

ELEMENTS OF CHEMICAL REACTION ENGINEERING

SIXTH EDITION

H. SCOTT FOGLER



INTERNATIONAL SERIES IN THE
PHYSICAL AND CHEMICAL ENGINEERING SCIENCES



Contents

Cover Page

About This eBook

Title Page

Copyright Page

Dedication Page

Contents

Introduction

A. Who Is the Intended Audience?

B. What Are the Goals of This Book?

C. What Is the Structure of CRE?

D. What Are the Components of the CRE Web Site?

E. Why Do We Assign Homework Problems?

F. Are There Other Web Site Resources?

G. How Can One's Critical Thinking and Creative
Thinking Skills Be Enhanced?

(<http://umich.edu/~scps/html/probsolv/strategy/crit-n-creat.htm>)

H. What's New in This Edition?

I. How Do I Say Thank You?

About the Author

1. Mole Balances

1.1 The Rate of Reaction, $-r_A$

1.2 The General Mole Balance Equation (GMBE)

1.3 Batch Reactors (BRs)

1.4 Continuous-Flow Reactors

1.5 Industrial Reactors

1.6 And Now... A Word from Our Sponsor–Safety 1
(AWFOS–S1 Safety)

Summary

CRE Web Site Materials

Questions, Simulations, and Problems

Supplementary Reading

2. Conversion and Reactor Sizing

2.1 Definition of Conversion

2.2 Batch Reactor Design Equations

2.3 Design Equations for Flow Reactors

2.4 Sizing Continuous-Flow Reactors

2.5 Reactors in Series

2.6 Some Further Definitions

2.7 And Now... A Word from Our Sponsor–Safety 2
(AWFOS–S2 The NFPA Diamond)

Summary

CRE Web Site Materials

Questions and Problems

Supplementary Reading

3. Rate Laws

3.1 Basic Definitions

3.2 The Rate Law

3.3 The Reaction-Rate Constant

3.4 Molecular Simulations

3.5 Present Status of Our Approach to Reactor Sizing
and Design

3.6 And Now... A Word from Our Sponsor–Safety 3
(AWFOS–S3 The GHS Diamond)

Summary

CRE Web Site Materials

Questions, Simulations, and Problems

Supplementary Reading

4. Stoichiometry

4.1 Batch Reactors (BRs)

4.2 Flow Systems

4.3 Reversible Reactions and Equilibrium Conversion

4.4 And Now... A Word from Our Sponsor–Safety 4
(AWFOS–S4 The Swiss Cheese Model)

Summary

CRE Web Site Materials

([http://www.umich.edu/~elements/6e/04chap/obj.html#/
/\)](http://www.umich.edu/~elements/6e/04chap/obj.html#/))

Questions and Problems

Questions

Computer Simulations and Experiments

Interactive Computer Games

Problems

Supplementary Reading

5. Isothermal Reactor Design: Conversion

5.1 Design Structure for Isothermal Reactors

5.2 Batch Reactors (BRs)

5.3 Continuous-Stirred Tank Reactors (CSTRs)

5.4 Tubular Reactors

5.5 Pressure Drop in Reactors

5.6 Synthesizing the Design of a Chemical Plant

5.7 And Now... A Word from Our Sponsor–Safety 5
(AWFOS–S5 A Safety Analysis of the Incident
Algorithm)

Summary

ODE Solver Algorithm

CRE Web Site Materials

Questions, Simulations, and Problems

Supplementary Reading

6. Isothermal Reactor Design: Moles and Molar Flow Rates

[6.1 The Moles and Molar Flow Rate Balance Algorithms](#)
[6.2 Mole Balances on CSTRs, PFRs, PBRs, and Batch Reactors](#)
[6.3 Application of the PFR Molar Flow Rate Algorithm to a Microreactor](#)
[6.4 Membrane Reactors](#)
[6.5 Unsteady-State Operation of Stirred Reactors](#)
[6.6 Semibatch Reactors](#)
[6.7 And Now... A Word from Our Sponsor–Safety 6 \(AWFOS–S6 The BowTie Diagram\)](#)
[Summary](#)
[ODE Solver Algorithm](#)
[CRE Web Site Materials](#)
[Questions, Simulations, and Problems](#)
[Supplementary Reading](#)

[7. Collection and Analysis of Rate Data](#)

[7.1 The Algorithm for Data Analysis](#)
[7.2 Determining the Reaction Order for Each of Two Reactants Using the Method of Excess](#)
[7.3 Integral Method](#)
[7.4 Differential Method of Analysis](#)
[7.5 Nonlinear Regression](#)
[7.6 Reaction-Rate Data from Differential Reactors](#)
[7.7 Experimental Planning](#)
[7.8 And Now... A Word from Our Sponsor–Safety 7 \(AWFOS–S7 Laboratory Safety\)](#)
[Summary](#)
[CRE Web Site Materials](#)
[Questions, Simulations, and Problems](#)
[Supplementary Reading](#)

[8. Multiple Reactions](#)

[8.1 Definitions](#)

8.2 Algorithm for Multiple Reactions

8.3 Parallel Reactions

8.4 Reactions in Series

8.5 Complex Reactions

8.6 Membrane Reactors to Improve Selectivity in Multiple Reactions

8.7 Sorting It All Out

8.8 The Fun Part

8.9 And Now... A Word from Our Sponsor—Safety 8 (AWFOS—S8 The Fire Triangle)

Summary

CRE Web Site Materials

Questions, Simulations, and Problems

Supplementary Reading

9. Reaction Mechanisms, Pathways, Bioreactions, and Bioreactors

9.1 Active Intermediates and Nonelementary Rate Laws

9.2 Enzymatic Reaction Fundamentals

9.3 Inhibition of Enzyme Reactions

9.4 Bioreactors and Biosynthesis

9.5 And Now... A Word from Our Sponsor—Safety 9 (AWFOS—S9 Process Safety Triangle)

Summary

CRE Web Site Materials

Questions, Simulations, and Problems

Supplementary Reading

10. Catalysis and Catalytic Reactors

10.1 Catalysts

10.2 Steps in a Catalytic Reaction

10.3 Synthesizing a Rate Law, Mechanism, and Rate-Limiting Step

10.4 Heterogeneous Data Analysis for Reactor Design

[10.5 Reaction Engineering in Microelectronic
Fabrication](#)
[10.6 Model Discrimination](#)
[10.7 Catalyst Deactivation](#)
[10.8 Reactors That Can Be Used to Help Offset
Catalyst Decay](#)
[Comparison of Model with Industrial Data](#)
[10.9 And Now... A Word from Our Sponsor–Safety 10
\(AWFOS–S10 Exxon Mobil Torrance Refinery
Explosion Involving a Straight–Through Transport
Reactor \[STTR\]\)](#)
[Summary](#)
[ODE Solver Algorithm](#)
[CRE Web Site Materials](#)
[Questions, Simulations, and Problems](#)
[Problems](#)
[Supplementary Reading](#)

[11. Nonisothermal Reactor Design: The Steady-State Energy Balance and Adiabatic PFR Applications](#)

[11.1 Rationale](#)
[11.2 The Energy Balance](#)
[11.3 The User-Friendly Energy Balance Equations](#)
[11.4 Adiabatic Operation \$\therefore Q = 0\$](#)
[11.5 Adiabatic Equilibrium Conversion](#)
[11.6 Reactor Staging with Interstage Cooling or
Heating](#)
[11.7 Optimum Feed Temperature](#)
[11.8 And Now... A Word from Our Sponsor–Safety 11
\(AWFOS–S11 Acronyms\)](#)
[Summary](#)
[CRE Web Site Materials](#)
[Questions, Simulations, and Problems](#)
[Supplementary Reading](#)

12. Steady-State Nonisothermal Reactor Design: Flow Reactors with Heat Exchange

12.1 Steady-State Tubular Reactor with Heat Exchange

12.2 Balance on the Heat-Transfer Fluid

12.3 Examples of the Algorithm for PFR/PBR Design with Heat Effects

12.4 CSTR with Heat Effects

12.5 Multiple Steady States (MSS)

12.6 Nonisothermal Multiple Chemical Reactions

12.7 Radial and Axial Temperature Variations in a Tubular Reactor

12.8 And Now... A Word from Our Sponsor—Safety

12 (AWFOS–S12 Safety Statistics)

Summary

CRE Web Site Materials

([http://www.umich.edu/~elements/6e/12chap/obj.html#/
/\)](http://www.umich.edu/~elements/6e/12chap/obj.html#/))

Questions, Simulations, and Problems

Supplementary Reading

13. Unsteady-State Nonisothermal Reactor Design

13.1 The Unsteady-State Energy Balance

13.2 Energy Balance on Batch Reactors (BRs)

13.3 Batch and Semibatch Reactors with a Heat Exchanger

13.4 Nonisothermal Multiple Reactions

13.5 And Now... A Word from Our Sponsor—Safety 13 (AWFOS–S13 Safety Analysis of the T2 Laboratories Incident)

Summary

CRE Web Site Materials

([http://www.umich.edu/~elements/6e/13chap/obj.html#/
/\)](http://www.umich.edu/~elements/6e/13chap/obj.html#/))

Questions, Simulations, and Problems

Supplementary Reading

14. Mass Transfer Limitations in Reacting Systems

14A Mass Transfer Fundamentals

14.1 Diffusion Fundamentals

14.2 Binary Diffusion

14.3 Modeling Diffusion with Chemical Reaction

14.4 The Mass Transfer Coefficient

14B Applications

14.5 Mass Transfer to a Single Particle

14.6 The Shrinking Core Model

14C Packed-Bed Applications

14.7 Mass Transfer-Limited Reactions in Packed Beds

14.8 Robert the Worrier

14.9 What If . . . ? (Parameter Sensitivity)

14.10 And Now... A Word from Our Sponsor—Safety

14 (AWFOS–S14 Sugar Dust Explosion)

Summary

CRE Web Site Materials

Questions, Simulations, and Problems

Supplementary Reading

15. Diffusion and Reaction

15.1 Diffusion and Reactions in Homogeneous Systems

15.2 Diffusion and Reactions in Spherical Catalyst Pellets

15.3 The Internal Effectiveness Factor

15.4 Falsified Kinetics

15.5 Overall Effectiveness Factor

15.6 Estimation of Diffusion- and Reaction-Limited Regimes

15.7 Mass Transfer and Reaction in a Packed Bed

15.8 Determination of Limiting Situations from Reaction-Rate Data

15.9 Multiphase Reactors in the Professional Reference Shelf

15.10 Fluidized Bed Reactors

15.11 Chemical Vapor Deposition (CVD)

15.12 And Now... A Word From Our Sponsor–Safety

15 (AWFOS–S15 Critical Thinking Questions Applied to Safety)

Summary

CRE Web Site Materials

(http://www.umich.edu/~elements/6e/15chap/obj.html#)

Questions, Simulations, and Problems

Supplementary Reading

16. Residence Time Distributions of Chemical Reactors

16.1 General Considerations

16.2 Measurement of the RTD

16.3 Characteristics of the RTD

16.4 RTD in Ideal Reactors

16.5 PFR/CSTR Series RTD

16.6 Diagnostics and Troubleshooting

16.7 And Now... A Word from Our Sponsor–Safety 16 (AWFOS–S16 Critical Thinking Actions)

Summary

CRE Web Site Materials

Questions, Simulations, and Problems

Supplementary Reading

17. Predicting Conversion Directly from the Residence Time Distribution

17.1 Modeling Nonideal Reactors Using the RTD

17.2 Zero Adjustable Parameter Models

17.3 Using Software Packages Such as Polymath to Find Maximum Mixedness Conversion

17.4 Tanks-in-Series One Parameter Model, n

17.5 RTD and Multiple Reactions

17.6 And Now... A Word from Our Sponsor–Safety 17
(AWFOS–S17 Brief Case History on an Air Preheater)

Summary

CRE Web Site Materials

Questions, Simulations, and Problems

Supplementary Reading

18. Models for Nonideal Reactors

18.1 Some Guidelines for Developing Models

18.2 Flow and Axial Dispersion of Inert Tracers in
Isothermal Reactors

18.3 Flow, Reaction, and Axial Dispersion

18.4 Flow, Reaction, and Axial Dispersion in
Isothermal Laminar-Flow Reactors and Finding Meno

18.5 Tanks-in-Series Model versus Dispersion Model

18.6 Numerical Solutions to Flows with Dispersion
and Reaction

18.7 Nonisothermal Flow with Radial and Axial
Variations in a Tubular Reactor

18.8 Two-Parameter Models—Modeling Real Reactors
with Combinations of Ideal Reactors

18.9 And Now... A Word from Our Sponsor–Safety 18
(AWFOS–S18 An Algorithm for Management of
Change (MoC))

Summary

CRE Web Site Materials

Questions, Simulations, and Problems

Supplementary Reading

A. Numerical Techniques

A.1 Useful Integrals in Chemical Reactor Design

A.2 Equal-Area Graphical Differentiation

A.3 Solutions to Differential Equations

A.3.B Coupled Differential Equations

A.3.C Second-Order Ordinary Differential Equations

A.4 Numerical Evaluation of Integrals

A.5 Semi-Log Graphs

A.6 Software Packages

B. Ideal Gas Constant and Conversion Factors

Ideal Gas Constant

Volume of Ideal Gas

Volume

Length

Pressure

Energy (Work)

Temperature

Mass

Viscosity

Force

Pressure

Work

Time Rate of Change of Energy with Time (Power)

Gravitational Conversion Factor

C. Thermodynamic Relationships Involving the Equilibrium
Constant

D. Software Packages

D.1 Polymath

D.2 Wolfram

D.3 Python

D.4 MATLAB

D.5 Excel

D.6 COMSOL

([http://www.umich.edu/~elements/6e/12chap/comsol.ht
ml](http://www.umich.edu/~elements/6e/12chap/comsol.html))

D.7 Aspen

D.8 Visual Encyclopedia of Equipment—Reactors
Section

D.9 Reactor Lab

E. Rate-Law Data

F. Nomenclature

G. Open-Ended Problems

G.1 ChemE Car

G.2 Effective Lubricant Design

G.3 Peach Bottom Nuclear Reactor

G.4 Underground Wet Oxidation

G.5 Hydrodesulfurization Reactor Design

G.6 Continuous Bioprocessing

G.7 Methanol Synthesis

G.8 Cajun Seafood Gumbo

G.9 Alcohol Metabolism

G.10 Methanol Poisoning

G.11 Safety

H. Use of Computational Chemistry Software Packages

H.1 Computational Chemical Reaction Engineering

I. How to Use the CRE Web Resources

I.1 CRE Web Resources Components

Index

Credits

i

ii

iii

iv

v

vi

vii

viii

ix

x

xi

xii

xiii

xiv

xv

xvi

xvii

xviii

xix

xx

xxi

xxii

xxiii

xxiv

xxv

xxvi

xxvii

xxviii

xxix

xxx

xxxi

xxxii

xxxiii

xxxiv

1

2

3

4

5

6

7

8

9

10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45

46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81

82

83

84

85

86

87

88

89

90

91

92

93

94

95

96

97

98

99

100

101

102

103

104

105

106

107

108

109

110

111

112

113

114

115

116

117

118

119

120

121

122

123

124

125

126

127

128

129

130

131

132

133

134

135

136

137

138

139

140

141

142

143

144

145

146

147

148

149

150

151

152

153

154

155

156

157

158

159

160

161

162

163

164

165

166

167

168

169

170

171

172

173

174

175

176

177

178

179

180

181

182

183

184

185

186

187

188

189

190

191

192

193

194

195

196

197

198

199

200

201

202

203

204

205

206

207

208

209

210

211

212

213

214

215

216

217

218

219

220

221

222

223

224

225

226

227

228

229

230

231

232

233

234

235

236

237

238

239

240

241

242

243

244

245

246

247

248

249

250

251

252

253

254

255

256

257

258

259

260

261

262

263

264

265

266

267

268

269

270

271

272

273

274

275

276

277

278

279

280

281

282

283

284

285

286

287

288

289

290

291

292

293

294

295

296

297

298

299

300

301

302

303

304

305

306

307

308

309

310

311

312

313

314

315

316

317

318

319

320

321

322

323

324

325

326

327

328

329

330

331

332

333

334

335

336

337

338

339

340

341

342

343

344

345

346

347

348

349

350

351

352

353

354

355

356

357

358

359

360

361

362

363

364

365

366

367

368

369

370

371

372

373

374

375

376

377

378

379

380

381

382

383

384

385

386

387

388

389

390

391

392

393

394

395

396

397

398

399

400

401

402

403

404

405

406

407

408

409

410

411

412

413

414

415

416

417

418

419

420

421

422

423

424

425

426

427

428

429

430

431

432

433

434

435

436

437

438

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440

441

442

443

444

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447

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618

619

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621

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699

700

701

702

703

704

705

706

707

708

709

710

711

712

713

714

715

716

717

718

719

720

721

722

723

724

725

726

727

728

729

730

731

732

733

734

735

736

737

738

739

740

741

742

743

744

745

746

747

748

749

750

751

752

753

754

755

756

757

758

759

760

761

762

763

764

765

766

767

768

769

770

771

772

773

774

775

776

777

778

779

780

781

782

783

784

785

786

787

788

789

790

791

792

793

794

795

796

797

798

799

800

801

802

803

804

805

806

807

808

809

810

811

812

813

814

815

816

817

818

819

820

821

822

823

824

825

826

827

828

829

830

831

832

833

834

835

836

837

838

839

840

841

842

843

844

845

846

847

848

849

850

851

852

853

854

855

856

857

858

859

860

861

862

863

864

865

866

867

868

869

870

871

872

873

874

875

876

877

878

879

880

881

882

883

884

885

886

887

888

889

890

891

892

893

894

895

896

897

898

899

900

901

902

903

904

905

906

907

908

909

910

911

912

913

914

915

916

917

918

919

920

921

922

923

924

925

926

927

928

929

930

931

932

933

934

935

936

937

938

939

940

941

942

943

944

945

946

947

948

949

950

951

952

953

954

955

956

957

958

959

960

961

962

963

964

965

966

967

968

969

970

971

972

973

974

975

976

977

978

979

980

981

982

983

984

985

986

987

988

989

990

991

992

993

994

995

996

997

998

999

1000

1001

1002

1003

1004

1005

1006

1007

1008

1009

1010

1011

1012

1013

1014

1015

1016

1017

1018

1019

1020

1021

1022

1023

1024

1025

1026

1027

1028

1029

1030

1031

1032

1033

1034

1035

1036

1037

1038

1039

1040

1041

1042

1043

1044

1045

1046

1047

1048

1049

1050

1051

1052

1053

1054

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Elements of Chemical Reaction Engineering

Sixth Edition

Elements of Chemical Reaction Engineering

Sixth Edition

H. Scott Fogler

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Engineering**

**and the Arthur F. Thurnau Professor
The University of Michigan, Ann Arbor**



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ScoutAutomatedPrintCode

Dedicated to

Janet Meadors Fogler

*For her companionship, encouragement,
sense of humor, love, and support throughout the years*

Contents

Introduction

About the Author

Chapter 1 Mole Balances

1.1 The Rate of Reaction, $-r_A$

1.2 The General Mole Balance Equation (GMBE)

1.3 Batch Reactors (BRs)

1.4 Continuous-Flow Reactors

1.4.1 Continuous-Stirred Tank Reactor (CSTR)

1.4.2 Tubular Reactor

1.4.3 Packed-Bed Reactor (PBR)

1.4.4 Well-Mixed “Fluidized” Catalytic Bed Reactor

1.5 Industrial Reactors

1.6 And Now... A Word from Our Sponsor—Safety 1 (AWFOS–S1 Safety)

1.6.1 What Is Chemical Process Safety?

1.6.2 Why Study Process Safety?

Chapter 2 Conversion and Reactor Sizing

2.1 Definition of Conversion

2.2 Batch Reactor Design Equations

2.3 Design Equations for Flow Reactors

2.3.1 CSTR (Also Known as a Backmix Reactor or a Vat)

2.3.2 Tubular Flow Reactor (PFR)

2.3.3 Packed-Bed Reactor (PBR)

2.4 Sizing Continuous-Flow Reactors

2.5 Reactors in Series

2.5.1 CSTRs in Series

2.5.2 PFRs in Series

2.5.3 Combinations of CSTRs and PFRs in Series

2.5.4 Comparing the CSTR and PFR Volumes and Reactor Sequencing

2.6 Some Further Definitions

2.6.1 Space Time

2.6.2 Space Velocity

2.7 And Now... A Word from Our Sponsor—Safety 2 (AWFOS–S2 The NFPA Diamond)

Chapter 3 Rate Laws

3.1 Basic Definitions

3.1.1 Relative Rates of Reaction

3.2 The Rate Law

3.2.1 Power Law Models and Elementary Rate Laws

3.2.2 Nonelementary Rate Laws

3.2.3 Reversible Reactions

3.3 The Reaction-Rate Constant

3.3.1 The Rate Constant k and Its Temperature Dependence

3.3.2 Interpretation of the Activation Energy

3.3.3 The Arrhenius Plot

3.4 Molecular Simulations

3.4.1 Historical Perspective

3.4.2 Stochastic Modeling of Reactions

3.5 Present Status of Our Approach to Reactor Sizing and Design

3.6 And Now... A Word from Our Sponsor—Safety 3 (AWFOS–S3 The GHS Diamond)

Chapter 4 Stoichiometry

4.1 Batch Reactors (BRs)

4.1.1 Batch Concentrations for the Generic Reaction, Equation (2-2)

4.2 Flow Systems

4.2.1 Equations for Concentrations in Flow Systems

4.2.2 Liquid-Phase Concentrations

4.2.3 Gas-Phase Concentrations

4.3 Reversible Reactions and Equilibrium

Conversion

4.4 *And Now... A Word from Our Sponsor—Safety* 4 (AWFOS–S4 The Swiss Cheese Model)

Chapter 5 Isothermal Reactor Design: Conversion

5.1 Design Structure for Isothermal Reactors

5.2 Batch Reactors (BRs)

5.2.1 Batch Reaction Times

5.3 Continuous-Stirred Tank Reactors (CSTRs)

5.3.1 A Single CSTR

5.3.2 CSTRs in Series

5.4 Tubular Reactors

5.4.1 Liquid-Phase Reactions in a PFR $\therefore v = v_0$

5.4.2 Gas-Phase Reactions in a PFR [$v = v_0 (1 + \epsilon X) (T/T_0)(P_0/P)$]

5.4.3 Effect of ϵ on Conversion

5.5 Pressure Drop in Reactors

5.5.1 Pressure Drop and the Rate Law

5.5.2 Flow Through a Packed Bed

5.5.3 Pressure Drop in Pipes

5.5.4 Analytical Solution for Reaction with Pressure Drop

5.5.5 Robert the Worrier Wonders: What If...

5.6 Synthesizing the Design of a Chemical Plant

5.7 *And Now... A Word from Our Sponsor—Safety*
5 (AWFOS–S5 A Safety Analysis of the
Incident Algorithm)

Chapter 6 Isothermal Reactor Design: Moles and Molar Flow
Rates

6.1 The Moles and Molar Flow Rate Balance
Algorithms

6.2 Mole Balances on CSTRs, PFRs, PBRs, and
Batch Reactors

6.2.1 *Liquid Phase*

6.2.2 *Gas Phase*

6.3 Application of the PFR Molar Flow Rate
Algorithm to a Microreactor

6.4 Membrane Reactors

6.5 Unsteady-State Operation of Stirred Reactors

6.6 Semibatch Reactors

6.6.1 *Motivation for Using a Semibatch*
Reactor

6.6.2 *Semibatch Reactor Mole Balances*

6.6.3 *Equilibrium Conversion*

6.7 *And Now... A Word from Our Sponsor—Safety*
6 (AWFOS–S6 The BowTie Diagram)

Chapter 7 Collection and Analysis of Rate Data

7.1 The Algorithm for Data Analysis

7.2 Determining the Reaction Order for Each of Two Reactants Using the Method of Excess

7.3 Integral Method

7.4 Differential Method of Analysis

7.4.1 Graphical Differentiation Method

7.4.2 Numerical Method

7.4.3 Finding the Rate-Law Parameters

7.5 Nonlinear Regression

7.5.1 Concentration–Time Data

7.5.2 Model Discrimination

7.6 Reaction-Rate Data from Differential Reactors

7.7 Experimental Planning

7.8 And Now... A Word from Our Sponsor—Safety 7 (AWFOS–S7 Laboratory Safety)

Chapter 8 Multiple Reactions

8.1 Definitions

8.1.1 Types of Reactions

8.1.2 Selectivity

8.1.3 Yield

8.1.4 Conversion

8.2 Algorithm for Multiple Reactions

8.2.1 Modifications to the Chapter 6 CRE Algorithm for Multiple Reactions

8.3 Parallel Reactions

8.3.1 Selectivity

8.3.2 Maximizing the Desired Product for One Reactant

8.3.3 Reactor Selection and Operating Conditions

8.4 Reactions in Series

8.5 Complex Reactions

8.5.1 Complex Gas-Phase Reactions in a PBR

8.5.2 Complex Liquid-Phase Reactions in a CSTR

8.5.3 Complex Liquid-Phase Reactions in a Semibatch Reactor

8.6 Membrane Reactors to Improve Selectivity in Multiple Reactions

8.7 Sorting It All Out

8.8 The Fun Part

8.9 And Now... A Word from Our Sponsor—Safety 8 (AWFOS–S8 The Fire Triangle)

8.9.1 The Fire Triangle

8.9.2 Defining Some Important Terms

8.9.3 Ways to Prevent Fires

8.9.4 Ways to Protect from Fires

Chapter 9 Reaction Mechanisms, Pathways, Bioreactions, and Bioreactors

9.1 Active Intermediates and Nonelementary Rate Laws

9.1.1 Pseudo-Steady-State Hypothesis (PSSH)

*9.1.2 If Two Molecules Must Collide, How Can
the Rate Law Be First Order?*

9.1.3 Searching for a Mechanism

9.1.4 Chain Reactions

9.2 Enzymatic Reaction Fundamentals

9.2.1 Enzyme–Substrate Complex

9.2.2 Mechanisms

9.2.3 Michaelis–Menten Equation

*9.2.4 Batch Reactor Calculations for Enzyme
Reactions*

9.3 Inhibition of Enzyme Reactions

9.3.1 Competitive Inhibition

9.3.2 Uncompetitive Inhibition

*9.3.3 Noncompetitive Inhibition (Mixed
Inhibition)*

9.3.4 Substrate Inhibition

9.4 Bioreactors and Biosynthesis

9.4.1 Cell Growth

9.4.2 Rate Laws

9.4.3 Stoichiometry

9.4.4 Mass Balances

9.4.5 Chemostats

9.4.6 CSTR Bioreactor Operation

9.4.7 Washout

*9.5 And Now... A Word from Our Sponsor—Safety
9 (AWFOS–S9 Process Safety Triangle)*

9.5.1 Levels of the Process Safety Triangle

9.5.2 Application to Process Safety

9.5.3 Examples of Process Safety Triangle

Chapter 10 Catalysis and Catalytic Reactors

10.1 Catalysts

10.1.1 Definitions

10.1.2 Catalyst Properties

10.1.3 Catalytic Gas–Solid Interactions

10.1.4 Classification of Catalysts

10.2 Steps in a Catalytic Reaction

*10.2.1 Mass Transfer Step 1: Diffusion from
the Bulk to the External Surface of the
Catalyst—An Overview*

*10.2.2 Mass Transfer Step 2: Internal
Diffusion—An Overview*

10.2.3 Adsorption Isotherms

10.2.4 Surface Reaction

10.2.5 Desorption

10.2.6 The Rate-Limiting Step

*10.3 Synthesizing a Rate Law, Mechanism, and
Rate-Limiting Step*

*10.3.1 Is the Adsorption of Cumene Rate-
Limiting?*

10.3.2 Is the Surface Reaction Rate-Limiting?

10.3.3 Is the Desorption of Benzene the Rate-Limiting Step (RLS)?

10.3.4 Summary of the Cumene Decomposition

10.3.5 Reforming Catalysts

10.3.6 Rate Laws Derived from the Pseudo-Steady-State Hypothesis (PSSH)

10.3.7 Temperature Dependence of the Rate Law

10.4 Heterogeneous Data Analysis for Reactor Design

10.4.1 Deducing a Rate Law from the Experimental Data

10.4.2 Finding a Mechanism Consistent with Experimental Observations

10.4.3 Evaluation of the Rate-Law Parameters

10.4.4 Reactor Design

10.5 Reaction Engineering in Microelectronic Fabrication

10.5.1 Overview

10.5.2 Chemical Vapor Deposition (CVD)

10.6 Model Discrimination

10.7 Catalyst Deactivation

10.7.1 Types of Catalyst Deactivation

10.7.2 Decay in Packed-Bed Reactors

10.8 Reactors That Can Be Used to Help Offset Catalyst Decay

10.8.1 Temperature–Time Trajectories

10.8.2 Moving-Bed Reactors

*10.8.3 Straight-Through Transport Reactors
(STTR)*

*10.9 And Now... A Word from Our Sponsor—
Safety 10 (AWFOS–S10 Exxon Mobil
Torrance Refinery Explosion Involving a
Straight–Through Transport Reactor [STTR])*

*Chapter 11 Nonisothermal Reactor Design: The Steady-State
Energy Balance and Adiabatic PFR Applications*

11.1 Rationale

11.2 The Energy Balance

11.2.1 First Law of Thermodynamics

11.2.2 Evaluating the Work Term

11.2.3 Overview of Energy Balances

11.3 The User-Friendly Energy Balance Equations

*11.3.1 Dissecting the Steady-State Molar Flow
Rates to Obtain the Heat of Reaction*

11.3.2 Dissecting the Enthalpies

11.3.3 Relating $\Delta H_{Rx}(T)$, ΔH_{Rx}° , and ΔC_P

11.4 Adiabatic Operation $\therefore \dot{Q} = 0$

11.4.1 Adiabatic Energy Balance

11.4.2 Adiabatic Tubular Reactor

11.5 Adiabatic Equilibrium Conversion

11.5.1 Equilibrium Conversion

11.6 Reactor Staging with Interstage Cooling or Heating

11.6.1 Exothermic Reactions

11.6.2 Endothermic Reactions

11.7 Optimum Feed Temperature

11.8 And Now... A Word from Our Sponsor— Safety 11 (AWFOS–S11 Acronyms)

Chapter 12 Steady-State Nonisothermal Reactor Design: Flow Reactors with Heat Exchange

12.1 Steady-State Tubular Reactor with Heat Exchange

12.1.1 Deriving the Energy Balance for a PFR

12.1.2 Applying the Algorithm to Flow Reactors with Heat Exchange

12.2 Balance on the Heat-Transfer Fluid

12.2.1 Co-Current Flow

12.2.2 Countercurrent Flow

12.3 Examples of the Algorithm for PFR/PBR Design with Heat Effects

12.3.1 Applying the Algorithm to an Exothermic Reaction

12.3.2 Applying the Algorithm to an Endothermic Reaction

12.4 CSTR with Heat Effects

12.4.1 Heat Added to the Reactor, \dot{Q}

12.5 Multiple Steady States (MSS)

12.5.1 Heat-Removed Term, $R(T)$

12.5.2 Heat-Generated Term, $G(T)$

12.5.3 Ignition–Extinction Curve

12.6 Nonisothermal Multiple Chemical Reactions

*12.6.1 Energy Balance for Multiple Reactions
in Plug-Flow Reactors*

*12.6.2 Energy Balance for Multiple Reactions
in a CSTR*

12.6.3 Series Reactions in a CSTR

12.6.4 Complex Reactions in a PFR

*12.7 Radial and Axial Temperature Variations in a
Tubular Reactor*

*12.8 And Now... A Word from Our Sponsor—
Safety 12 (AWFOS–S12 Safety Statistics)*

*12.8.1 The Process Safety Across the
Chemical Engineering Curriculum Web
site*

12.8.2 Safety Statistics

*12.8.3 Additional Resources CCPS and
SACHE*

Chapter 13 Unsteady-State Nonisothermal Reactor Design

13.1 The Unsteady-State Energy Balance

13.2 Energy Balance on Batch Reactors (BRs)

*13.2.1 Adiabatic Operation of a Batch
Reactor*

*13.2.2 Case History of a Batch Reactor with
Interrupted Isothermal Operation
Causing a **Runaway Reaction***

*13.3 Batch and Semibatch Reactors with a Heat
Exchanger*

13.3.1 Startup of a CSTR

13.3.2 Semibatch Operation

13.4 Nonisothermal Multiple Reactions

*13.5 And Now... A Word from Our Sponsor—
Safety 13 (AWFOS–S13 Safety Analysis of
the T2 Laboratories Incident)*

Chapter 14 Mass Transfer Limitations in Reacting Systems

14.1 Diffusion Fundamentals

14.1.1 Definitions

14.1.2 Molar Flux: W_A

14.1.3 Fick's First Law

14.2 Binary Diffusion

14.2.1 Evaluating the Molar Flux

14.2.2 Diffusion and Convective Transport

14.2.3 Boundary Conditions

*14.2.4 Temperature and Pressure Dependence
of D_{AB}*

14.3 Modeling Diffusion with Chemical Reaction

*14.3.1 Diffusion through a Stagnant Film to a
Particle*

14.4 The Mass Transfer Coefficient

14.5 Mass Transfer to a Single Particle

14.5.1 First-Order Rate Laws

14.5.2 Limiting Regimes

14.6 The Shrinking Core Model

*14.6.1 Dust Explosions, Particle Dissolution,
and Catalyst Regeneration*

14.7 Mass Transfer–Limited Reactions in Packed
Beds

14.8 Robert the Worrier

14.9 What If ... ? (Parameter Sensitivity)

14.10 *And Now... A Word from Our Sponsor—
Safety 14 (AWFOS–S14 Sugar Dust
Explosion)*

Chapter 15 Diffusion and Reaction

15.1 Diffusion and Reactions in Homogeneous
Systems

15.2 Diffusion and Reactions in Spherical Catalyst
Pellets

15.2.1 Effective Diffusivity

*15.2.2 Derivation of the Differential Equation
Describing Diffusion and Reaction in a
Single Spherical Catalyst Pellet*

*15.2.3 Writing the Diffusion with the Catalytic
Reaction Equation in Dimensionless
Form*

*15.2.4 Solution to the Differential Equation
for a First-Order Reaction*

15.3 The Internal Effectiveness Factor

*15.3.1 Isothermal First-Order Catalytic
Reactions*

*15.3.2 Effectiveness Factors with Volume
Change with Reaction*

*15.3.3 Internal-Diffusion-Limited Reactions
Other Than First Order*

*15.3.4 Weisz–Prater Criterion for Internal
Diffusion Limitations*

15.4 Falsified Kinetics

15.5 Overall Effectiveness Factor

15.6 Estimation of Diffusion- and Reaction-
Limited Regimes

*15.6.1 Mears Criterion for External Diffusion
Limitations*

15.7 Mass Transfer and Reaction in a Packed Bed

15.8 Determination of Limiting Situations from
Reaction-Rate Data

15.9 Multiphase Reactors in the Professional
Reference Shelf

15.9.1 Slurry Reactors

15.9.2 Trickle Bed Reactors

15.10 Fluidized Bed Reactors

15.11 Chemical Vapor Deposition (CVD)

15.12 *And Now... A Word from Our Sponsor—*
Safety 15 (AWFOS–S15 Critical Thinking
Questions Applied to Safety)

*Chapter 16 Residence Time Distributions of Chemical
Reactors*

16.1 General Considerations

*16.1.1 Residence Time Distribution (RTD)
Function*

16.2 Measurement of the RTD

16.2.1 Pulse Input Experiment

16.2.2 Step Tracer Experiment

16.3 Characteristics of the RTD

16.3.1 Integral Relationships

16.3.2 Mean Residence Time

16.3.3 Other Moments of the RTD

16.3.4 Normalized RTD Function, $E(\Theta)$

16.3.5 Internal-Age Distribution, $I(\alpha)$

16.4 RTD in Ideal Reactors

16.4.1 RTDs in Batch and Plug-Flow Reactors

16.4.2 Single-CSTR RTD

16.4.3 Laminar-Flow Reactor (LFR)

16.5 PFR/CSTR Series RTD

16.6 Diagnostics and Troubleshooting

16.6.1 General Comments

*16.6.2 Simple Diagnostics and
Troubleshooting Using the RTD for
Ideal Reactors*

*16.7 And Now... A Word from Our Sponsor—
Safety 16 (AWFOS–S16 Critical Thinking
Actions)*

*Chapter 17 Predicting Conversion Directly from the Residence
Time Distribution*

17.1 Modeling Nonideal Reactors Using the RTD

17.1.1 Modeling and Mixing Overview

17.1.2 Mixing

17.2 Zero Adjustable Parameter Models

17.2.1 Segregation Model

17.2.2 Maximum Mixedness Model

*17.3 Using Software Packages Such as Polymath to
Find Maximum Mixedness Conversion*

*17.3.1 Comparing Segregation and Maximum
Mixedness Predictions*

17.4 Tanks-in-Series One Parameter Model, n

*17.4.1 Find the Number of T-I-S to Model the
Real Reactor*

*17.4.2 Calculating Conversion for the T-I-S
Model*

*17.4.3 Tanks-in-Series versus Segregation for
a First-Order Reaction*

17.5 RTD and Multiple Reactions

17.5.1 Segregation Model

17.5.2 Maximum Mixedness

17.6 And Now... A Word from Our Sponsor—

*Safety 17 (AWFOS–S17 Brief Case History on
an Air Preheater)*

Chapter 18 Models for Nonideal Reactors

18.1 Some Guidelines for Developing Models

18.1.1 One-Parameter Models

18.1.2 Two-Parameter Models

*18.2 Flow and Axial Dispersion of Inert Tracers in
Isothermal Reactors*

18.2.1 Balances on Inert Tracers

*18.2.2 Boundary Conditions for Flow and
Reaction*

18.3 Flow, Reaction, and Axial Dispersion

18.3.1 Balance Equations

18.3.2 Solution for a Closed-Closed System

*18.4 Flow, Reaction, and Axial Dispersion in
Isothermal Laminar-Flow Reactors and
Finding **Meno***

*18.4.1 Determine the Dispersion Coefficient
(D_a) and the Péclet Number (Pe_r)*

18.4.2 Correlations for D_a

18.4.3 Dispersion in Packed Beds

18.4.4 Experimental Determination of D_a

18.5 Tanks-in-Series Model versus Dispersion
Model

18.6 Numerical Solutions to Flows with Dispersion
and Reaction

18.7 Nonisothermal Flow with Radial and Axial
Variations in a Tubular Reactor

18.7.1 Molar Flux

18.7.2 Energy Flux

18.7.3 Energy Balance

18.8 Two-Parameter Models—Modeling Real
Reactors with Combinations of Ideal Reactors

*18.8.1 Real CSTR Modeled Using Bypassing
and Dead Space*

*18.8.2 Real CSTR Modeled as Two CSTRs
with Interchange*

*18.8.3 Other Models of Nonideal Reactors
Using CSTRs and PFRs*

*18.8.4 Applications to Pharmacokinetic
Modeling*

18.9 And Now... A Word from Our Sponsor—
Safety 18 (AWFOS–S18 An Algorithm for
Management of Change (MoC))

Appendix A Numerical Techniques

A.1 Useful Integrals in Chemical Reactor Design

A.2 Equal-Area Graphical Differentiation

A.3 Solutions to Differential Equations

*A.3.A First-Order Ordinary Differential
Equations*

A.3.B Coupled Differential Equations

*A.3.C Second-Order Ordinary Differential
Equations*

A.4 Numerical Evaluation of Integrals

A.5 Semi-Log Graphs

A.6 Software Packages

Appendix B Ideal Gas Constant and Conversion Factors

*Appendix C Thermodynamic Relationships Involving the
Equilibrium Constant*

Appendix D Software Packages

D.1 Polymath

D.1.A About Polymath

(<http://www.umich.edu/~elements/6e/software/polymath.html>)

D.1.B Polymath Tutorials

(<http://www.umich.edu/~elements/6e/software/polymath-tutorial.html>)

D.1.C Living Example Problems

D.2 Wolfram

D.3 Python

D.4 MATLAB

D.5 Excel

D.6 COMSOL

(<http://www.umich.edu/~elements/6e/12chap/comsol.html>)

D.7 Aspen

D.8 Visual Encyclopedia of Equipment—Reactors Section

D.9 Reactor Lab

Appendix E Rate-Law Data

Appendix F Nomenclature

Appendix G Open-Ended Problems

G.1 Chem-E-Car

G.2 Effective Lubricant Design

G.3 Peach Bottom Nuclear Reactor

G.4 Underground Wet Oxidation

G.5 Hydrodesulfurization Reactor Design

G.6 Continuous Bioprocessing

G.7 Methanol Synthesis

G.8 Cajun Seafood Gumbo

G.9 Alcohol Metabolism

G.10 Methanol Poisoning

G.11 Safety

Appendix H Use of Computational Chemistry Software Packages

H.1 Computational Chemical Reaction Engineering

Appendix I How to Use the CRE Web Resources

I.1 CRE Web Resources Components

Index

Introduction

The man who has ceased to learn ought not to be
allowed
to wander around loose in these dangerous days.

—M. M. Coady

A. WHO IS THE INTENDED AUDIENCE?

This book was written with today's students in mind. It provides instantaneous access to information; does not waste time on extraneous details; cuts right to the point; uses more bullets to make information easier to access; and includes new, novel problems on chemical reaction engineering (e.g., solar energy).¹ The interaction between the text and Web site (<http://www.umich.edu/~elements/6e/>) breaks new ground and provides one of the most comprehensive active learning resources available. With the advent of sliders in both Wolfram and Python, students can explore the reactions and the reactor in which they occur, by carrying out simulation experiments and then writing a set of conclusions to describe what they found.

¹ This Introduction is a condensed version of the full Preface/Introduction found on the Web site (<http://www.umich.edu/~elements/6e/toc/Preface->

Complete.pdf).

This book and interactive Web site are intended for use as both an undergraduate-level and a graduate-level text in chemical reaction engineering. The undergraduate course/courses usually focus on Chapters 1–13; the graduate course material includes topics such as diffusion limitations, effectiveness factors (discussed in Chapters 14 and 15), nonideal reactors, and residence time distribution (discussed in Chapters 16–18) along with the additional material and Professional Reference Shelf (PRS) on the Web site.

This edition emphasizes chemical reactor safety by ending each chapter with a safety lesson called *And Now... A Word From Our Sponsor-Safety (AWFOS–S)*. These lessons can also be found on the Web site at <http://umich.edu/~safeche/>.

B. WHAT ARE THE GOALS OF THIS BOOK?

B.1 To Have Fun Learning Chemical Reaction Engineering (CRE)

Chemical reaction engineering (CRE) is a great subject that is fun to learn and is the heart of chemical engineering. I have tried to provide a little Michigan humor as we go. Take a look at the humorous YouTube videos (e.g., “Black Widow” or “Chemical Engineering Gone Wrong”) that illustrate certain principles in the text. These videos were made by chemical engineering students at the universities of Alabama and Michigan. In addition, I have found that students enjoy the Interactive Computer Games (ICGs) that, along with the

videos, are linked from the CRE homepage (<http://www.umich.edu/~elements/6e/index.html>).

B.2 To Develop a Fundamental Understanding of Reaction Engineering

The second goal of this book is to help the reader clearly understand the fundamentals of CRE. This goal is achieved by presenting a structure that allows the reader to solve reaction engineering problems through reasoning rather than through memorization and recall of numerous equations and the restrictions and conditions under which each equation applies (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>).

B.3 To Enhance Thinking Skills

A third goal of this text is to enhance critical thinking skills and creative thinking skills. How does the book help enhance your critical and creative thinking skills? We discuss ways to achieve this enhancement in Table P-2, Critical Thinking Questions; Table P-3, Critical Thinking Actions; and Table P-4, Practicing Creative Thinking, in the complete preface on the CRE Web site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>) and also from the Problem Solving Web site (<http://umich.edu/~scps/>).

C. WHAT IS THE STRUCTURE OF CRE?

C.1 What Are the Concepts That Form the Foundation of CRE?

The strategy behind the presentation of material is to build continually on a few basic ideas in CRE to solve a wide variety of problems. The building blocks of CRE and the primary algorithm allow us to solve isothermal CRE problems through logic rather than memorization. We start with the Mole Balance Building Block ([Chapter 1](#)) and then place the other blocks one at a time on top of the others until we reach the Evaluate Block ([Chapter 5](#)), by which time we can solve a multitude of isothermal CRE problems. As we study each block, we need to make sure we understand everything in that block and be sure not to cut corners by leaving anything out so we don't wind up with a stack of cylindrical blocks. An animation of what happens to such a stack is shown at the end of Lecture 1 notes

(<http://www.umich.edu/%7Eelements/6e/lectures/umich.html>).

For nonisothermal reactions, we replace the “Combine” building block in [Figure I-1](#) with the “Energy Balance” building block because nonisothermal reactions almost always require a computer-generated solution. Consequently, we don't need the “Combine” block because the computer combines everything for us. From these pillars and building blocks, we construct our CRE algorithm:

Mole Balance + Rate Laws + Stoichiometry + Energy Balance + Combine → Solution

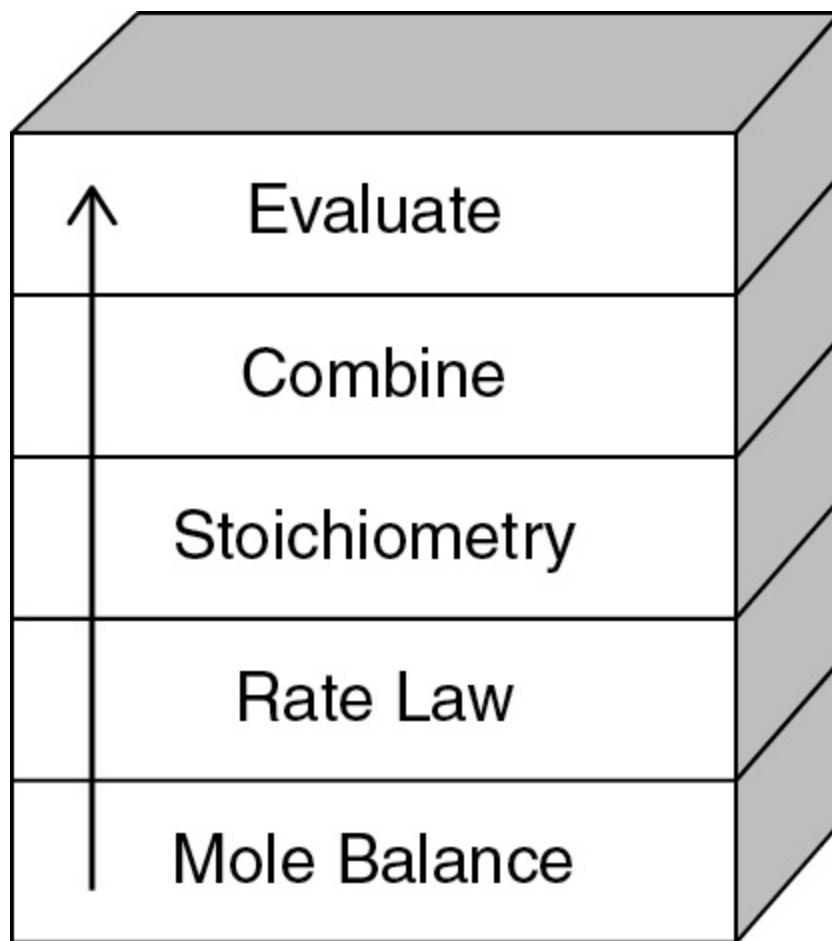


Figure I-1 Building blocks.

C.2 What Is the Sequence of Topics in Which This Book Can Be Used?

The selection and order of topics and chapters are shown in **Figure P-3** in the Complete Preface/Introduction on the Web site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>). There are notes in the margins, which are meant to serve two purposes. First, they act as guides or commentary as one reads through the material. Second, they identify key equations and relationships that are used to solve CRE problems.

D. WHAT ARE THE COMPONENTS OF THE CRE WEB SITE?

The interactive companion Web site material has been significantly updated and is a novel, and integral part of this book. The main purposes of the Web site are to serve as an interactive part of the text with enrichment resources. The home page for the CRE Web site (<http://www.umich.edu/~elements/6e/index.html>) is shown in Figure I-2. For discussion of how to use the Web site and text interactively, see Appendix I.

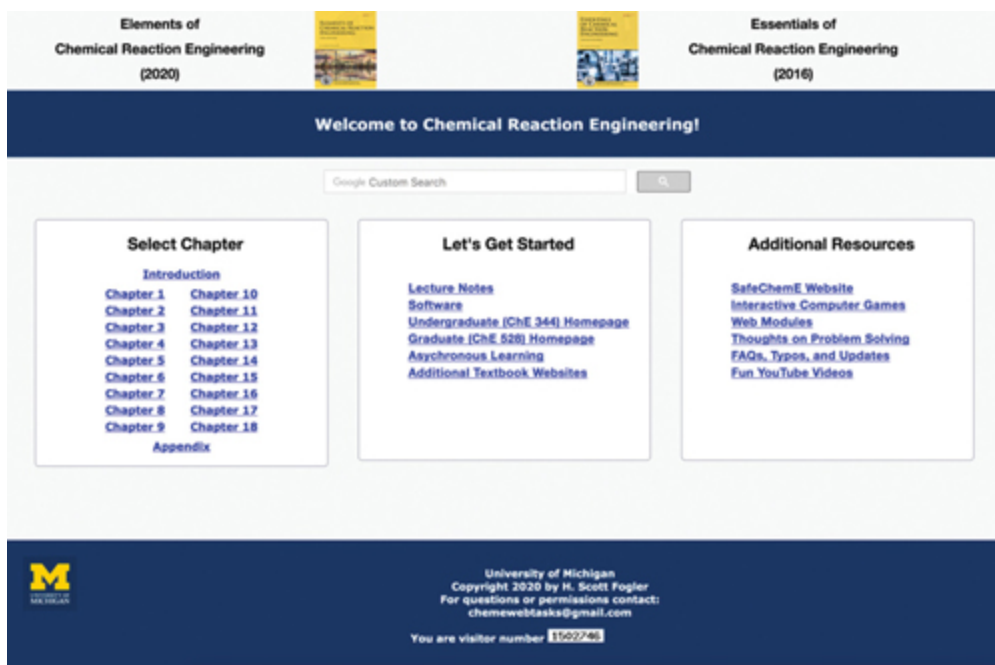


Figure I-2 Screen shot of the book's companion Web site (<http://www.umich.edu/~elements/6e/index.html>).

The objectives of the Web site are fourfold:

1. To facilitate the interactive learning of CRE by using the companion Web site and Wolfram and Python sliders to explore Living Example Problems to gain a deep understanding of the reaction and the reactors in which they take place.
2. To provide additional technical material in the extended material and in the Professional Reference Shelf.
3. To provide tutorial information and self-assessment exercises such as the i>clicker questions.
4. To make the learning of CRE fun through the use of interactive games, LEP simulations, and computer experiments, which allow one to use Inquiry-Based Learning (IBL) to explore the concepts of CRE.

D.1 How to Use the Web Site

I would like to expand a bit on a couple of things that we use extensively, namely the useful links. These items can be accessed by clicking on the Chapter number on the Home Page. After clicking on Chapter 1 shown in Figure I-3, one will arrive at

Useful Links

Living Example Problems Polymath, Python, Matlab and Wolfram	Extra Help Multiple Resources extra problems, screencasts and lecture notes	Additional Materials New Technical Material, Detailed Derivations and Web Modules	Professional Reference Shelf Material important to the practicing engineer that is not necessarily covered in all CRE courses.	Computer Simulation Problem Statements Digital problems using Wolfram and Python as well as Matlab and Polymath	YouTube Videos Humorous videos covering topics varying from example problems to light hearted breaks from studying
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Evaluation

Self Tests Interactive problems with solutions to provide extra practice of concepts	i>Clicker Questions Interactive multiple choice questions to help access your understanding of the material
--	--

Figure I-3 Access to useful links

(<http://www.umich.edu/~elements/6e/01chap/obj.html#/>).

The important point I want to make here is the list of all resources shown in [Figures I-3 and I-4](#). In addition to listing the objectives for this chapter, you will find all the major hot buttons, such as

Useful Links



Evaluation



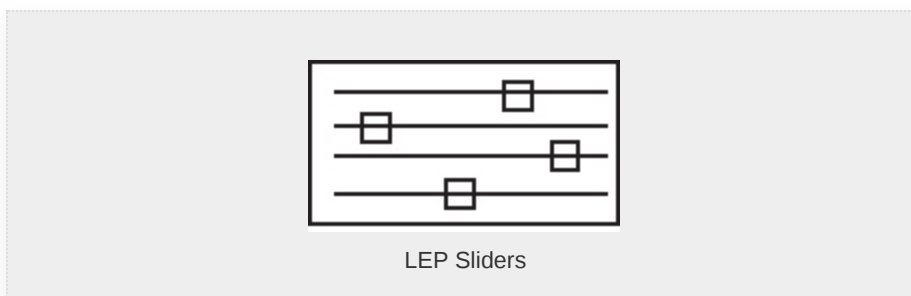
Figure I-4 Useful links.

The *Living Example Problems* (LEPs), including *COMSOL*, have all numerical Example Problems programmed and read for use with the click of a button. The *Extra Help* includes interactive notes, screen casts, and techniques that facilitate learning and studying. The *Additional Material* and *Professional Reference Shelf* provide expanded derivations and material that is relevant to CRE, but did not make the final cut owing to limitations of the thickness of the book; that is, students can't concentrate about CRE if their backpacks are so heavy they are suffering from carrying them. The *Self Tests* and *i>Clicker Questions* help readers gauge their level of understanding.

D.2 Living Example Problems (LEPs)

What are LEPs? LEPs are **Living Example Problems** that are really simulations that can be used to carry out experiments on the reactor and the reactions occurring inside the reactor. Here, rather than being stuck with the parameter values the author gives, the LEPs allow you to change the value of a parameter and see its effect on the reactor's operation. LEPs have been unique to this book since their invention and inclusion in the Third Edition of this title, published in 1999. However, Wolfram and Python have allowed us to take LEPs to a new level, resulting in a minor paradigm shift. The LEPs use simulation software, which can be downloaded directly onto one's own computer in order to "play with" the key variables and assumptions. Using the LEPs to explore the problem and asking "What if...?" questions provide students with the opportunity to practice critical and creative thinking skills. To guide students in using these simulations, questions for each chapter are given on the Web site (e.g., <http://www.umich.edu/~elements/6e/12chap/obj.html>).² In this edition, there are more than 80 interactive simulations (LEPs) provided on the Web site. It is the author's strong belief that using the LEP sliders will develop an intuitive feel for Chemical Reaction Engineering (CRE).

²See Introduction section D and Appendix I for ideas on how to use the LEPs.



The simulations labeled **Stop and Smell the Roses** are comprehensive-interactive simulations that will provide significant insight and an intuitive feel for the reactor and the reaction when you take the time to explore the parameters using the Wolfram or Python sliders. #wellworthyourtime

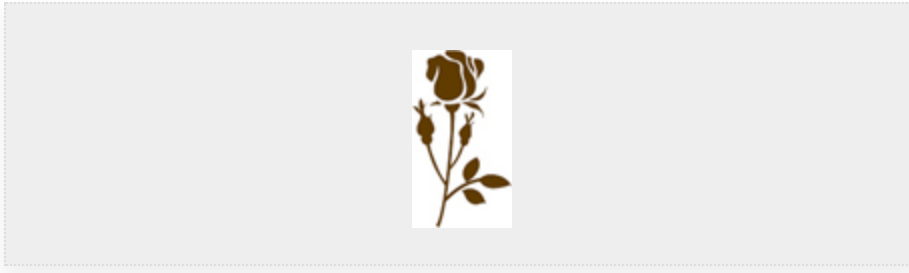


Figure I-5 shows a screen shot of the LEPs for Chapter 5. One simply clicks on the hot button of the desired programming language (Wolfram, Python) and the program loads, then uses the sliders to explore the reactors operating variables and the property parameters.

Chapter 5: Isothermal Reactor Design: Conversion

Living Example Problems

Note: When downloading Python code files over Chrome browser, you may see a security warning. We assure you that these files are secure and you may keep them on your computer.

Living Example Problem	Polymath™ Code	Python Code	MATLAB Code	Wolfram CDF Code *	AspenTech™
Example 5-3 Plug-flow reactor	LEP-5-3.pol	LEP-5-3.py	LEP-5-3.zip	LEP-5-3.cdf	
Example 5-4 Pressure Drop in a Packed Bed		LEP-5-4.py		LEP-5-4.cdf	
Example 5-5 Effect of pressure drop on conversion	LEP-5-5.pol	LEP-5-5.py	LEP-5-5.zip	LEP-5-5.cdf	
Example 5-6 Robert Worries what if...	LEP-5-6.pol	LEP-5-6.py		LEP-5-6.cdf	
Example 5-7 Calculating X in a reactor with Pressure drop	LEP-5-7.pol	LEP-5-7.py	LEP-5-7.zip	LEP-5-7.cdf	Tutorial, ASPEN Backup File
Example 5-8 Reversible gas-phase reaction in a packed bed with pressure drop	LEP-5-8.pol	LEP-5-8.py	LEP-5-8.zip	LEP-5-8.cdf	

1. **LEP** : Click [here](#) to view LEP Tutorials
2. **Polymath** : Click [here](#) to view Polymath Tutorials
3. **Python** : Click [here](#) to view Python Tutorials
4. **MATLAB** : Click [here](#) to view MATLAB Tutorials
5. **Wolfram** : Click [here](#) to download Wolfram CDF Player. You can run the CDF code, download Wolfram CDF Player for free. Click [here](#) to view Wolfram Tutorials

Figure I-5 Living Example Problems (LEPs).

It has been shown that students using **inquiry-based learning (IBL)** have a much greater understanding of information than students educated by traditional methods (*Univers. J. Educ. Res.*, 2(1), 37–41 (2014)).^{3,4} The learning was most definitely enhanced when it came to questions that required interpretation such as, “Why did the temperature profile go through a minimum?” Each chapter has a section on Computer

Simulations and Experiments that will guide students in practicing **IBL**. Students have commented that the Wolfram slider LEPs are a very efficient way to study the operation of a chemical reactor. For example, one can carry out a simulation experiment on the reactor (e.g., LEP 13-2) to investigate what conditions would lead to unsafe operation.

³ Ibid, Adbi, A.

⁴ Documentation of the advantages of IBL can be found at *Studies in Higher Education*, 38(9), 1239–1258 (2013),
<https://www.tandfonline.com/doi/abs/10.1080/03075079.2011.616584>

You will note the tutorials listed just below the screen shot of the Living Example Problems page. There are 11 Polymath tutorials, and one LEP tutorial for each Polymath, Wolfram, Python, and MATLAB in later chapters. There are also six COMSOL tutorials. To access the LEP software you want to use, that is, Polymath, Wolfram, Python, or MATLAB, just click on the appropriate hot button, and then load and run the LEPs in the software you have chosen. Homework problems using the LEPs have been added to each chapter that requires the use of Wolfram, Python, and Polymath. The use of the LEP sliders will allow students to vary the reaction and reactor parameters to get a thorough understanding of the Computer Simulation Problems.

D.3 Extra Help

The components of Extra Help are shown in Figure I-6.

Extra Help

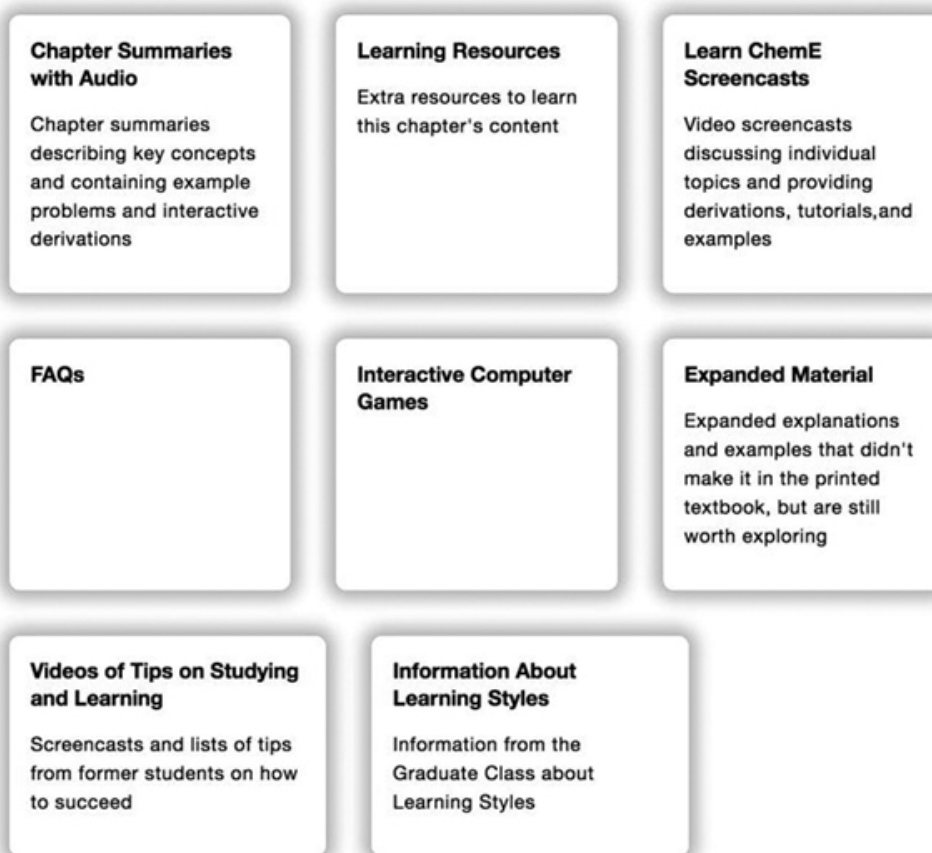


Figure I-6 Screen shot of Extra Help.

The *Learning Resources* give an overview of the material in each chapter through the Interactive *Summary Notes*. These notes include on-demand derivations of key equations, audio explanations, additional resources such as *Interactive Computer Games (ICGs)*, computer simulations and experiments, Web modules of novel applications of CRE, solved problems, study aids, *Frequently Asked Questions (FAQs)*, Microsoft PowerPoint lecture slides, and links to *LearnChemE videos*. The Web modules consist of a number of examples that apply key CRE concepts to both standard and

nonstandard reaction engineering problems (e.g., glow sticks, the use of wetlands to degrade toxic chemicals, and pharmacokinetics of death from a cobra bite). The Web modules can be loaded directly from the CRE Web site (http://www.umich.edu/~elements/6e/web_mod/index.html). These resources are described in Appendix I.

D.4 Additional Material

The additional material shown in Figure I-7 includes derivations, examples, and novel applications of CRE principles that build on the CRE algorithm in the text.

Additional Materials

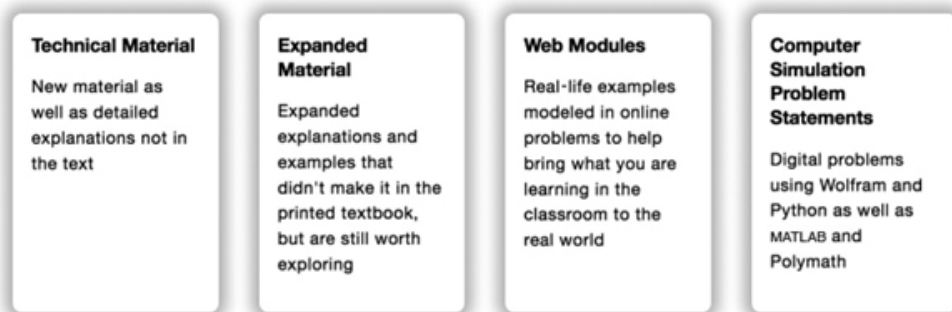


Figure I-7 Screen shot of Additional Materials.

D.5 Professional Reference Shelf

This material is important to the practicing engineer, such as details of the industrial reactor design for the oxidation of SO_2 and design of spherical reactors and other material that is typically not included in the majority of chemical reaction engineering courses.

D.6 Computer Simulations, Experiments, and Problems

As discussed in section D.2, these problems help guide students to understand how the parameters and operating conditions affect the reaction and the reactors. These problems are in the printed version of the second edition of *Essentials of Chemical Reaction Engineering*, and the sixth edition of *Elements of Chemical Reaction Engineering*, but not in the printed version of the fifth edition of *Elements of Chemical Reaction Engineering*.

D.7 YouTube Videos

Here, you will find links to humorous YouTube videos made by students in Professor Alan Lane's 2008 chemical reaction engineering class at the University of Alabama, as well as videos from the University of Michigan's 2011 CRE class, which includes the ever-popular chemical engineering classic, "Reaction Engineering Gone Wrong." If you have a humorous YouTube video on CRE, I would be happy to consider linking to it.

D.8 COMSOL

The COMSOL Multiphysics software is a partial differential equation solver that is used with [Chapters 13 and 18](#) to view both axial and radial temperature and concentration profiles. For users of this text, COMSOL has provided a special Web site that includes a step-by-step tutorial, along with examples. See [Figure 18-15 on page 964](#) and also (<https://www.comsol.com/books/elements-of-chemical->

reaction-engineering-5th/models). Further details are given in the Living Example Problems on the Web site.

E. WHY DO WE ASSIGN HOMEWORK PROBLEMS?

The working of homework problems facilitates a *true understanding* of CRE. After reading a chapter, the student may feel they have an understanding of the material. However, when attempting a new or slightly different application of CRE in a homework problem, students sometimes need to go back and reread different parts of the chapter to get the level of understanding needed to eventually solve the homework problem. **Polymath** is a most user-friendly software and is recommended to solve these end-of-chapter problems.

I would like to point out research has shown (*J. Exp. Psychol. Learn. Mem. Cogn.*, 40, 106–114 (2014)) that if you ask a question of the material before reading the material you will have greater retention. Consequently, the first question of every chapter will have such a question on that chapter's material. For Chapter 1, the question is, “Is the generation term, G , the only term in the mole balance that varies for each type of reactor?” The questions that follow are qualitative in Q1-2_A and Q2-3_A, and so on.

It is recommended that students first work through *Computer Simulation Problems* that use MATLAB, Python, and Wolfram before going on to other problems. These example problems are a key resource. The subscript letter (A, B, C, or D) after

each problem number denotes the difficulty of the problem (i.e., A = easy; D = difficult). The A- and B-level problems should be worked before tackling the more challenging homework problems in a given chapter.

F. ARE THERE OTHER WEB SITE RESOURCES?

CRE Web Site

(<http://www.umich.edu/~elements/6e/index.html>). A complete description of all the educational resources and ways to use them can be found in [Appendix I](#).

Safety Web Site. During the past two years, a safety Web site has been developed for all core chemical engineering courses (<http://umich.edu/~safeche/>). A section at the end of each chapter called *And Now... A Word From Our Sponsor-Safety (AWFOS-S)* has taken the tutorials and distributed them in chapters throughout the text. A safety module for both the T2 Laboratory incident ([http://umich.edu/~safeche/assets/pdf/courses/Problems/CRE/344ReactionEngrModule\(1\)PS-T2.pdf](http://umich.edu/~safeche/assets/pdf/courses/Problems/CRE/344ReactionEngrModule(1)PS-T2.pdf)) and the Monsanto incident ([http://umich.edu/~safeche/assets/pdf/courses/Problems/CRE/344ReactionEngrModule\(2\)PS-Monsanto.pdf](http://umich.edu/~safeche/assets/pdf/courses/Problems/CRE/344ReactionEngrModule(2)PS-Monsanto.pdf)) can be found on the safety Web site. A safety algorithm is included in both of these modules.

What Entertainment Is on the Web Site?

A. YouTube Videos. The humorous videos are discussed in Section D, what are the components of the CRE Web site, above.

B. Interactive Computer Games (ICGs). Students have found the Interactive Computer Games to be both fun and extremely useful for reviewing the important chapter concepts and then applying them to real problems in a unique and entertaining fashion. The following ICGs are available on the Web site:

- Quiz Show I (Ch. 1)
- Reactor Staging (Ch. 2)
- Quiz Show II (Ch. 4)
- Murder Mystery (Ch. 5)
- Tic Tac (Ch. 5)
- Ecology (Ch. 7)
- The Great Race (Ch. 8)
- Enzyme Man (Ch. 9)
- Catalysis (Ch. 10)
- Heat Effects I (Ch. 12)
- Heat Effects II (Ch. 12)

As you play these interactive games, you will be asked a number of questions related to the corresponding material in the textbook. The ICG keeps track of all the correct answers and at the end of the game displays a coded performance

number that reflects how well you mastered the material in the text. Instructors have a manual to decode the performance number.

G. HOW CAN ONE'S CRITICAL THINKING AND CREATIVE THINKING SKILLS BE ENHANCED?

([HTTP://UMICH.EDU/~SCPS/HTML/PROBSO LV/STRATEGY/CRIT-N-CREAT.HTM](http://umich.edu/~scps/html/probsoLV/strategy/crit-n-creat.htm))

A third goal of this book is to enhance critical and creative thinking skills. How does one enhance their critical thinking skills? Answer: By learning how to ask critical thinking questions and taking critical thinking actions of the type given on the Web site in Tables P-2 and P-3. Further discussion is found in the Complete Preface-Introduction on the Web site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>).

The goal to enhance creative thinking skills is achieved by using a number of problems that are open-ended to various degrees. With these, students can practice their *creative skills* by exploring the example problems, as outlined at the beginning of the homework problems of each chapter, and by making up and solving an original problem using the suggestions in Table P-4 on the Web site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>).

One of the major goals at the undergraduate level is to bring students to the point where they can solve complex reaction problems, such as multiple reactions with heat effects, and then ask “What if . . . ?” questions and look for optimum operating conditions and unsafe operating conditions. The solution to one problem exemplifies this goal: the Manufacture of Styrene (Chapter 12, Problem P12-26_C). This problem is particularly interesting because two reactions are endothermic and one is exothermic.

1. Ethylbenzene \rightarrow Styrene + Hydrogen: Endothermic
2. Ethylbenzene \rightarrow Benzene + Ethylene: Endothermic
3. Ethylbenzene + Hydrogen \rightarrow Toluene + Methane: Exothermic

The student could get further practice in critical and creative thinking skills by adding any of the following exercises (x), (y), and (z) to any of the end-of-chapter homework problems.

1. (x) How could you make this problem easier? More difficult?
2. (y) Critique your answer by writing a critical thinking question.
3. (z) Describe two ways you could work this problem incorrectly.

H. WHAT'S NEW IN THIS EDITION?

This textbook and Web site interaction is a mini paradigm shift in active learning. There is a symbiotic relationship between the Web site and the textbook that allows the student to get an intuitive feel of the reactions and reactors. Here the students use the software packages of Wolfram, Python, MATLAB, and

Polymath to explore the reactions and the reactors. In addition, this edition maintains all the strengths of the previous editions of *Elements of Chemical Reaction Engineering* by using algorithms that allow students to learn chemical reaction engineering through logic rather than memorization. Figure I-8 shows the Extra Help associated with the Chapter 1 material.

Chapter 1: Mole Balances

Extra Help

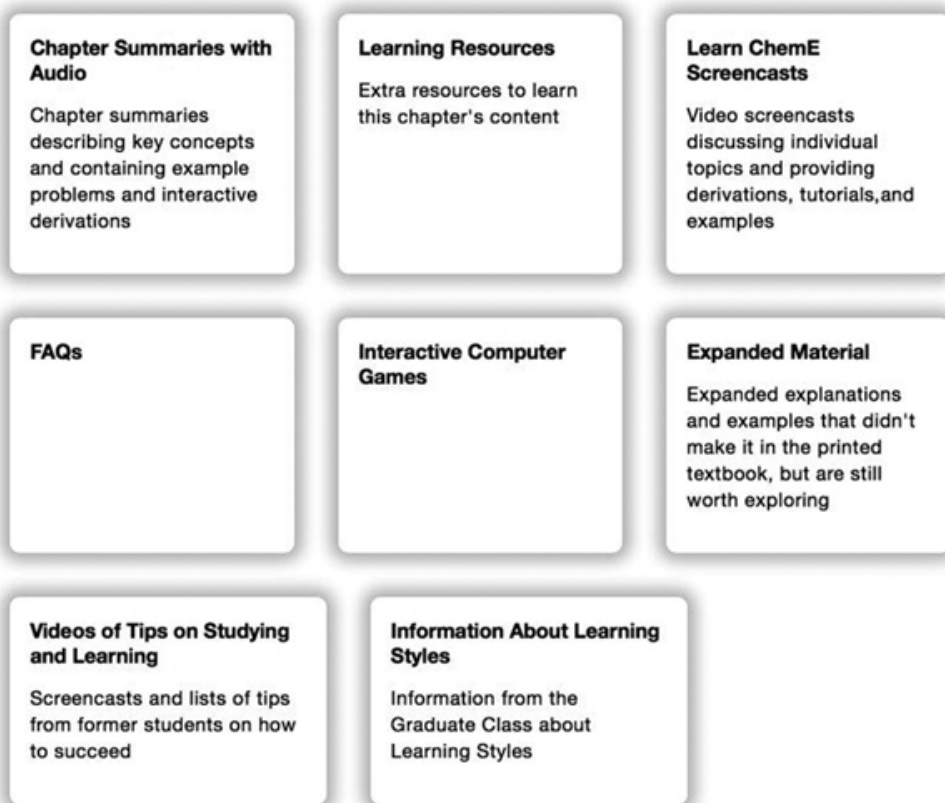




Figure I-8 Screen shot of Extra Help.

The Web site has been greatly expanded to address the Felder/Solomon Inventory of Different Learning Styles⁵ through interactive Summary Notes, i>clicker questions and

Interactive Computer Games (ICGs). For example, as discussed in Appendix I the Global Learner can get an overview of the chapter material from the Summary Notes; the Sequential Learner can use all the i>clicker questions and  hot buttons; and the active learner can interact with the ICGs and use the  hot buttons in the Summary Notes.

⁵<https://www.engr.ncsu.edu/stem-resources/legacy-site/>

The Web site for this new edition provides thorough interactive example problems using Polymath, Wolfram, Python, and MATLAB. These software packages are used to perform experiments on the reactor and the reactions and to then write a set of conclusions describing what the experiments revealed. In addition, there is a Safety Section at the end of each chapter that is linked to the safety Web site (<http://umich.edu/~safeche/>).

As with the past edition, an Aspen tech tutorial is provided for four example problems on the CRE Web site (<http://www.umich.edu/~elements/6e/software/aspen.html>).

And most importantly we have to always remember that:

*Hopefully all intensive laws tend often to have exceptions.
Very important concepts take orderly, responsible statements.
Virtually all laws intrinsically are natural thoughts. General observations become laws under experimentation.*

I. HOW DO I SAY THANK YOU?

There are so many colleagues and students who contributed to this book that it would require another chapter to thank them all in an appropriate manner. I again acknowledge all my friends, students, and colleagues for their contributions to the sixth edition of *Elements of Chemical Reaction Engineering*. I would like to give special recognition as follows.

First of all, I am indebted to Ame and Catherine Vennema family, whose gift of an endowed chair greatly facilitated the completion of this project. My colleague Dr. Nihat Gürmen coauthored the original Web site during the writing of the fourth edition of *Elements of Chemical Reaction Engineering*. He has been a wonderful colleague to work with. I also would like to thank University of Michigan undergraduate ChE students who served early on as webmasters for the CRE Web site namely Arthur Shih, Maria Quigley, Brendan Kirchner, and Ben Griessmann. More recently CSE students, Jun Kyungjun Kim, Elsa Wang, Wen He, Kiran Thwardas, Tony Hanchi Zhang, Arav Agarwal, and Lisa Ju Young Kim worked on both the CRE Web site and the Safety Web site.

Michael B. Cutlip, coauthor of Polymath, not only gave suggestions and a critical reading of the first edition, but also, most importantly, provided continuous support and encouragement throughout the course of this project. Professor Chau-Chyun Chen provided two AspenTech examples. Ed Fontes at COMSOL Multiphysics not only provided encouragement, but also provided a COMSOL Web site containing a tutorial with CRE examples. Julie Nahil, senior content producer at Pearson for all of my book projects, has

been fantastic throughout. She provided encouragement, attention to detail, and a great sense of humor, which were greatly appreciated. Indian Institute of Technology (IIT)–Guwahati chemical engineering graduate Mayur Tikmani was amazing in helping to get this text to the compositor in time. He provided all of the Wolfram coding for the LEP examples; when necessary, checked and corrected all the Polymath, Wolfram, Python, and MATLAB tutorials on the CRE Web site; and also helped proofread all the chapters. A number of summer interns have helped with preparation of the additional material for the book, especially the Safety Web site, as well as related material. Kaushik Nagaraj developed and provided the MATLAB coding for the simulations in Section 3.5 while Jakub Wlodarczyk (Warsaw University of Technology, Poland) checked all of the i>clicker questions and solutions. Students from Indian Institute of Technology, Bombay, who contributed to AWFOS-S at the end of each chapter include Kaushik Nagaraj, Triesha Singh, Reshma Kalyan Sundaram, Kshitiz Parihar, Manan Agarwal, Kushal Mittal, and Sahil Kulkarni. Vaibav Jain from IIT Delhi worked on the Solutions Manual. From the University of Michigan, Kara Steshetz, Alec Driesenga, Maeve Gillis, and Lydia Peters also worked on the Safety material.

I would like to thank the following people for various different reasons: Waheed Al-Masry, David Bogle, Lee Brown, Hank Browning, Thorwald Brun, John Chen, Stu Churchill, Dave Clough, Jim Duderstadt, Tom Edgar, John Falconer, Claudio Vilas Boas Favero, Rich Felder, Asterios Gavriilidis, Sharon

Glotzer, Joe Goddard, Robert Hesketh, Mark Hoefner, Jay Jorgenson, Lloyd Kemp, Kartic Khilar, Costas Kravaris, Steve LeBlanc, Charlie Little, Kasper Lund, the Magnuson family, Joe Martin, Susan Montgomery, our parents, Guiseppe Parravano, Max Peters, Sid Sapakie, Phil Savage, Jerry Schultz, Johannes Schwank, Mordechai Shacham, Nirala Singh who class-tested this edition, Michael Stamatakis, Klaus Timmerhaus, my good friend Jim Wilkes, June Wispelwey, my grandchildren Max and Joe (aka “Jofo”) Fogler, Sophia and Nicolas Bellini, my children, Peter, Rob, and Kristi, my parents, the Emeritus Faculty Friday Lunch Group, and the Starbucks staff at Plymouth Road Mall, where most of my final editing of this book was accomplished.

Laura Bracken is very much a part of this book. I appreciate her excellent deciphering of equations and scribbles, her organization, her discovery of mistakes and inconsistencies, and her attention to detail in working with the galleys and page proofs. Through all this was her ever-present wonderful disposition. Thanks, Radar!!

Finally, to my wife Janet, love and thanks. Not only did she type the first edition of this book—can you believe on a Royal Select typewriter!—she also was a sounding board for so many things in this edition. She was always willing to help with the wording and sentence structure. For example, I often asked her, “Is this the correct phrase or word to use here?” or “Should I mention Jofostan here?” Jan also helped me learn that creativity involves knowing what to leave out. Without

her enormous help and support the project would never have been possible.

HSF
Ann Arbor, Michigan
May 2020

Updates, FAQs, Web Modules, LEPs, exciting new applications, and typographical errors can all be accessed from the Home page on the companion Web site:

www.umich.edu/~elements/6e/index.html



About the Author



H. Scott Fogler is the Ame and Catherine Vennema professor of chemical engineering and the Arthur F. Thurnau professor at the University of Michigan in Ann Arbor. He was recognized as a 2020 Michigan Distinguished Professor of the year, and was the 2009 National President of the American Institute of Chemical Engineers (AIChE), a 50,000-member organization. He received his B.S. from the University of Illinois and his M.S. and Ph.D. from the University of Colorado. He is also the author of the *Essentials of Chemical Reaction Engineering, Second -Edition*, and coauthor, with Steven LeBlanc and Benjamin Rizzo, of *Strategies for Creative Problem Solving, Third Edition*.

Professor Fogler's research interests include flow and reaction in porous media, wax and asphaltene deposition, asphaltene flocculation kinetics, gelation kinetics, colloidal phenomena, and catalyzed dissolution. He has been research advisor to 49

Ph.D. students and has more than 250 refereed publications in these areas. Fogler has chaired ASEE's Chemical Engineering Division, served as director of the AIChE, and earned the Warren K. Lewis Award from AIChE for contributions to chemical engineering education. He also received the Chemical Manufacturers Association's National Catalyst Award, and the 2010 Malcom E. Pruitt Award from the Council for Chemical Research (CCR), and the 2019 Van Antwerpen Award from AIChE. He is the recipient of 12 named lectureships and is associate editor of *Energy & Fuels*. On April 15, 2016, Scott received a *doctor honoris causa* degree from the Universitat Rovira i Virgili, Tarragona, Spain.

1. Mole Balances

The first step to knowledge is to know that we are ignorant.

—Socrates (470–399 B.C.)

The Wide, Wild World of Chemical Reaction Engineering

Chemical kinetics is the study of chemical reaction rates and reaction mechanisms. The study of chemical reaction engineering (CRE) combines the study of chemical kinetics with the reactors in which the reactions occur. Chemical kinetics and reactor design are at the heart of producing almost all industrial chemicals, such as the manufacture of phthalic anhydride shown in [Figure 1-1](#). It is primarily a knowledge of chemical kinetics and reactor design that distinguishes the chemical engineer from other engineers. The selection of a reaction system that operates in the safest and most efficient manner can be the key to the economic success or failure of a chemical plant. For example, if a reaction system produces a large amount of undesirable product, subsequent purification and separation of the desired product could make the entire process economically unfeasible.

How is a chemical engineer different from other engineers?

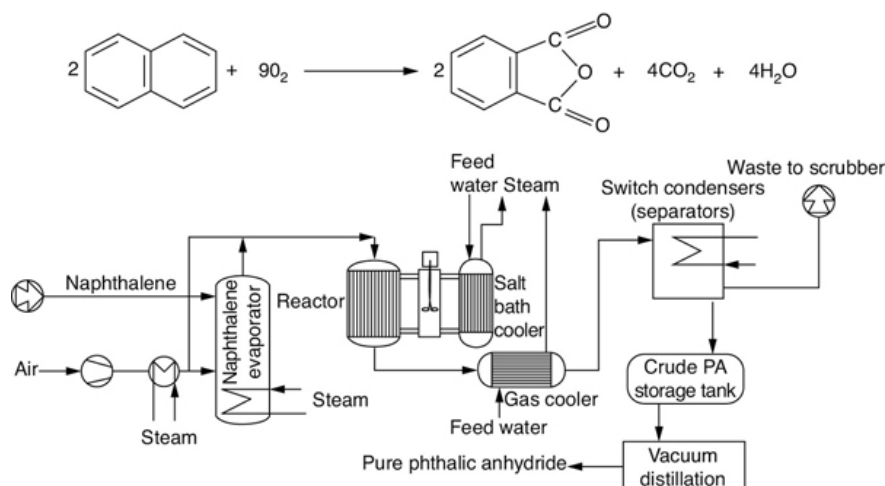


Figure 1-1 Manufacture of phthalic anhydride.

The chemical reaction engineering (**CRE**) principles learned here can also be applied in many areas, such as waste water treatment, microelectronics, nanoparticles fabrication, and pharmacokinetics of living systems, in addition to the more traditional areas of the manufacture of chemicals and pharmaceuticals. Some of the examples that illustrate the wide application of CRE principles in this book are shown in [Figure 1-2](#). These examples, which can be found either in the text or as Web modules, include modeling smog in the Los Angeles (L.A.) basin ([Chapter 1 Web module](#)), the digestive system of a hippopotamus ([Chapter 2 Web module](#)) on the CRE Web site, (www.umich.edu/~elements/6e/index.html), and molecular CRE ([Chapter 3 Web module](#)). Also shown are the manufacture of ethylene glycol (antifreeze), where three of the most common types of industrial reactors are used ([Chapters 5 and 6](#)), and the use of wetlands to degrade toxic chemicals ([Chapter 7](#) on the CRE Web site). Other examples shown are the solid–liquid kinetics of acid–rock interactions to improve oil recovery ([Chapter 7](#)); pharmacokinetics of cobra bites ([Chapter 8 Web module](#)); free-radical scavengers used in the design of motor oils ([Chapter 9](#)); enzyme kinetics ([Chapter 9](#)) and drug delivery pharmacokinetics ([Chapter 9](#) on the CRE

Web site); heat effects, runaway reactions, and plant safety (Chapters 11–13); and increasing the octane number of gasoline and the manufacture of computer chips (Chapter 10).

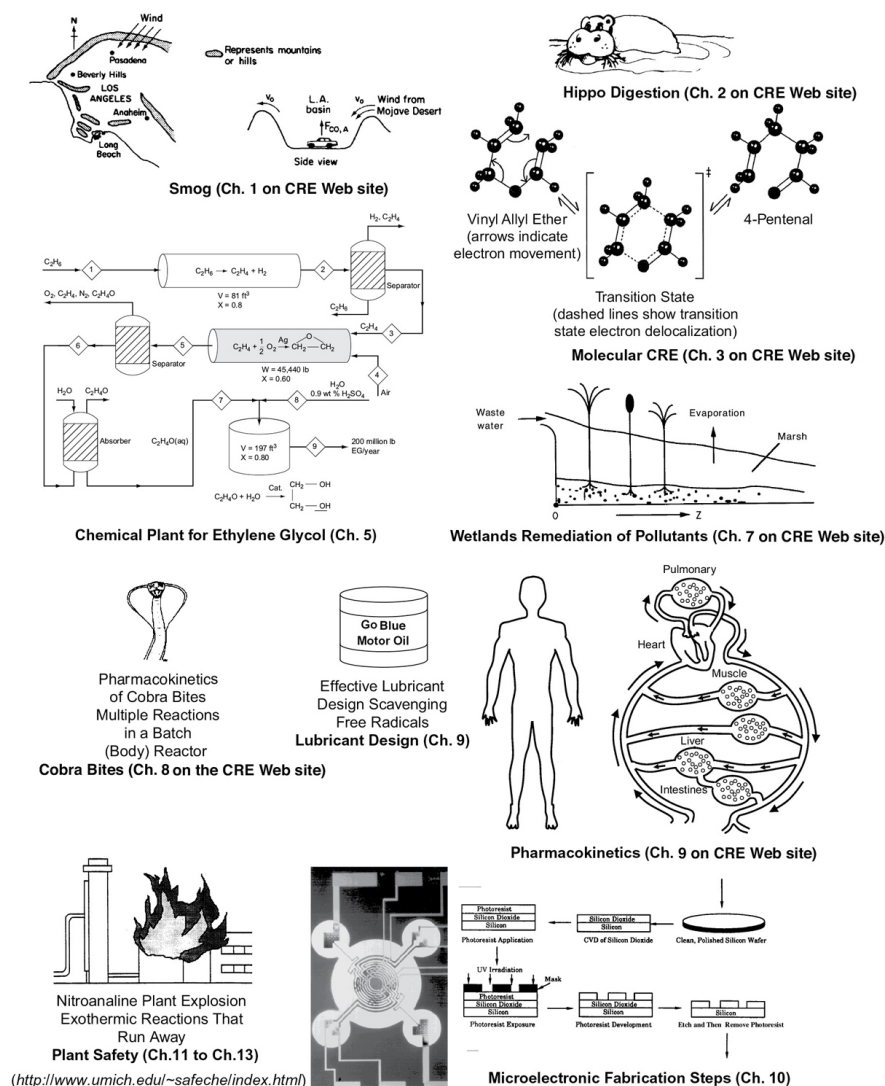


Figure 1-2 The wide world of CRE applications.

Overview. This chapter develops the first building block of chemical reaction engineering, *mole balances*, which will be used continually throughout the text. After completing this chapter, you will be able to:

- Describe and define the rate of reaction
- Derive the general mole balance equation
- Apply the general mole balance equation to the four most common types of industrial reactors

Before entering into discussions of the conditions that affect chemical reaction rates mechanisms and reactor design, it is necessary to account for the various chemical species entering, leaving, reacting, and accumulating in a system. This accounting process is achieved through overall mole balances on individual species in the reacting system. In this chapter, we develop a general mole balance that can be applied to any species (usually a chemical compound) entering, leaving, reacting, and accumulating within the reaction system volume. After defining the rate of reaction, $-r_A$, we show how the general mole balance equation (GMBE) may be used to develop a preliminary form of the design equations of the most common industrial reactors (<http://encyclopedia.che.engin.umich.edu/Pages/Reactors/menu.html>).

- Batch Reactor (BR)
- Continuous-Stirred Tank Reactor (CSTR)
- Plug-Flow Reactor (PFR)
- Packed-Bed Reactor (PBR)

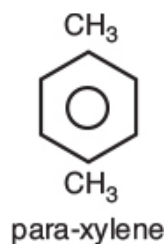
In developing these equations, the assumptions pertaining to the modeling of each type of reactor are delineated. Finally, a brief summary and series of short review questions and problems are given at the end of the chapter.

1.1 THE RATE OF REACTION, $-R_A$

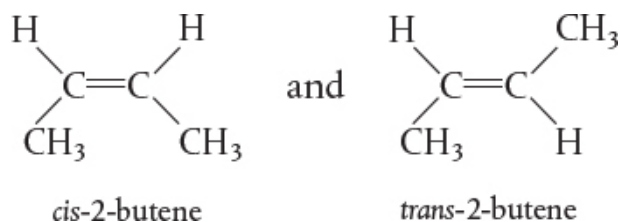
Identify

- Kind
- Number
- Configuration

The rate of reaction tells us how fast the number of moles of one chemical species are being consumed to form another chemical species. The term *chemical species* refers to any chemical component or element with a given *identity*. The *identity* of a chemical species is determined by the *kind*, *number*, and *configuration* of that species' atoms. For example, the species para-xylene is made up of a



fixed number of specific atoms in a definite molecular arrangement or configuration. The structure shown illustrates the kind, number, and configuration of atoms on a molecular level. Even though two chemical compounds have exactly the same kind and number of atoms of each element, they could still be different species because of different configurations. For example, 2-butene has four carbon atoms and eight hydrogen atoms; however, the atoms in this compound can form two different arrangements.



As a consequence of the different configurations, these two isomers display different chemical and physical properties. Therefore, we consider them as two different species, even though each has the same number of atoms of each element.

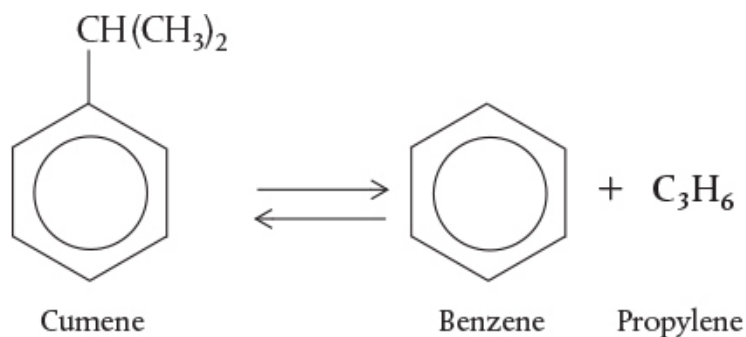
When has a chemical reaction taken place?

We say that a *chemical reaction* has taken place when a detectable number of molecules of one or more species have lost their identity and assumed a new form by a change in the kind or number of atoms in the compound and/or by a change in structure or configuration of these atoms. In this classical approach to chemical change, it is assumed that the total mass

is neither created nor destroyed when a chemical reaction occurs. The mass referred to is the total collective mass of all the different species in the system. However, when considering the individual species involved in a particular reaction, we do speak of the rate of disappearance of mass of a particular species. *The rate of disappearance of a species, say species A, is the number of A molecules that lose their chemical identity per unit time per unit volume through the breaking and subsequent re-forming of chemical bonds during the course of the reaction.* In order for a particular species to “appear” in the system, some prescribed fraction of another species must lose its chemical identity.

Definition of Rate of Reaction

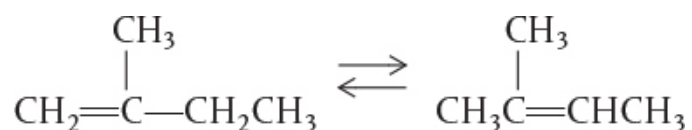
There are three basic ways a species may lose its chemical identity: decomposition, combination, and isomerization. In *decomposition*, the molecule loses its identity by being broken down into smaller molecules, atoms, or atom fragments. For example, if benzene and propylene are formed from a cumene molecule,



A species can lose its identity by

- Decomposition
- Combination
- Isomerization

the cumene molecule has lost its identity (i.e., disappeared) by breaking its bonds to form these molecules. A second way that a molecule may lose its chemical identity is through *combination* with another molecule or atom. In the above reaction, the propylene molecule would lose its chemical identity if the reaction were carried out in the reverse direction, so that it combined with benzene to form cumene. The third way a species may lose its chemical identity is through *isomerization*, such as the reaction

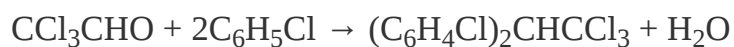


Here, although the molecule neither adds other molecules to itself nor breaks into smaller molecules, it still loses its identity through a change in configuration.

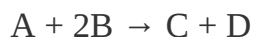
To summarize this point, we say that a given number of molecules (i.e., moles) of a particular chemical species have reacted or disappeared when the molecules have lost their chemical identity.

The rate at which a given chemical reaction proceeds can be expressed in different ways by referring it to different chemical species in the reaction. To illustrate, consider the reaction of chlorobenzene with chloral in the presence of

fuming sulfuric acid to produce the banned insecticide DDT (dichlorodiphenyl trichloroethane).



Letting the symbol A represent chloral, B be chlorobenzene, C be DDT, and D be H_2O , we obtain



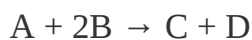
What is $-r_A$?

The rate of reaction, $-r_A$, is the number of moles of A (e.g., chloral) reacting (disappearing) per unit time per unit volume ($\text{mol}/\text{dm}^3\cdot\text{s}$).

The numerical value of the rate of disappearance of reactant A, $-r_A$, is a positive number.

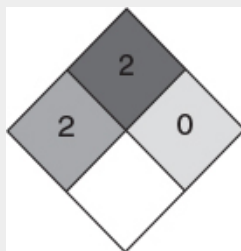
Example 1–1 Rates of Disappearance and Formation

Chloral is being consumed at a rate of 10 moles per second per m^3 when reacting with chlorobenzene to form DDT and water in the reaction described above. In symbol form, the reaction is written as



Write the rates of disappearance and formation (i.e., generation; $\text{mol}/\text{m}^3\cdot\text{s}$) for each species in this reaction when the rate of reaction of chloral [A] ($-r_{\text{A}}$) is as $10 \text{ mol}/\text{m}^3\cdot\text{s}$.

NFPA Diamond



DDT See [Section 2.7](#)

Solution

(a) Rate of disappearance of A = $-r_{\text{A}} = 10 \text{ mol}/\text{m}^3\cdot\text{s}$
Chloral[A]

:

Rate of formation of A = $r_{\text{A}} = -10 \text{ mol}/\text{m}^3\cdot\text{s}$

(b) For every mole of chloral that disappears, two
Chlorobenz moles of chlorobenzene [B] also disappear.
ene[B]:

Rate of disappearance of B = $-r_B = -2r_A = 20 \text{ mol/m}^3 \cdot \text{s}$

Rate of formation of B = $r_B = -20 \text{ mol/m}^3 \cdot \text{s}$

(c) For every mole of chloral that disappears, one mole of DDT [C] appears. $r_C = -r_A$

DDT[C]:

Rate of disappearance of C = $-r_C = -10 \text{ mol/m}^3 \cdot \text{s}$

Rate of formation of C = $r_C = -r_A = -(-10 \text{ mol/m}^3 \cdot \text{s}) = 10 \text{ mol/m}^3 \cdot \text{s}$

(d) Same relationship to chloral as the relationship to DDT

Water[D]:

Rate of formation of D = $r_D = 10 \text{ mol/m}^3 \cdot \text{s}$

Rate of disappearance of D = $-r_D = -10 \text{ mol/m}^3 \cdot \text{s}$

$$-r_A = 10 \text{ mol A/m}^3 \cdot \text{s}^\dagger$$

$$r_A = -10 \text{ mol A/m}^3 \cdot \text{s}$$

Equation (3-1) page 77

Then

$$\frac{r_A}{-1} = \frac{r_B}{-2} = \frac{r_C}{1} = \frac{r_D}{1}$$

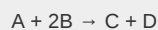
$$r_B = 2(r_A) = -20 \text{ mol B/m}^3 \cdot \text{s}$$

$$-r_B = 20 \text{ mol B/m}^3 \cdot \text{s}$$

$$r_C = -r_A = 10 \text{ mol C/m}^3 \cdot \text{s}$$

$$r_D = -r_A = 10 \text{ mol D/m}^3 \cdot \text{s}$$

[†]Tutorial Video: <https://www.youtube.com/watch?v=6mAqX31RRJU>



The convention

$$-r_A = 10 \text{ mol A/m}^3 \cdot \text{s}$$

$$r_A = -10 \text{ mol A/m}^3 \cdot \text{s}$$

$$-r_B = 20 \text{ mol B/m}^3 \cdot \text{s}$$

$$r_B = -20 \text{ mol B/m}^3 \cdot \text{s}$$

$$r_C = 10 \text{ mol C/m}^3 \cdot \text{s}$$

Analysis: The purpose of this example is to better understand the convention for the rate of reaction. The symbol r_j is the rate of formation (generation) of species j . If species j is a reactant, the numerical value of r_j will be a negative number. If species j is a product, then r_j will be a positive number. The rate of reaction, $-r_A$, is the rate of disappearance of reactant A and must be a positive number. A mnemonic relationship to help remember how to obtain relative rates of reaction of A to B, and so on, is given by Equation (3-1) on page 77.

In Equation (3-1) in Chapter 3, we will delineate the prescribed relationship between the rate of formation of one species, r_j (e.g., DDT [C]), and the rate of disappearance of another species, $-r_i$ (e.g., chlorobenzene [B]), in a chemical reaction.

Heterogeneous reactions involve more than one phase. In heterogeneous reaction systems, the rate of reaction is usually expressed in measures other than volume, such as reaction surface area or catalyst weight. For a gas–solid catalytic reaction, the gas molecules must interact with the solid catalyst surface for the reaction to take place, as described in Chapter 10.

What is $-r'_A$?

The dimensions of this heterogeneous reaction rate, $-r'_A$ (prime), *are the number of moles of A reacting per unit time per unit mass of catalyst* (e.g., mol/s·g catalyst).

Definition of r_j

Most of the introductory discussions on chemical reaction engineering in this book focus on homogeneous systems, in which case we simply say that r_j *is the rate of formation of species j per unit volume*. It is the number of moles of species j generated per unit volume per unit time.

We can say four things about the reaction rate r_j : r_j is

The rate law does not depend on the type of reactor used!!

- **The rate of formation of species j (mole/time/volume)**
- **An algebraic equation**
- **Independent of the type of reactor (e.g., batch or continuous flow) in which the reaction is carried out**
- **Solely a function of the properties of the reacting materials and reaction conditions (e.g., species concentration, temperature, pressure, or type of catalyst, if any) at a point in the system**

What is $-r_A$ a function of?

However, because the properties and reaction conditions of the reacting materials may vary with position in a chemical reactor, r_j can in turn be a function of position and can vary from point to point in the system. This concept is utilized in flow reactors.

The *reaction-rate law* relates the rate of reaction to species concentration and temperature as will be shown in [Chapter 3](#). The chemical reaction-rate-law is essentially an algebraic equation involving concentration, not a differential equation.¹ For example, the algebraic form of the rate law for $-r_A$ for the reaction



may be a linear function of concentration,

$$-r_A = kC_A \quad (1-1)$$

¹ For further elaboration on this point, see *Chem. Eng. Sci.*, 25, 337 (1970); B. L. Crynes and H. S. Fogler, eds., *AIChE Modular Instruction Series E: Kinetics*, 1, 1 New York: AIChE, 1981; and R. L. Kabel, "Rates," *Chem. Eng. Commun.*, 9, 15 (1981).

or it may be some other algebraic function of concentration, such as Equation [3-6](#) shown in [Chapter 3](#),

$$-r_A = kC_A^2 \quad (1-2)$$

OR

$$-r_A = \frac{k_1 C_A}{1 + k_2 C_A}$$

The rate law is an algebraic equation.

For a given reaction, the particular concentration dependence that the rate law follows (i.e., $-r_A = kC_A$ or $-r_A = kC_A^2$ or ...)

must be determined from *experimental observation*. Equation (1-2) states that the rate of disappearance of A is equal to a rate constant k (which is a function of temperature) times the square of the concentration of A. As noted earlier, by convention, r_A is the rate of formation of A; consequently, $-r_A$ is the rate of disappearance of A. Throughout this book, the phrase *rate of generation* means exactly the same as the phrase *rate of formation*, and these phrases are used interchangeably.

The convention

1.2 THE GENERAL MOLE BALANCE EQUATION (GMBE)

To perform a mole balance on any system, the system boundaries must first be specified. The volume enclosed by these boundaries is referred to as the *system volume*. We shall perform a mole balance on species j in a system volume, where species j represents the particular chemical species of interest, such as water or NaOH (Figure 1-3).

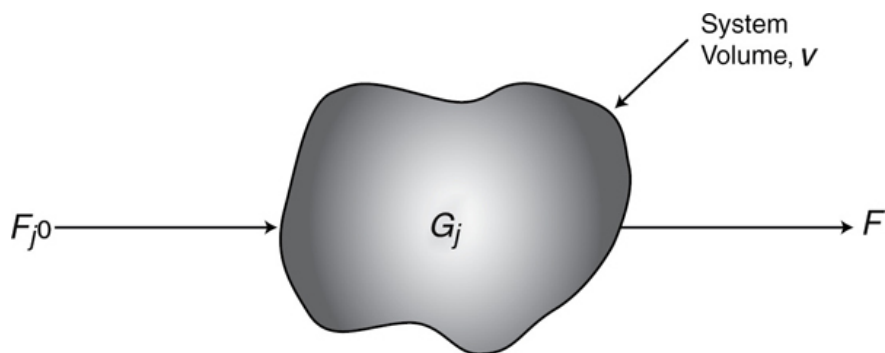


Figure 1-3 Mole balance on species j in a system volume, V .

A mole balance on species j at any instant in time, t , yields the following equation:

Mole balance

$$\begin{array}{ccccccccc}
 \left[\begin{array}{c} \text{Rate of flow} \\ \text{of } j \text{ into} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] & - & \left[\begin{array}{c} \text{Rate of flow} \\ \text{of } j \text{ out of} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] & + & \left[\begin{array}{c} \text{Rate of generation} \\ \text{of } j \text{ by chemical} \\ \text{reaction within} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] & = & \left[\begin{array}{c} \text{Rate of} \\ \text{accumulation} \\ \text{of } j \text{ within} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] \\
 \text{In} & - & \text{Out} & + & \text{Generation} & = & \text{Accumulation} \\
 F_{j0} & - & F_j & + & G_j & = & \frac{dN_j}{dt} \quad (1-3)
 \end{array}$$

Accumulation: In this equation, N_j represents the number of moles of species j in the system at time t and $\left(\frac{dN_j}{dt}\right)$ is the rate of accumulation of species j within the system volume.

Generation: If all the system variables (e.g., temperature, catalytic activity, and concentration of the chemical species) are spatially uniform throughout the system volume, the rate of generation of species j , G_j (moles/time) is just the product of the reaction volume, V , and the rate of formation of species j , r_j .

$$G_j = r_j \cdot V$$

$$\frac{\text{moles}}{\text{time}} = \frac{\text{moles}}{\text{time} \cdot \text{volume}} \cdot \text{volume}$$

Now suppose that the rate of formation of species j for the reaction varies with position in the system volume. That is, it has a value r_{j1} at location 1, which is surrounded by a small volume, ΔV_1 , within which the rate is uniform; similarly, the reaction rate has a value at location 2 and an associated volume, r_{j2} , and so on (Figure 1-4).

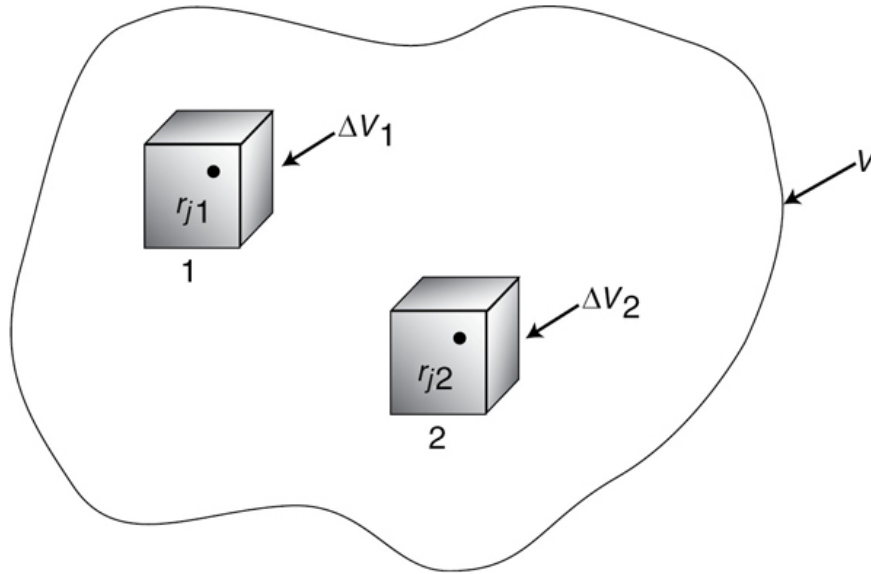


Figure 1-4 Dividing up the system volume, V .

The rate of generation, ΔG_{j1} , in terms of r_{j1} and subvolume ΔV_1 , is

$$\Delta G_{j1} = r_{j1} \Delta V_1$$

Similar expressions can be written for ΔG_{j2} and the other system subvolumes, ΔV_i . The total rate of generation within the system volume is the sum of all the rates of generation in each of the subvolumes. If the total system volume is divided into M subvolumes, the total rate of generation is

$$G_j = \sum_{i=1}^M \Delta G_{ji} = \sum_{i=1}^M r_{ji} \Delta V_i$$

By taking the appropriate limits (i.e., let $M \rightarrow \infty$ and $\Delta V \rightarrow 0$) and making use of the definition of an integral, we can rewrite the foregoing equation in the form

$$G_j = \int^V r_j dV$$

From this equation, we see that r_j will be an indirect function of position, since the properties of the reacting materials and reaction conditions (e.g., concentration, temperature) can have different values at different locations in the reactor volume.

We now replace G_j in Equation (1-3), that is,

$$F_{j0} - F_j + G_j = \frac{dN_j}{dt} \quad (1-3)$$

by its integral form to yield a form of the general mole balance equation for any chemical species j that is entering, leaving, reacting, and/or accumulating within any system volume V .

$$\boxed{F_{j0} - F_j + \int^V r_j dV = \frac{dN_j}{dt}} \quad (1-4)$$

This is a basic equation for chemical reaction engineering.

From this general mole balance equation, we can develop the *design* equations for the various types of industrial reactors: batch, semibatch, and continuous-flow. Upon evaluation of these equations, we can determine the time (batch), reactor volume or catalyst weight (continuous-flow) necessary to convert a specified amount of the reactants into products.

1.3 BATCH REACTORS (BRS)

When is a batch reactor used?

A batch reactor is used for small-scale operation, for testing new processes that have not been fully developed, for the manufacture of expensive products, and for processes that are difficult to convert to continuous operations. The reactor can

be charged (i.e., filled) through the holes at the top (see [Figure 1-5\(a\)](#)). The batch reactor has the advantage of high conversions that can be obtained by leaving the reactant in the reactor for long periods of time, but it also has the disadvantages of high labor costs per batch, the variability of products from batch to batch, and the difficulty of large-scale production (see Industrial Reactor Photos in *Professional Reference Shelf* [PRS]

(<http://www.umich.edu/~elements/6e/01chap/prof-reactors.html>) on the CRE Web sites, www.umich.edu/~elements/6e/index.html). Also see <http://encyclopedia.che.engin.umich.edu/Pages/Reactors/menu.html>.

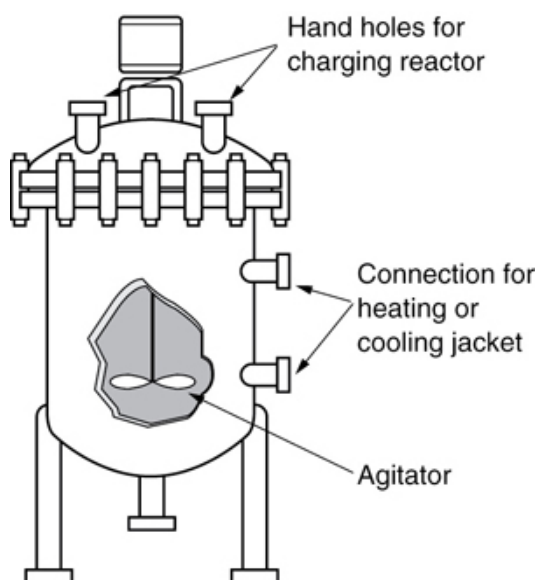
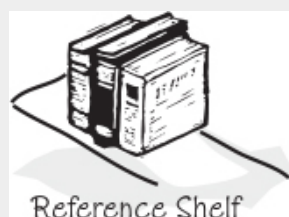


Figure 1-5(a) Simple batch homogeneous batch reactor (BR). [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

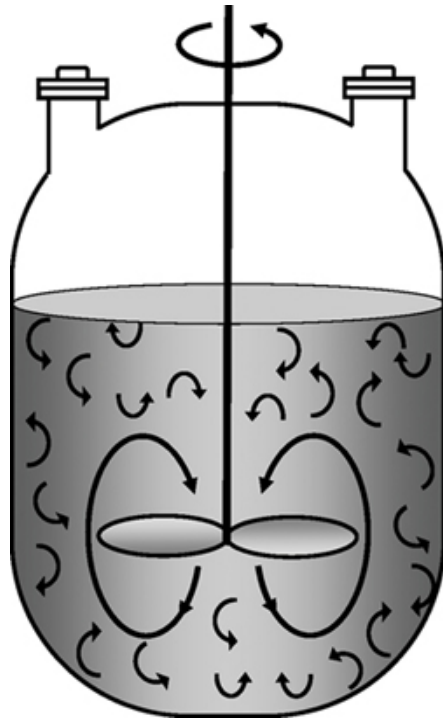


Figure 1-5(b) Batch reactor mixing patterns. Further descriptions and photos of the batch reactors can be found in both the *Visual Encyclopedia of Equipment* and in the *Professional Reference Shelf* on the CRE Web site.

Also see

<http://encyclopedia.che.engin.umich.edu/Pages/Reactors/Batch/Batch.html>.

A batch reactor has neither inflow nor outflow of reactants or products while the reaction is being carried out: $F_{j0} = F_j = 0$. The resulting general mole balance on species j is

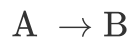
$$\frac{dN_j}{dt} = \int^V r_j dV$$

If the reaction mixture is perfectly mixed (Figure 1-5(b)) so that there is no variation in the rate of reaction throughout the reactor volume, we can take r_j out of the integral, integrate, and write the differential form of the mole balance, that is,

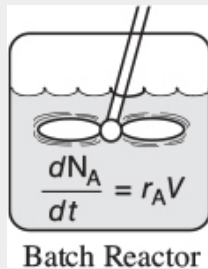
$$\boxed{\frac{dN_j}{dt} = r_j V} \quad (1-5)$$

Perfect mixing

Let's consider the isomerization of species A in a batch reactor



As the reaction proceeds, the number of moles of A decreases and the number of moles of B increases, as shown in Figure 1-6.



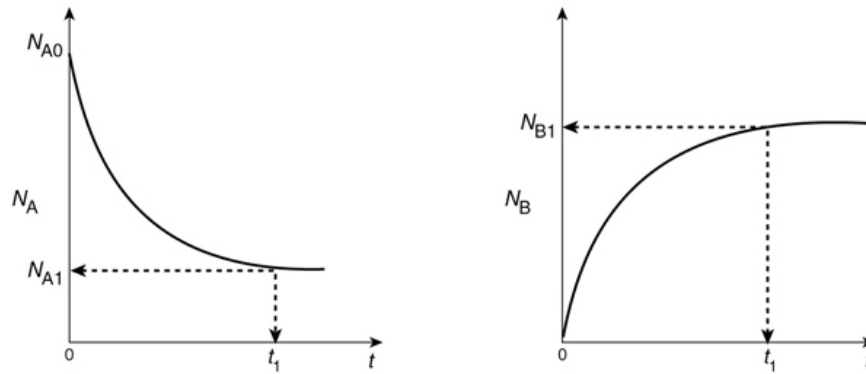


Figure 1-6 Mole-time trajectories.

We might ask what time, t_1 , is necessary to reduce the initial number of moles from N_{A0} to a final desired number N_{A1} .

Applying Equation (1-5) to the isomerization

$$\frac{dN_A}{dt} = r_A V$$

rearranging,

$$dt = \frac{dN_A}{r_A V}$$

and integrating with limits that at $t = 0$, then $N_A = N_{A0}$, and at $t = t_1$, then $N_A = N_{A1}$, we obtain

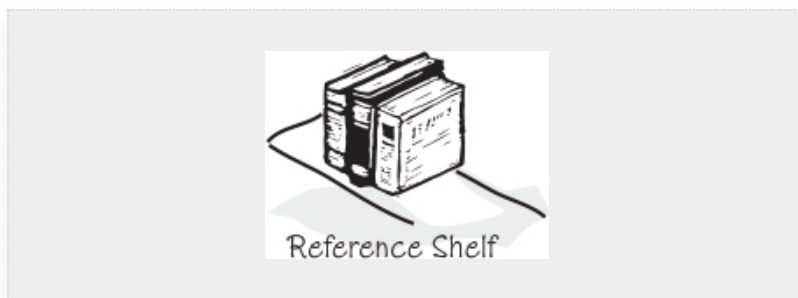
$$t_1 = \int_{N_{A1}}^{N_{A0}} \frac{dN_A}{-r_A V} \quad (1-6)$$

This equation is the integral form of the mole balance on a batch reactor. It gives the time, t_1 , necessary to reduce the number of moles from N_{A0} to N_{A1} and also to form N_{B1} moles of B.

1.4 CONTINUOUS-FLOW REACTORS

Continuous-flow reactors are almost always operated at steady state. We will consider three types: the *continuous-stirred tank reactor* (CSTR), the *plug-flow reactor* (PFR), and the *packed-*

bed reactor (PBR). Detailed physical descriptions of these reactors can be found in both the *Professional Reference Shelf (PRS)*, (<http://www.umich.edu/~elements/6e/01chap/prof.html>) for Chapter 1 and in the *Visual Encyclopedia of Equipment*, <http://encyclopedia.che.engin.umich.edu/Pages/Reactors/CSTR/CSTR.html>, and on the CRE Web site.



1.4.1 Continuous-Stirred Tank Reactor (CSTR)

What is a CSTR used for?

A type of reactor commonly used in industrial processing is the stirred tank operated continuously (Figure 1-7). It is referred to as the *continuous-stirred tank reactor* (CSTR) or *vat*, or *backmix reactor*, and is primarily used for

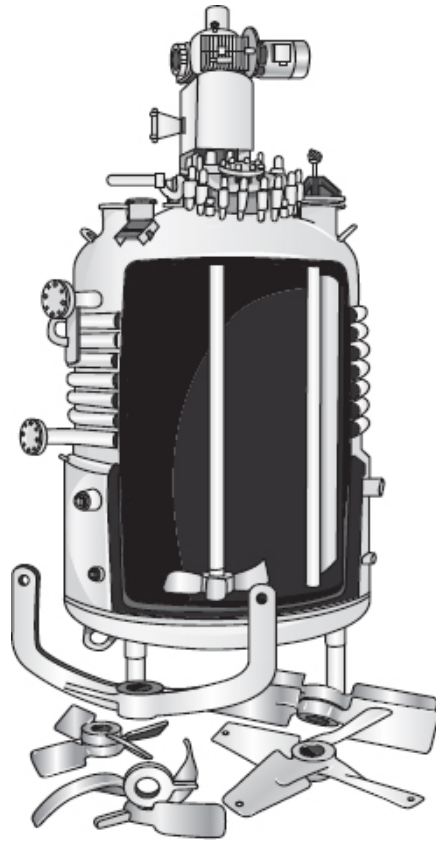


Figure 1-7(a) CSTR/batch reactor.

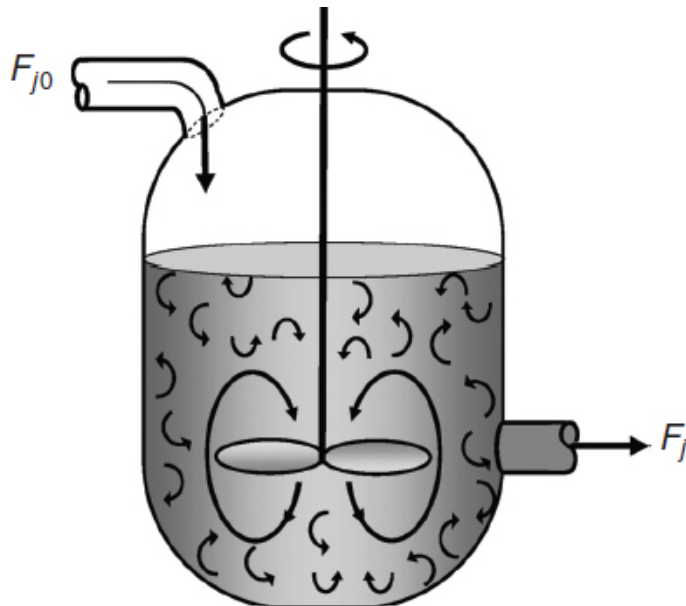


Figure 1-7(b) CSTR mixing patterns.

Also see

<http://encyclopedia.che.engin.umich.edu/Pages/Reactors/CSTR/CSTR.html>.

liquid-phase reactions. It is normally operated **at steady state** and is assumed to be **perfectly mixed**; consequently, there is no time dependence or position dependence of the temperature, concentration, or reaction rate inside the CSTR. That is, every variable is the same at every point inside the reactor. Because the temperature and concentration are identical everywhere within the reaction vessel, they are the same at the *exit point* as they are elsewhere in the tank. Thus, the temperature and concentration in the exit stream are modeled as being the same as those inside the reactor. In systems where mixing is highly *nonideal*, the well-mixed model is inadequate, and we must resort to other modeling techniques, such as residence time distributions, to obtain meaningful results. This topic of nonideal mixing is discussed in [Chapters 16 and 17](#), while nonideal flow reactors are discussed in [Chapter 18](#).

When the general mole balance equation

$$F_{j0} - F_j + \int^V r_j dV = \frac{dN_j}{dt} \quad (1-4)$$

GMBE

is applied to a CSTR operated at steady state (i.e., conditions do not change with time),

$$\frac{dN_j}{dt} = 0$$

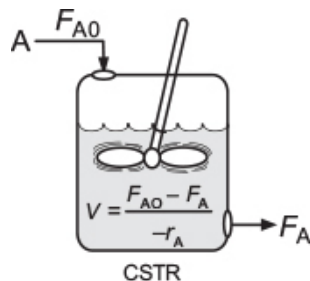
in which there are no spatial variations in the rate of reaction (i.e., perfect mixing),

$$\int^V r_j dV = V r_j$$

The ideal CSTR is assumed to be perfectly mixed.

it takes the familiar form known sometimes called *the design equation* for a CSTR

$$V = \frac{F_{j0} - F_j}{-r_j} \quad (1-7)$$



The CSTR design equation gives the reactor volume V necessary to reduce the entering molar flow rate of species j from F_{j0} to the exit molar flow rate F_j , when species j is disappearing at a rate of $-r_j$. We note that the CSTR is modeled such that the conditions in the exit stream (e.g., concentration and temperature) **are identical** to those in the tank. The molar flow rate F_j is just the product of the concentration of species j and the volumetric flow rate v

$$\begin{array}{l} F_j = C_j \cdot v \\ \frac{\text{moles}}{\text{time}} = \frac{\text{moles}}{\text{volume}} \cdot \frac{\text{Volume}}{\text{time}} \end{array} \quad (1-8)$$

Applying Equation (1-8) at the entrance of the reactor one obtains

$$F_{j0} = C_{j0} \cdot v_0$$

Consequently, we can substitute for F_{j0} and F_j into Equation (1-7) to write a balance on species A in terms of concentration, as

$$V = \frac{v_0 C_{A0} - v C_A}{-r_A} \quad (1-9)$$

The ideal CSTR mole balance equation is an algebraic equation, not a differential equation.

1.4.2 Tubular Reactor

In addition to the CSTR and batch reactors, another type of reactor commonly used in industry is the *tubular reactor*. It consists of a cylindrical pipe and is normally operated at steady state, as is the CSTR. Tubular reactors are used most often for *gas-phase reactions*. A schematic and a photograph of industrial tubular reactors are shown in Figure 1-8.

When is a tubular reactor most often used?

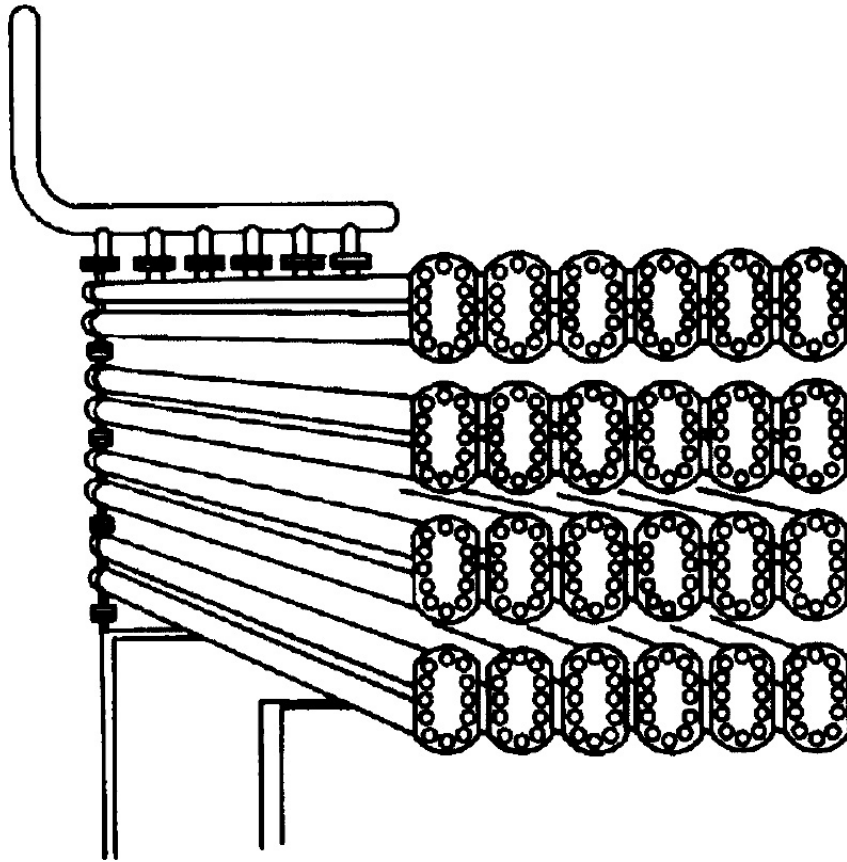


Figure 1-8(a) Tubular reactor schematic. Longitudinal tubular reactor. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

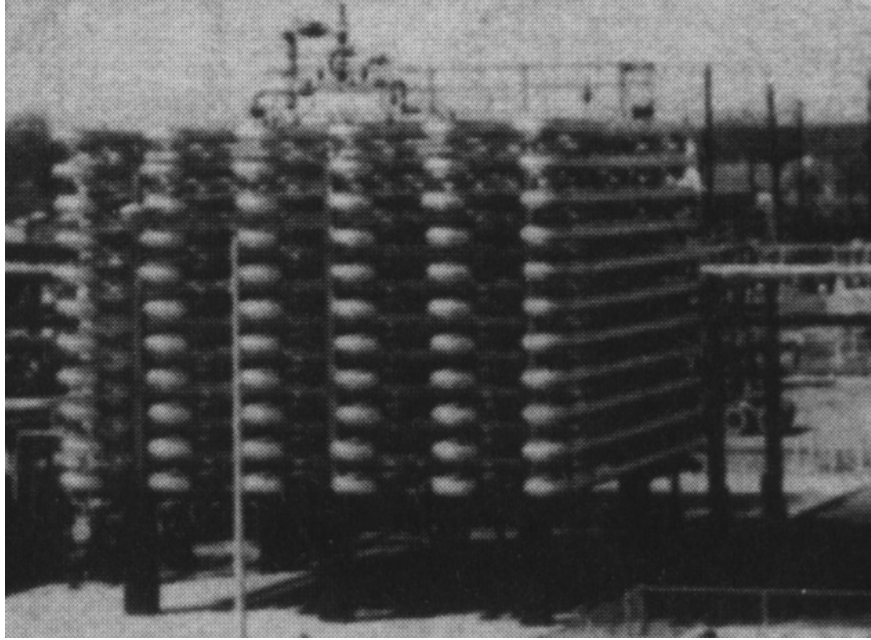


Figure 1-8(b) Tubular reactor photo. Tubular reactor for production of Dimersol G. (Photo courtesy of Editions Techniq Institut Français du Pétrole.)

Also see

<http://encyclopedia.che.engin.umich.edu/Pages/Reactors/PFR/PFR.html>.

In the tubular reactor, the reactants are continually consumed as they flow down the length of the reactor. In modeling the tubular reactor, we assume that the concentration varies continuously in the axial direction through the reactor. Consequently, the *reaction rate*, which is a function of concentration for all but zero-order reactions (cf. Equation 3-2), will *also* vary axially. For the purposes of the material presented here, we consider systems in which the flow field may be modeled by that of a plug-flow profile (e.g., uniform radial velocity as in turbulent flow), as shown in Figure 1-9. That is, there is no radial variation in reaction rate, and the reactor is referred to as a *plug-flow reactor* (PFR). (The

laminar-flow reactor (LFR) is discussed in Chapters 16–18, along with a discussion of nonideal reactors.)

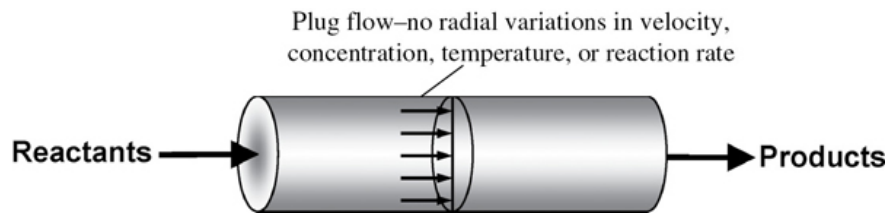


Figure 1-9 Plug-flow tubular reactor.

Also see PRS and *Visual Encyclopedia of Equipment*.

The general mole balance equation is given by Equation (1-4):

$$F_{j0} - F_j + \int_V r_j dV = \frac{dN_j}{dt} \quad (1-4)$$

The equation we will use to design PFRs at steady state can be developed in two ways: (1) directly from Equation (1-4) by differentiating with respect to volume V , and then rearranging the result *or* (2) from a mole balance on species j in a differential segment of the reactor volume ΔV . Let's choose the second way to arrive at the differential form of the PFR mole balance. The differential volume, ΔV , shown in Figure 1-10, will be chosen sufficiently small such that there are no spatial variations in reaction rate within this volume. Thus the generation term, ΔG_j , is

$$\Delta G_j = \int^{\Delta V} r_j dV = r_j \Delta V$$

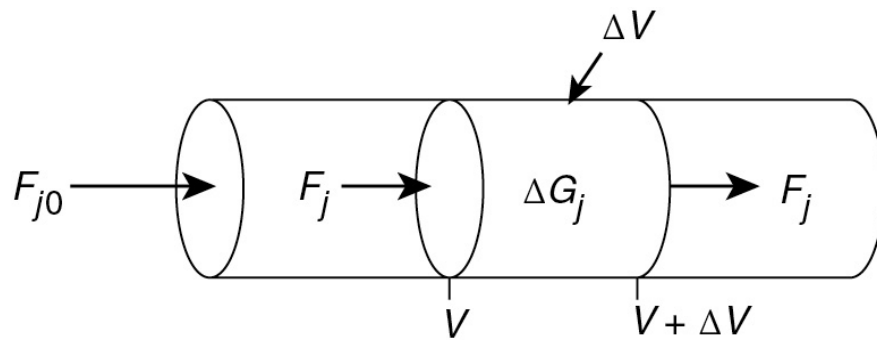


Figure 1-10 Mole balance on species j in volume ΔV .

$\left[\begin{array}{c} \text{Molar flow} \\ \text{rate of species } j \\ \text{In at } v \\ \text{moles/time} \end{array} \right]$	-	$\left[\begin{array}{c} \text{Molar flow} \\ \text{rate of species } j \\ \text{out at } (V + \Delta V) \\ \text{moles/time} \end{array} \right]$	+	$\left[\begin{array}{c} \text{Molar rate of} \\ \text{Generation} \\ \text{of species } j \\ \text{within } \Delta V \\ \text{moles/time} \end{array} \right]$	=	$\left[\begin{array}{c} \text{Molar rate of} \\ \text{Accumulation} \\ \text{of species } j \\ \text{within } \Delta V \\ \text{moles/time} \end{array} \right]$
In	-	Out	+	Generation	=	Accumulation
$F_{j V}$	-	$F_{j V+\Delta V}$	+	$r_j \Delta V$	=	0 (1-10)

Dividing Equation (1-10) by ΔV and rearranging

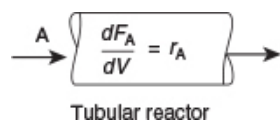
$$\left[\frac{F_{j|V+\Delta V} - F_{j|V}}{\Delta V} \right] = r_j$$

we note the term in brackets resembles the definition of a derivative

$$\lim_{\Delta x \rightarrow 0} \left[\frac{f(x+\Delta x) - f(x)}{\Delta x} \right] = \frac{df}{dx}$$

Taking the limit as ΔV approaches zero, we obtain the differential form of steady-state mole balance on a PFR

$$\boxed{\frac{dF_j}{dV} = r_j} \quad (1-11)$$



We could have made the cylindrical reactor on which we carried out our mole balance an irregularly shaped reactor, such as the one shown in [Figure 1-11](#) for reactant species A. *However*, we see that by applying Equation (1-10), the result would yield the same equation (i.e., Equation (1-11)). For species A, the mole balance is

$$\boxed{\frac{dF_A}{dV} = r_A} \quad (1-12)$$

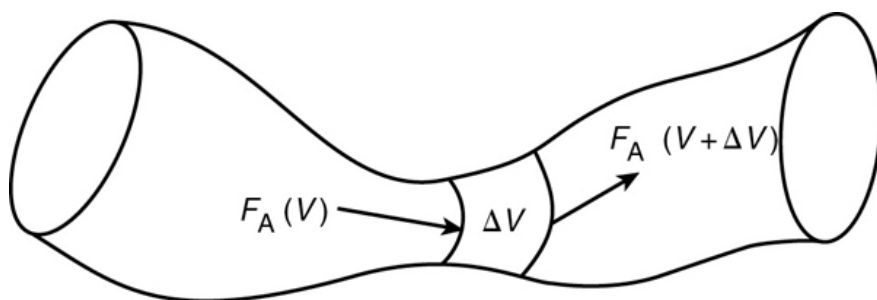


Figure 1-11 Pablo Picasso's reactor.

Picasso's reactor

Consequently, we see that Equation (1-11) applies equally well to our model of tubular reactors of variable and constant cross-sectional area, although it is doubtful that one would find a reactor of the shape shown in [Figure 1-11](#) unless it were designed by Pablo Picasso or perhaps one of his followers.

The conclusion drawn from the application of the design equation to Picasso's reactor is an important one: the degree of completion of a reaction achieved in an ideal plug-flow reactor (PFR) does not depend on its shape, only on its total volume.

Lets again consider the isomerization $A \rightarrow B$, this time in a PFR. As the reactants proceed down the reactor, A is consumed by chemical reaction and B is produced.

Consequently, the molar flow rate F_A decreases as shown in Figure 1-12(a) while F_B increases as the reactor volume V increases, as shown in Figure 1-12(b).

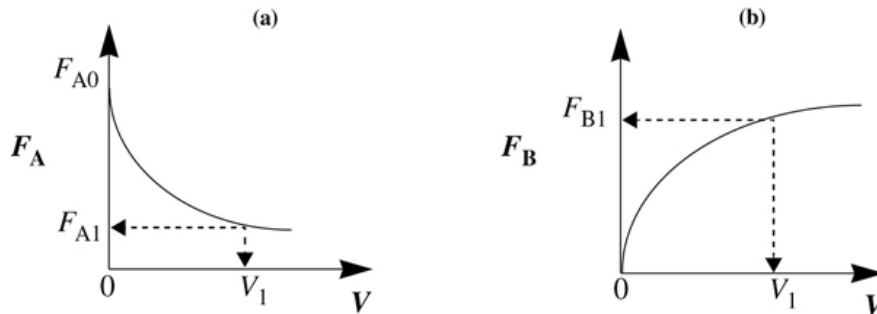


Figure 1-12 Profiles of molar flow rates in a PFR.

$$V = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r_A}$$

We now ask, “What is the reactor volume V_1 necessary to reduce the entering molar flow rate of A from F_{A0} to an exit flow rate F_{A1} ?” Rearranging Equation (1-12) in the form

$$dV = \frac{dF_A}{r_A}$$

and integrating with limits at $V = 0$, then $F_A = F_{A0}$, and at $V = V_1$, then $F_A = F_{A1}$

$$\boxed{V_1 - \int_{F_{A0}}^{F_{A1}} \frac{dF_A}{r_A} = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r_A}} \quad (1-13)$$

V_1 is the volume necessary to reduce the entering molar flow rate F_{A0} to some specified value F_{A1} and also the volume necessary to produce a molar flow rate of B of F_{B1} .

1.4.3 Packed-Bed Reactor (PBR)

The principal difference between reactor design calculations involving homogeneous reactions and those involving fluid–

solid heterogeneous reactions is that for the latter, the reaction takes place on the surface of the catalyst (see [Figure 10-5](#)).

The greater the mass of a given catalyst, the greater the reactive surface area. Consequently, the reaction rate is based on mass of solid catalyst, W , rather than on reactor volume, V . For a fluid–solid heterogeneous system, the rate of reaction of a species A, $-r'_A$, is defined as

$$-r'_A = \text{mol A reacted} / (\text{time} \times \text{mass of catalyst})$$

The mass of solid catalyst is used because the amount of catalyst is what is important to the rate of product formation. We note that by multiplying the heterogeneous reaction rate, $-r'_A$, by the bulk catalyst density, $\rho_b \left(\frac{\text{mass}}{\text{volume}} \right)$, we can obtain the reaction rate per unit volume, $-r_A$.

$$-r_A = \rho_b (-r'_A)$$

$$\left(\frac{\text{mol}}{\text{dm}^3 \cdot \text{s}} \right) = \left(\frac{\text{g}}{\text{dm}^3} \right) \left(\frac{\text{mol}}{\text{g} \cdot \text{s}} \right)$$

The reactor volume that contains the catalyst is of secondary significance. [Figure 1-13](#) shows a schematic of an industrial catalytic reactor with vertical tubes packed with solid catalyst.

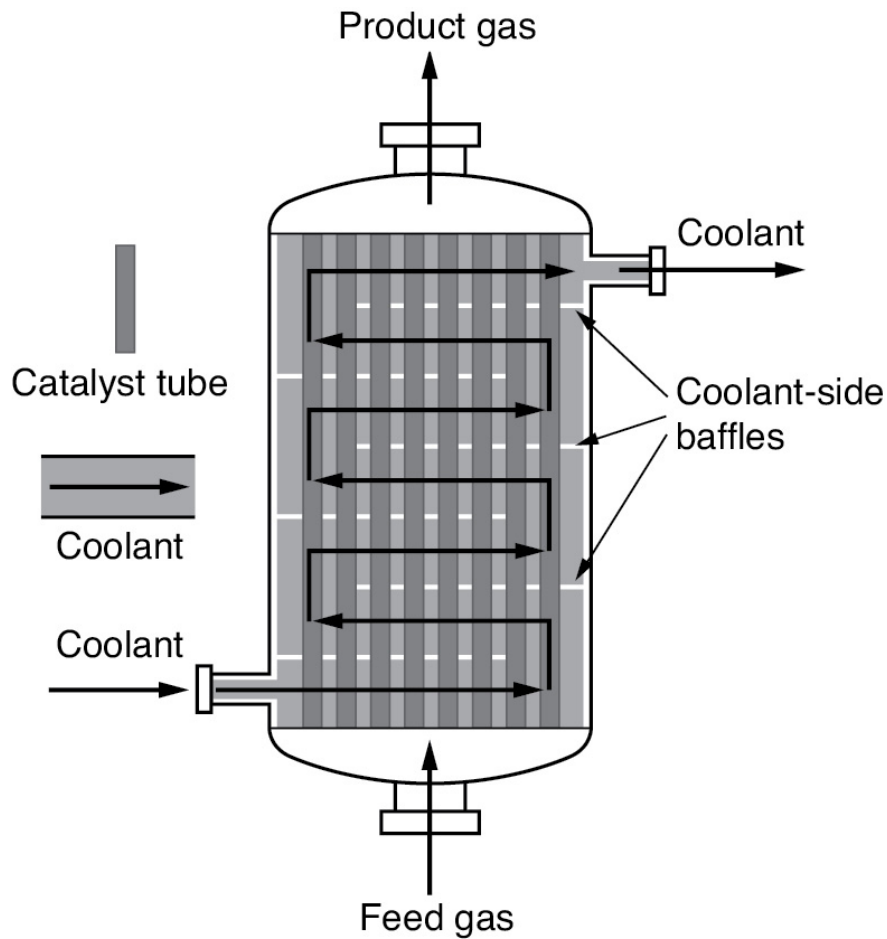


Figure 1-13 Longitudinal catalytic packed-bed reactor. Also see <http://encyclopedia.che.engin.umich.edu/Pages/Reactors/PBR/PBR.html>.

In the three idealized types of reactors just discussed (the perfectly mixed batch reactor [BR], the plug-flow tubular reactor [PFR]), and the perfectly mixed continuous-stirred tank reactor [CSTR]), the design equations (i.e., mole balances) were developed based on reactor volume. The derivation of the design equation for a packed-bed catalytic reactor (PBR) will be carried out in a manner analogous to the development of the tubular design equation. To accomplish this derivation, we simply replace the volume coordinate, V , in Equation (1-10)

with the catalyst mass (i.e., weight) coordinate W (Figure 1-14).

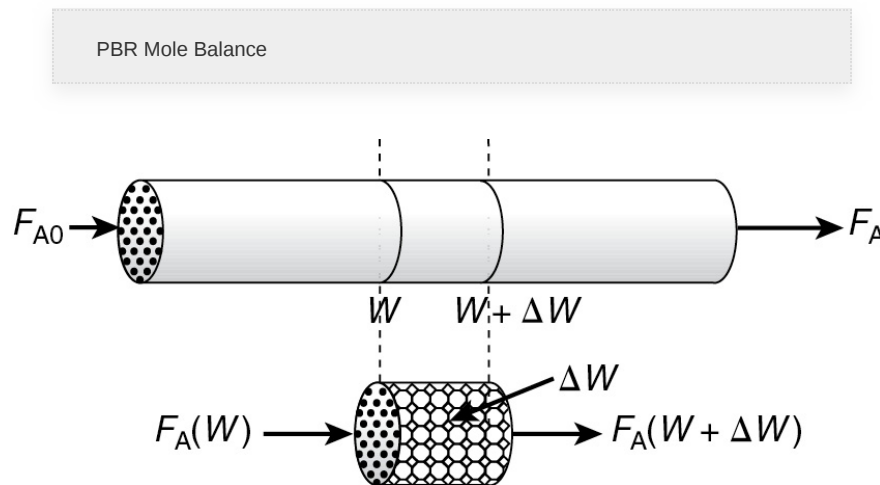


Figure 1-14 Packed-bed reactor schematic.

As with the PFR, the PBR is assumed to have no radial gradients in concentration, temperature, or reaction rate. The generalized mole balance on species A over catalyst weight ΔW results in the equation

$$\begin{array}{ccccccc} \text{In} & - & \text{Out} & + & \text{Generation} & = & \text{Accumulation} \\ F_{A|W} & - & F_{A|(w+\Delta w)} & + & r'_A \Delta W & = & 0 \end{array} \quad (1-14)$$

The dimensions of the generation term in Equation (1-14) are

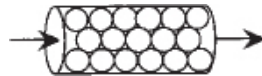
$$(r'_A) \Delta W \equiv \frac{\text{moles A}}{(\text{time})(\text{mass of catalyst})} \cdot (\text{mass of catalyst}) \equiv \frac{\text{moles A}}{\text{time}}$$

which are, as expected, the same dimensions of the molar flow rate F_A . After dividing Equation (1-14) by ΔW and taking the limit as $\Delta W \rightarrow 0$, we arrive at the differential form of the mole balance for a packed-bed reactor:

$$\boxed{\frac{dF_A}{dW} = r'_A} \quad (1-15)$$

Use the differential form of design equation for catalyst decay and pressure drop.

When pressure drop through the reactor (see [Section 5.5](#)) and catalyst decay (see [Section 10.7 in Chapter 10](#)) are neglected, the integral form of the packed-catalyst-bed design equation can be used to calculate the catalyst weight



$$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A} = \int_{F_A}^{F_{A0}} \frac{dF_A}{-r'_A} \quad (1-16)$$

You can use the integral form **only** when there is no ΔP and no catalyst decay.

W is the catalyst weight necessary to reduce the entering molar flow rate of species A, F_{A0} , down to a molar flow rate F_A .

1.4.4 Well-Mixed “Fluidized” Catalytic Bed Reactor

For particulate catalytic gas-phase systems, the fluidized bed is also in common use. Depending of the flow regime, it can be modeled anywhere between a straight through transport reactor ([Chapter 10](#)) to a fluidized bed that is analogous to a CSTR ([section 1.4.1](#)), which is shown in [Figure 1-15](#).

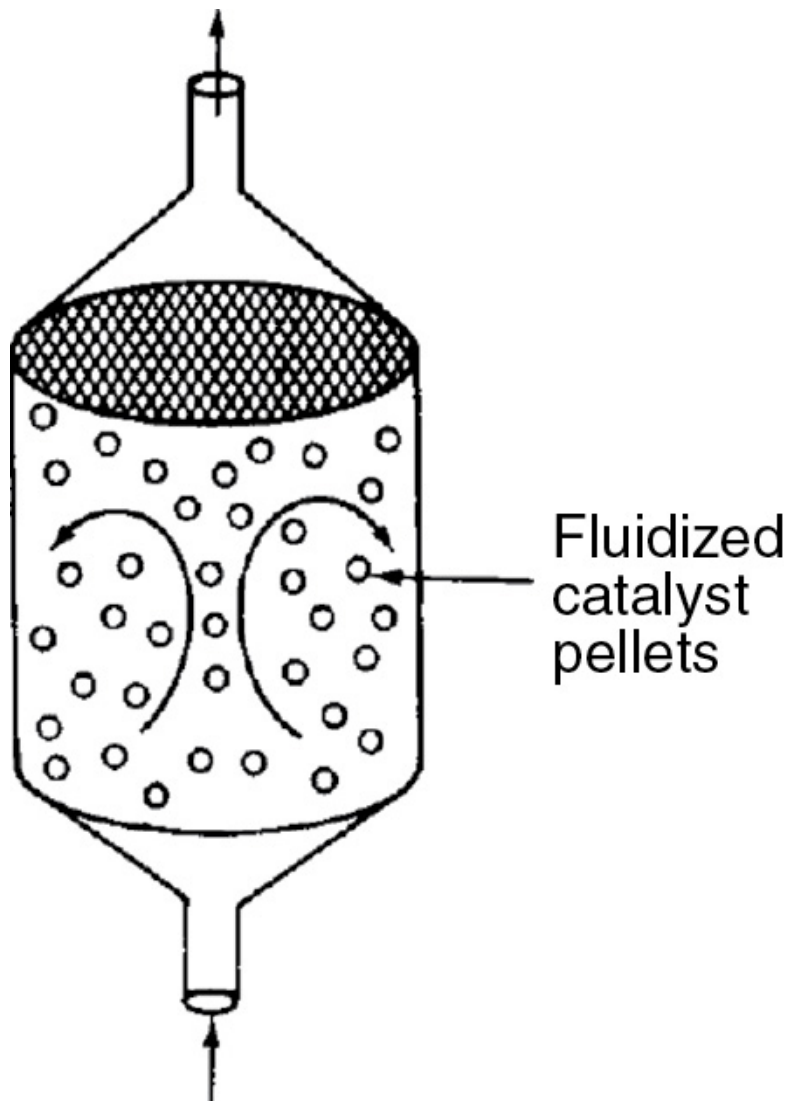


Figure 1-15 Well-mixed fluidized bed modeled as a CSTR.

A mole balance on species A in a well-mixed “fluidized” bed is

$$F_{A0} - F_A + r'_A W = 0 \quad (1-17)$$

Dividing by the catalyst weight W , we arrive at the Equation (1-18) that gives the catalyst weight necessary to reduce the molar rate entering from, F_{A0} (mol/s) to the molar rate leaving, F_A , (mol/s) when species A is disappearing at a rate, r'_A (mol/s·gcat) the design equation

$$W = \frac{F_{A0} - F_A}{-r'_A} \quad (1-18)$$

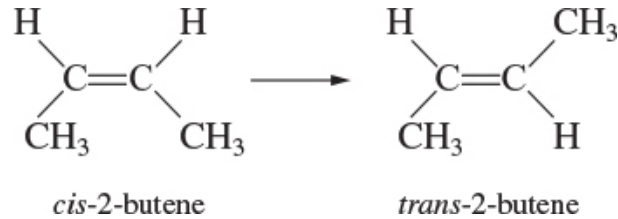
Looking Ahead



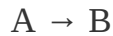
For some insight into “things to come,” consider the following example of how one can use the tubular reactor design in Equation (1-11).

Example 1–2 How Large Is the Reactor Volume?

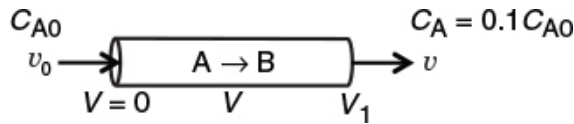
Let's consider the liquid phase *cis*–*trans* isomerization of 2–butene



which we will write symbolically as



The reaction is first order in A ($-r_A = kC_A$) and is carried out in a tubular reactor in which the volumetric flow rate, v , is constant, that is, $v = v_0$.



1. Without solving any equations, sketch what you think the concentration profile (C_A as a function of V) would look like.
2. Derive an equation relating the reactor volume to the entering and exiting concentrations of A, the rate constant k , and the volumetric flow rate v_0 .
3. Determine the reactor volume, V_1 , necessary to reduce the exiting concentration to 10% of the entering concentration, that is, $C_A = 0.1C_{A0}$, when the volumetric flow rate v_0 is 10 dm³/min (i.e., liters/min) and the specific reaction rate, k , is 0.23. min^{–1}.

Solution

1. Sketch C_A as a function of V .

Species A is consumed as we move down the reactor, and as a result, both the molar flow rate of A and the concentration of A will decrease. Because the volumetric flow rate is constant, $v = v_0$, one can use Equation (1-8) to obtain the concentration of A, $C_A = F_A/v_0$, and then by comparison with the plot in Figure 1-12, obtain the concentration of A as a function of reactor volume, as shown in Figure E1-2.1.

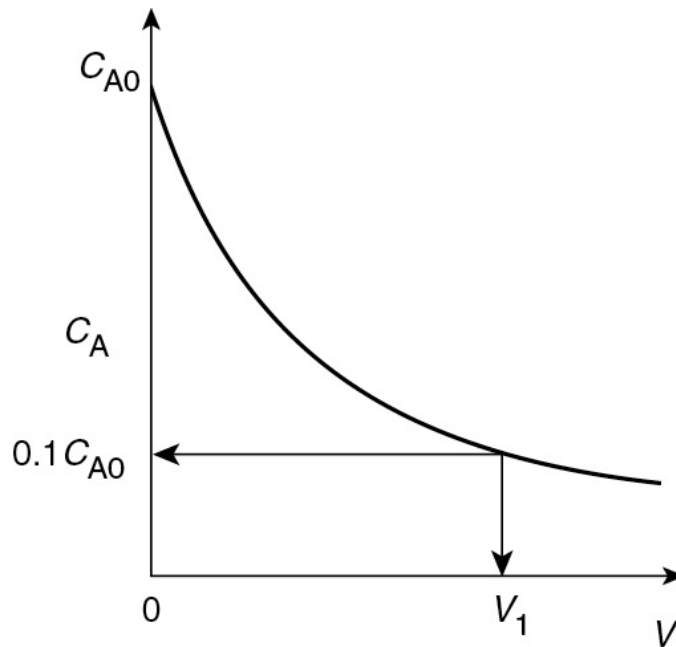


Figure E1-2.1 Concentration profile.

2. Derive an equation relating V , v_0 , k , C_{A0} , and C_A .

For a tubular reactor, the mole balance on species A ($j = A$) was shown to be given by Equation (1-11). Then for species A ($j = A$)

Mole Balance:

$$\frac{dF_A}{dV} = r_A \quad (1-12)$$

For a first-order reaction, the rate law (as will be discussed in Chapter 3, Equation (3-5)) is

Rate Law:

$$-r_A = kC_A \quad (\text{E1-2.1})$$

Because the volumetric flow rate, v , is constant ($v = v_0$), as it is for virtually all liquid-phase reactions,

$$\frac{dF_A}{dV} = \frac{d(C_A v)}{dV} = \frac{d(C_A v_0)}{dV} = v_0 \frac{dC_A}{dV} = r_A \quad (\text{E1-2.2})$$

Reactor sizing

Multiplying both sides of Equation (E1-2.2) by minus one and then substituting Equation (E1-2.1) yields

Combine:

$$-\frac{v_0 dC_A}{dV} = -r_A = kC_A \quad (\text{E1-2.3})$$

Separating the variables and rearranging gives

$$-\frac{v_0}{k} \left(\frac{dC_A}{C_A} \right) = dV$$

Using the conditions at the entrance of the reactor that when $V = 0$, then $C_A = C_{A0}$

$$-\frac{v_0}{k} \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^V dV \quad (\text{E1-2.4})$$

Carrying out the integration of Equation (E1-2.4) gives

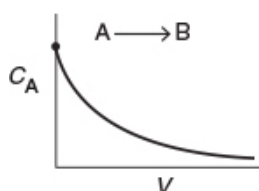
Solve:

$$V = \frac{v_0}{k} \ln \frac{C_{A0}}{C_A} \quad (\text{E1-2.5})$$

We can also rearrange Equation (E1-2.5) to solve for the concentration of A as a function of reactor volume to obtain

$$C_A = C_{A0} \exp(-kV/v_0)$$

Concentration profile



3. Calculate the volume V . We want to find the volume, V_1 , at which $C_A = \frac{1}{10} C_{A0}$ when $k = 0.23 \text{ min}^{-1}$ and $v_0 = 10 \text{ dm}^3/\text{min}$.

Evaluate:

Substituting C_{A0} , C_A , v_0 , and k in Equation (E1-2.5), we have

$$V = \frac{10 \text{ dm}^3/\text{min}}{0.23 \text{ min}^{-1}} \ln \frac{C_{A0}}{0.1 C_{A0}} = \frac{10 \text{ dm}^3}{0.23} \ln 10 = 100 \text{ dm}^3 \text{ (i.e., 100L ; } 0.1 \text{ m}^3 \text{)}$$

Ans. We see that a reactor volume of 0.1 m^3 is necessary to convert 90% of species A entering (i.e., $C_A = 0.1 C_{A0}$) into product B for the parameters given.

Let's now calculate the reactor volume necessary to an even smaller concentration say $(1/100)^{\text{th}}$ of the entering concentration, that is,

$$C_A = 0.01 C_0$$

$$V = \frac{10 \text{ dm}^3/\text{min}}{0.23 \text{ min}^{-1}} \ln \frac{C_{A0}}{0.01 C_{A0}} = \frac{10 \text{ dm}^3}{0.23} \ln 100 = 200 \text{ dm}^3 \text{ Ans.}$$

Note: We see that a larger reactor (200 dm^3) is needed to reduce the exit concentration to a smaller fraction of the entering concentration (e.g., $C_A = 0.01 C_{A0}$).

Analysis: For this irreversible liquid-phase first-order reaction (i.e., $-r_A = kC_A$) being carried out in a PFR, the concentration of the reactant decreases exponentially down the length (i.e., volume V) of the reactor. The more that species A is consumed and converted to product B, the larger must be the reactor volume. The purpose of the example was to give a vision of the types of calculations we will be carrying out as we study chemical reaction engineering (CRE).

Example 1–3 Numerical Solutions to Example 1-2
Problem: How Large Is the Reactor Volume?

Now we will turn Example 1-2 into a *Living Example Problem* (LEP) where we can vary parameters to learn their effect on the volume and/or exit concentrations. We could use Polymath, Wolfram, or Python to solve the combined mole balance and rate law to determine the concentration profile. In this example, we will use *Polymath*.

We begin by rewriting the mole balance, Equation (E1-2.2), in Polymath notation form

Mole Balances

$$\frac{d(Ca)}{d(V)} = ra/v_0 \quad (\text{E1-3.1})$$

$$\frac{d(Cb)}{d(V)} = rb/v_0 \quad (\text{E1-3.2})$$

Rate Law

$$ra = -k^* Ca \quad (\text{E1-3.3})$$

$$rb = -ra \quad (\text{E1-3.4})$$

$$k = 0.23$$

$$v_0 = 10$$

Polymath Formulation

A Polymath tutorial to solve the ordinary differential equations (ODEs) can be found on the Web site (http://www.umich.edu/~elements/6e/tutorials/ODE_Equation_Tutorial.pdf) and

http://www.umich.edu/~elements/6e/tutorials/Polymath_tutorials.html).

The parameter values are $k = 0.23 \text{ min}^{-1}$, $v_0 = 10 \text{ dm}^3/\text{min}$ and $C_A = 10 \text{ mole/dm}^3$. The initial and final values for the integration wrt the volume V are $V = 0$ and $V = 100 \text{ dm}^3$.

The output from the Polymath solution is given in Table E1-3.1 and the axial concentration profiles from species A and B are shown in Figure E1-3.1.

TABLE E1-3.1 POLYMATH PROGRAM AND OUTPUT FOR ISOTHERMAL PFR

		Calculated values of DEQ variables		
Differential equations		Variable	Initial value	Final value
1	$d(C_b)/d(V) = r_b/v_o$	1 Ca	10.	1.002588
2	$d(C_a)/d(V) = r_a/v_o$	2 Cb	0	8.997412
Explicit equations		3 k	0.23	0.23
1	$v_o = 10$	4 ra	-2.3	-0.2305953
2	$k = 0.23$	5 rb	2.3	0.2305953
3	$r_a = -k \cdot C_a$	6 V	0	100.
4	$r_b = -r_a$	7 vo	10.	10.

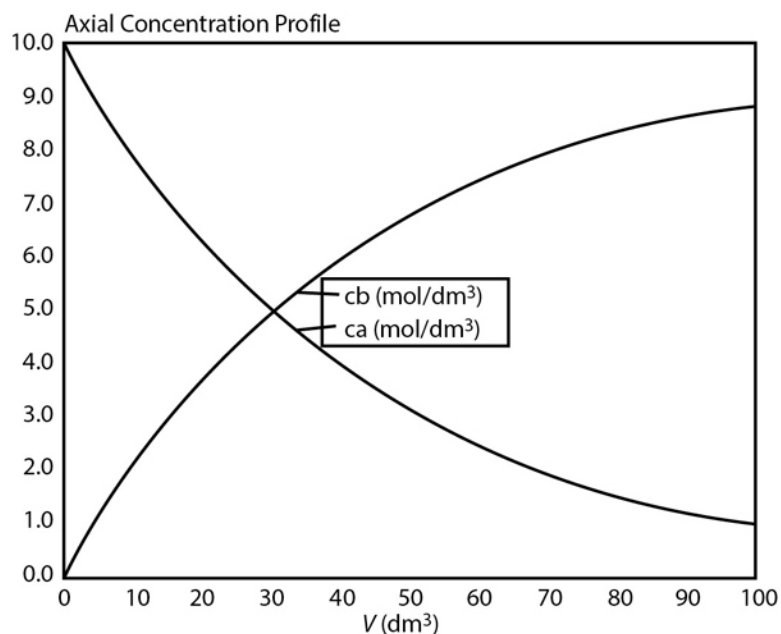
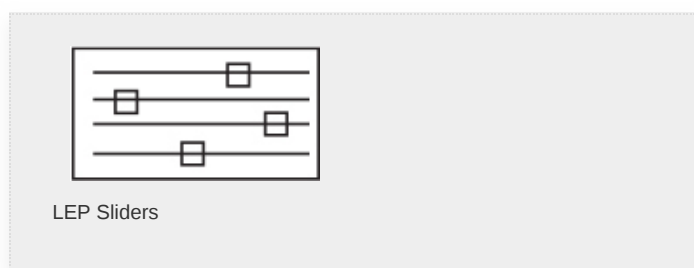


Figure E1-3.1 Axial concentration profiles for A and B.

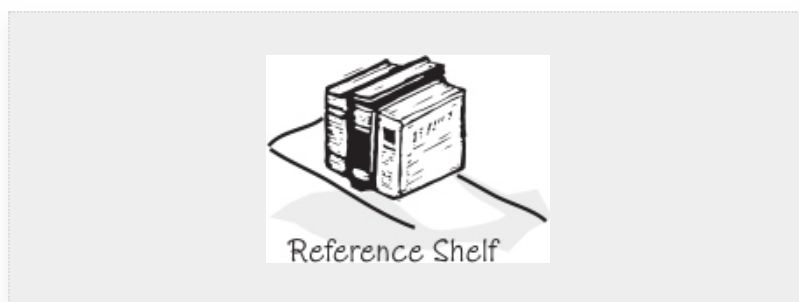


Analysis: Because Polymath will be used extensively in later chapters to solve non-linear ordinary differential equations (ODEs), we introduce it here so that the reader can start to become familiar with it. Figure E1-3.1 shows how the concentrations of species A and B vary down the length of the PFR. In order to become familiar with Polymath, the reader is encouraged to solve the foxes and rabbits problem using Polymath (P1-3_B(a)) and then study the dynamics of the reaction using Wolfram or Python (P1-3_B(b)).

1.5 INDUSTRIAL REACTORS

Be sure to view the actual photographs of industrial reactors on the CRE Web site so you will know them when you run into them. There are also links to view reactors on different Web sites. The CRE Web site also includes a portion of the *Visual Encyclopedia of Equipment*, encyclopedia.che.engin.umich.edu, “Chemical Reactors” developed by Dr. Susan Montgomery and her students at the University of Michigan. Also see *Professional Reference Shelf* on the CRE Web site for “Reactors for Liquid-Phase and Gas-Phase Reactions,” along with photos of industrial reactors, and Expanded Material on the CRE Web site.²

² *Chem. Eng.*, 63(10), 211 (1956). See also *AIChE Modular Instruction Series E*, 5 (1984).



In this chapter, and on the CRE Web site, we've introduced each of the major types of industrial reactors: batch, stirred tank, tubular, and fixed bed (packed bed). Many variations and modifications of these commercial reactors (e.g., semibatch, fluidized bed) are in current use and these reactors will be discussed in Chapters 6 and 10, respectively. For further elaboration, refer to the detailed discussion of industrial reactors given by Walas.³

³ S. M. Walas, *Reaction Kinetics for Chemical Engineers*, New York: McGraw-Hill, 1959, Chap. 11.

<http://encyclopedia.che.engin.umich.edu/Pages/Reactors/menu.html>

The CRE Web site describes industrial reactors, along with typical feed and operating conditions. In addition, two solved example problems for Chapter 1 can be found on the CRE Web site, <http://www.umich.edu/~elements/6e>.

1.6 AND NOW... A WORD FROM OUR SPONSOR—SAFETY 1 (AWFOS—S1 SAFETY)

A note to students: In this sixth edition of *Elements of Chemical Reaction Engineering*, I am including a section at the end of each chapter to bring a greater awareness to process safety. A critical aspect of process safety is “anticipating” what could go wrong in a chemical process and ensuring it won’t go wrong. Equipment and processes involving exothermic chemical reactions are some of the most at risk in a chemical plant. Consequently, each chapter will end with a segment “And Now... A Word From Our Sponsor—Safety” (AWFOS—S). In addition, to highlight process safety across the chemical engineering curriculum, a Web site (<http://umich.edu/~safeche/>) has been developed that features a safety module specific to every core chemical engineering lecture course plus lab safety. In this chapter, we define process safety along with a very brief discussion on why it is important to study process safety.

1.6.1 What Is Chemical Process Safety?

Chemical process safety is a blend of engineering and management practices focused on preventing accidents, namely explosions, fires, and toxic releases that result in loss of life and property.

1.6.2 Why Study Process Safety?



Figure 1-16 T2 Laboratories (see Chapter 13).

Industrial disasters such as UCIL Bhopal, T2 Laboratories, BP Texas City, and Flixborough have collectively killed and injured thousands of people and caused billions of dollars in damage to chemical plants and nearby communities. Accidents such as these occur because chemical engineering processes are some of the most potentially dangerous due to extreme operating conditions and the use of explosive, reactive, and flammable materials. What surprises people is that most of these chemical engineering accidents, such as those listed in the Chemical Safety Board Videos on the companion Web site (<http://umich.edu/~safeche/>) were preventable. They were the result of poor engineering decisions, made by people who lacked fundamental understanding of basic chemical engineering concepts and chemical engineering safety. Thus, knowing the fundamentals of chemical engineering and process safety may save your life and the lives of innocent people, and prevent the loss of millions of dollars of material and equipment.

Engineers have an ethical and professional obligation to work only in areas for which they are competent and qualified. The best way to prevent future industrial disasters is to understand how to effectively and safely design, operate, and troubleshoot

chemical processes. To prepare a prevention plan, we must take the time and effort to understand chemical processes and chemical process safety. To help achieve this understanding, the last section of every chapter has a tutorial, AWFOS–S, that can help you prevent accidents.

A comparison of process safety and personal safety is very succinctly given on the Web site

(http://www.energysafetycanada.com/files/pdf/Personal_vs_Process_Safety_v3.pdf).

Closure. The goal of this text is to weave the fundamentals of chemical reaction engineering into a structure or algorithm that is easy to use and apply to a variety of problems. We have just finished the first building block of this algorithm: mole balances.



This algorithm and its corresponding building blocks will be developed and discussed in the following chapters:

- Mole Balance, [Chapters 1 and 2](#)
- Rate Law, [Chapter 3](#)
- Stoichiometry, [Chapter 4](#)
- Isothermal Reactor Design, [Chapter 5](#)

Combine

Evaluate

- Energy Balance, [Chapters 11–13](#)

With this algorithm, one can approach and solve chemical reaction engineering problems through logic rather than memorization.

A Word of Caution: The falling CRE Tower. As we proceed through the next five chapters, we will see how these building blocks form a tower. Now, if one cuts corners when studying this material, the building blocks become cylinders and as a result the tower becomes unstable and all of the understanding of CRE falls apart. See

<http://www.umich.edu/~elements/6e/01chap/assets/player/KeynoteDHTMLPlayer.html#3>.

SUMMARY

Each chapter summary gives the key points of the chapter that need to be remembered and carried into succeeding chapters.

1. A mole balance on species j , which enters, leaves, reacts, and accumulates in a system volume V , is

$$F_{j0} - F_j + \int^V r_j dV = \frac{dN_j}{dt} \quad (\text{S1-1})$$

If, and only if, the contents of the reactor are well mixed will the mole balance (Equation (S1-1)) on species A give

$$F_{A0} - F_A + r_A V = \frac{dN_A}{dt} \quad (\text{S1-2})$$



2. The kinetic rate law for r_j is

1. The rate of formation of species j per unit volume (e.g., mol/s·dm³)
2. Solely a function of the properties of reacting materials and reaction conditions (e.g., concentration [activities], temperature, pressure, catalyst, or solvent [if any]) and does not depend on reactor type
3. An intensive quantity (i.e., it does not depend on the total amount)
4. An algebraic equation, not a differential equation (e.g., $-r_A = kC_A$ or $-r_A = kC_A^2$)


For homogeneous catalytic systems, typical units of $-r_j$ may be gram moles per second per liter; for heterogeneous systems, typical units of r'_j may be gram moles per second per gram of catalyst. By convention, $-r_A$ is the rate of disappearance of species A and r_A is the rate of formation of species A.

3. Mole balances on species A in four common reactors are shown in Table S1-1.


TABLE S1-1 SUMMARY OF REACTOR MOLE BALANCES

Reactor	Comments	Mole Balance Differential Form	Algebraic Form	Integral Form
	Batch	$\frac{dN_A}{dt} = r_A V$		$t_1 = \int_{N_{A1}}^{N_{A0}} \frac{dN_A}{-r_A V}$
	Continuous Stirred-Tank Reactor (CSTR)	—	$V = \frac{F_{A0} - F_A}{-r_A}$	—


st
at
e


 P St $\frac{dF_A}{dV} = r_A$
 F e
 R a
 d
 y
 st
 at
 e

$$V_1 = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r_A}$$


 P St $\frac{dF_A}{dV} = r'_A$
 B e
 R a
 d
 y
 st
 at
 e

$$W_1 = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r'_A}$$


 F St —
 lu e
 id a
 iz d
 e y
 d st
 C at
 S e
 T
 R

$$W = \frac{F_{A0} - F_A}{-r'_A} \quad \text{—}$$

CRE WEB SITE MATERIALS

(<http://www.umich.edu/~elements/6e/01chap/obj.html#/>)

Useful Links

Living Example Problems

Polymath, Python, Matlab and Wolfram

Extra Help

Multiple Resources extra problems, screencasts and lecture notes

Additional Materials

New Technical Material, Detailed Derivations and Web Modules

Professional Reference Shelf

Material important to the practicing engineer that is not necessarily covered in all CRE courses.

YouTube Videos

Humorous videos covering topics varying from example problems to light hearted breaks from studying

Evaluation

Self Tests

Interactive problems with solutions to provide extra practice of concepts

Clicker Questions

Interactive multiple choice questions to help access your understanding of the material

Getting Unstuck on a Problem



(http://www.umich.edu/~elements/6e/01chap/iclicker_ch1_q1.html)

Smog in L.A. Web Module



Photograph by Radoslaw Lecyk/Shutterstock

(http://www.umich.edu/~elements/6e/web_mod/la_basin/index.htm)

Living Example Problem:

<http://www.umich.edu/~elements/6e/01chap/live.html>

Interactive Computer Games

(<http://www.umich.edu/~elements/6e/icm/index.html>)

A. Quiz Show I

(<http://www.umich.edu/~elements/6e/icm/kinchal1.html>)



This game could help prepare you for the AIChE student chapter Jeopardy Competition held each year at the Annual AIChE meeting.

QUESTIONS, SIMULATIONS, AND PROBLEMS

I wish I had an answer for that, because I'm getting tired of answering that question.

—Yogi Berra, New York Yankees
Sports Illustrated, June 11, 1984

The subscript to each of the problem numbers indicates the level of difficulty, that is, A, least difficult; B, moderate

difficulty; C, fairly difficult; D, (double black diamond), most difficult. A = • B = ■ C = ♦ D = ♦♦ For example, P1-5_B means “1” is the Chapter number, “5” is the problem number, “_B” is the problem difficulty, in this case B means moderate difficulty.

Before solving the problems, state or sketch qualitatively the expected results or trends.

Questions

Q1-1_A QBR Questions Before Reading. Research has shown (*J. Exp. Psychol. Learn. Mem. Cogn.*, 40, 106–114 (2014)) that if you ask a question of the material before reading the material you will have greater retention. Consequently, the first question of every chapter will have such a question on that chapter’s material. For Chapter 1, the question is “Is the generation term, G, the only term in the mole balance that varies for each type of reactor?”

Q1-2_A Go to Chapter 1 Evaluation on the Web site. Click on **i>Clicker Questions** (http://www.umich.edu/~elements/6e/01chap/iclicker_ch1_q1.html) and view at least five i>clicker questions. Choose one that could be used as is, or a variation thereof, to be included on the next exam. You also could consider the opposite case: explaining why the question should *not* be on the next exam. In either case, explain your reasoning.



i>Clicker
Questions

Q1-3_A What if... the PFR in **Example 1-2** were replaced by a CSTR, what would be its volume?

Q1-4_A What if... you were asked to rework **Example 1-2** to calculate the time to reduce the number of moles of A to 1% if its initial value for a constant volume BR, what would you say? Would you do it? If your answer is “yes,” go ahead and calculate it; if your answer is “NO, I won’t do it!” then suggest two ways to work this problem incorrectly.

Q1-5_A Read through the Introduction. Write a paragraph describing both the content goals and the intellectual goals of the course and text. Also describe what’s on the Web site and how the Web site can be used with the text and course.

Q1-6_A Go to **Chapter 1 Useful Links** (<http://www.umich.edu/~elements/6e/01chap/obj.html#/>) and click on Professional Reference Shelf to view the photos and schematics of real reactors. Write a paragraph describing two or more of the reactors. What similarities and differences do you observe between the reactors on the Web site (e.g., www.loebequipment.com), and in the text? How do the used reactor prices compare with those in Table 1-1?

Q1-7_A What assumptions were made in the derivation of the design equation for: **(a)** The batch reactor (BR)? **(b)** The CSTR? **(c)** The plug-flow reactor (PFR)? **(d)** The packed-bed reactor (PBR)? **(e)** State in words the meanings of $-r_A$ and r'_A .

Q1-8_A Fill out the following table for each of the reactors discussed in this chapter, BR, CSTR, PBR, and Fluidized Bed:

Type of Reactor	Characteristics	Phases Present	Usage	Advantages	Disadvantages

Q1-9_A Define Chemical Process Safety and list four reasons we need to study it and why it is particularly relevant to CRE (<http://umich.edu/~safeche/index.html>).

Q1-10_A Go to **Chapter 1 Extra Help** on the Web site and click on **LearnChemE ScreenCasts** (<http://www.umich.edu/~elements/6e/01chap/learn-cheme-videos.html>). Choose one of the LearnChemE videos and critique it for such things as **(a)** value, **(b)** clarity, **(c)** visuals, and **(d)** how well it held your interest. (Score 1–7; 7 = outstanding, 1 = poor)

Q1-11_A Go to **Chapter 1 Extra Help** on the Web site and click on **LearnChemE ScreenCasts** (<http://www.umich.edu/~elements/6e/01chap/learn-cheme-videos.html>) the **How to Study** screencast and list three ways that screencasts can help you learn the material.

Q1-12_A Go to **Extra Help** then click on **Videos of Tips on Studying and Learning**. Go to **Chapter 1** (<http://www.umich.edu/~elements/6e/01chap/obj.html#/video-tips/>).

1. View one of the 5- to 6-minute video tutorials and list two of the most important points in the video. List what two things you think this screencast did well?
2. After viewing the three screencasts on How to Study (<http://www.learncheme.com/student-resources/how-to-study-resources>), describe the most efficient way to study. In video 3 How to Study, the author of this book has a very different view of one of the points suggested. What do you think it is?
3. View the video 13 Study Tips**** (4 Stars) (<https://www.youtube.com/watch?v=eVlvxHJdql8&feature=youtu.be>). List four of the tips that you think might help your study habits.
4. Rate each of the sites on video tips, (1) Not Helpful, (5) Very Helpful.

Computer Simulations and Experiments

Before running your experiments, stop a moment and try to predict how your curves will change shape as you change a variable (cf. Q1-1_A).

P1-1_A

1. Revisit **Example 1-3**.

Wolfram and Python

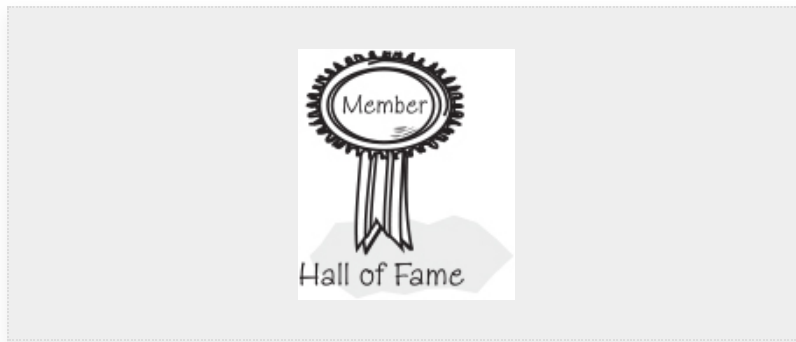
1. Describe how C_A and C_B change when you experiment with varying the volumetric flow rate, u_0 , and the specific reaction rate, k , and then write a conclusion about your experiments.
2. Click on the description of reversible reaction $A \rightleftharpoons B$ to understand how the rate law becomes $-r_A = k \left[C_A - \frac{C_B}{K_e} \right]$. Set K_e at its minimum value and vary k and u_0 . Next, set K_e at its maximum value and vary k and u_0 . Write a couple sentences describing how varying k , u_0 , and K_e affect the concentration profiles. We will learn more about K_e in [Section 3.2](#).
3. After reviewing *Generating Ideas and Solutions* on the Web site ([http://www.umich.edu/~elements/6e/toc/SCPS,3rdEdBook\(Ch07\).pdf](http://www.umich.edu/~elements/6e/toc/SCPS,3rdEdBook(Ch07).pdf)), choose one of the brainstorming techniques (e.g., lateral thinking) to suggest two questions that should be included in this problem.

Polymath

4. Modify the Polymath program to consider the case where the reaction is reversible as discussed in part (ii) above with $K_e = 3$. How do your results (i.e., C_A) compare with the irreversible reaction case?

Problems

P1-2_B Schematic diagrams of the Los Angeles basin are shown in Figure P1-2_B. The basin floor covers approximately 700 square miles ($2 \times 10^{10} \text{ ft}^2$) and is almost completely surrounded by mountain ranges. If one assumes an inversion height in the basin of 2,000 ft, the corresponding volume of air in the basin is $4 \times 10^{13} \text{ ft}^3$. We shall use this system volume to model the accumulation and depletion of air pollutants. As a very rough first approximation, we shall treat the Los Angeles basin as a well-mixed container (analogous to a CSTR) in which there are no spatial variations in pollutant concentrations.



Photograph by Radoslaw
Lecyk/Shutterstock

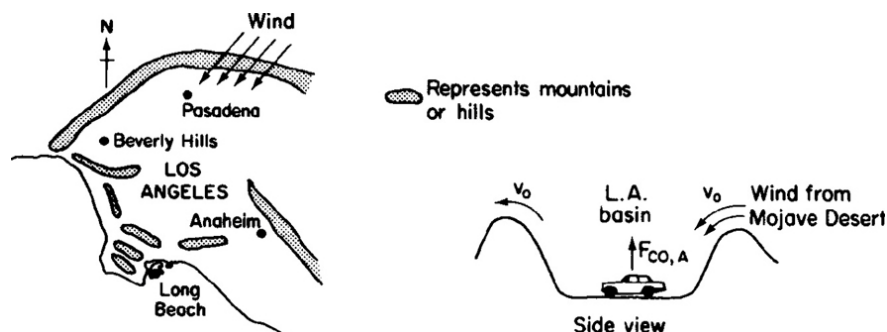


Figure P1-2_B Schematic diagrams of the Los Angeles basin.

(http://www.umich.edu/~elements/6e/web_mod/la_basin/index.htm)

We shall perform an unsteady-state mole balance (Equation (1-4)) on CO as it is depleted from the basin area by a Santa Ana wind. Santa Ana winds are high-velocity winds that originate in the Mojave Desert just to the northeast of Los Angeles.

Load the **Smog in Los Angeles Basin Web Module**. Use the data in the module to work parts 1–12 (a) through (h) given in the module. Load the **Living Example Polymath code** and explore the problem. For part (i), vary the parameters v_0 , a , and b , and write a paragraph describing what you find.

There is heavier traffic in the L.A. basin in the mornings and in the evenings as workers go to and from work in downtown L.A. Consequently, the flow of CO into the L.A. basin might be better represented by the sine function over a 24-hour period.

P1-3_B This problem focuses on using Polymath, an ordinary differential equation (ODE) solver, and also a nonlinear equation (NLE) solver. These equation solvers will be used extensively in later chapters. Information on how to obtain and load the Polymath Software is given in **Appendix D** and on the CRE Web site.

1. Professor Sven Köttlov has a son-in-law, Štěpán Dolež, who has a farm near Riča, Jofostan where there are initially 500 rabbits (x) and 200 foxes (y). Use Polymath or MATLAB to plot the concentration of foxes and rabbits as a function of time for a period of up to 500 days. The predator–prey relationships are given by the following set of coupled ordinary differential equations:

$$\begin{aligned}\frac{dx}{dt} &= k_1x - k_2x \cdot y \\ \frac{dy}{dt} &= k_3x \cdot y - k_4y\end{aligned}$$



Constant for growth of rabbits $k_1 = 0.02 \text{ day}^{-1}$

Constant for death of rabbits $k_2 = 0.00004/(\text{day} \times \text{no. of foxes})$

Constant for growth of foxes after eating rabbits $k_3 = 0.0004/(\text{day} \times \text{no. of rabbits})$

Constant for death of foxes $k_4 = 0.04 \text{ day}^{-1}$

What do your results look like for the case of $k_3 = 0.00004/(\text{day} \times \text{no. of rabbits})$ and $t_{\text{final}} = 800$ days? Also, plot the number of foxes versus the number of rabbits. Explain why the curves look the way they do.

Polymath Tutorial (<https://www.youtube.com/watch?v=nyJmt6cTiL4>)

2. Using Wolfram and/or Python in the Chapter 1 LEP on the Web site, what parameters would you change to convert the foxes versus rabbits plot from an oval to a circle? Suggest reasons that could cause this shape change to occur.
3. We will now consider the situation in which the rabbits contracted a deadly virus also called *rabbit measles (measlii)*. The death rate is $r_{\text{Death}} = k_D x$ with $k_D = 0.005 \text{ day}^{-1}$. Now plot the fox and rabbit concentrations as a function of time and also plot the foxes versus rabbits. Describe, if possible, the minimum growth rate at which the death rate does not contribute to the net decrease in the total rabbit population.
4. Use Polymath or MATLAB to solve the following set of nonlinear algebraic equations

$$\begin{aligned}x^3y - 4y^2 + 3x &= 1 \\ 6y^2 - 9xy &= 5\end{aligned}$$

with initial guesses of $x = 2, y = 2$. Try to become familiar with the edit keys in Polymath and MATLAB. See the CRE Web site for instructions. You will need to know how to use this solver in later chapters involving CSTRs.

Screen shots on how to run Polymath are shown at the end of
Summary Notes for Chapter 1 or on the CRE Web site,
www.umich.edu/~elements/6e/software/polymath-tutorial.html.

Interactive Computer Games

P1-4_A Find the Interactive Computer Games (ICG) on the
CRE Web site
(<http://www.umich.edu/~elements/6e/icg/index.html>).
Read the description of the Kinetic Challenge module
(<http://www.umich.edu/~elements/6e/icm/kinchal1.html>
) and then go to the installation instructions
(<http://www.umich.edu/~elements/6e/icm/install.html>)
to install the module on your computer. Play this game
and then record your performance number, which
indicates your mastery of the material.

Jeopardy Game Held at Annual AIChE Student Chapter
Meeting

ICM Quiz Show ICG

Mole Balance	Reactions	Rate Laws
100	100	100
200	200	200
300	300	300

ICG Kinetics Challenge 1 Performance #

Problems

P1-5_A OEQ (*Old Exam Question*) The reaction



takes place in an unsteady CSTR. The feed is only A and
B in equimolar proportions. Which of the following sets
of equations gives the correct set of mole balances on A,

B, and C? Species A and B are disappearing and species C is being formed. Circle the correct answer where all the mole balances are correct. **(a) (b)**

$$F_{B0} - F_A - \int^V r_A dV = \frac{dN_A}{dt}$$

$$1. \quad F_{B0} - F_B - \int^V r_A dV = \frac{dN_B}{dt}$$

$$-F_C + 2 \int^V r_A dV = \frac{dN_C}{dt}$$

$$F_{A0} - F_A + \int^V r_A dV = \frac{dN_A}{dt}$$

$$2. \quad F_{A0} - F_B + \int^V r_A dV = \frac{dN_B}{dt}$$

$$-F_C - 2 \int^V r_A dV = \frac{dN_C}{dt}$$

$$F_{A0} - F_A + \int_0^V r_A dV = \frac{dN_A}{dt}$$

$$3. \quad F_{A0} - F_B + \int^V r_A dV = \frac{dN_B}{dt}$$

$$-F_C + \int^V r_C dV = \frac{dN_C}{dt}$$

$$F_{B0} - F_A - \int^V r_A dV = \frac{dN_A}{dt}$$

$$4. \quad F_{B0} - F_{A0} - \int^V r_A dV = \frac{dN_B}{dt}$$

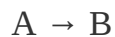
$$-F_C + \int^V r_C dV = \frac{dN_C}{dt}$$

5. None of the above.

This problem was written in honor of Ann Arbor, Michigan's own Grammy winning artist, Bob Seger

(https://www.youtube.com/channel/UComKJVf5rNLI_RfC_rbt7qg/videos).

P1-6B The reaction



is to be carried out isothermally in a continuous-flow reactor. The entering volumetric flow rate v_0 is $10 \text{ dm}^3/\text{h}$.

Note: $F_A = C_A v$. For a constant volumetric flow rate $v = v_0$, then $F_A = C_A v_0$. Also, $C_{A0} = F_{A0}/v_0 = ([15 \text{ mol/h}]/[10 \text{ dm}^3/\text{h}])0.5 \text{ mol/dm}^3$.

Calculate both the CSTR and PFR volumes necessary to consume 99% of A (i.e., $C_A = 0.01C_{A0}$) when the entering molar flow rate is 5 mol/h , assuming the reaction rate $-r_A$ is

1. $-r_A = k$ with $k = 0.05 \frac{\text{mol}}{\text{h} \cdot \text{dm}^3}$ [**Ans.:** $V_{\text{CSTR}} = 99 \text{ dm}^3$]
2. $-r_A = k_{CA}$ with 0.0001 s^{-1}
3. $-r_A = kC_A^2$ with $k = 300 \frac{\text{dm}^3}{\text{mol} \cdot \text{h}}$ [**Ans.:** $V_{\text{CSTR}} = 660 \text{ dm}^3$]
4. Repeat (a), (b), and/or (c) to calculate the time necessary to consume 99.9% of species A in a 1000 dm^3 constant-volume batch reactor with $C_{A0} = 0.5 \text{ mol/dm}^3$.

P1-7A Enrico Fermi (1901–1954) Problems (EFP). Enrico

Fermi was an Italian physicist who received the Nobel Prize for his work on nuclear processes. Fermi was famous for his “Back of the Envelope Order of Magnitude Calculation” to obtain an estimate of the answer through *logic* and then to make reasonable assumptions. He used a process to set bounds on the answer by saying it is probably larger than one number and smaller than another, and arrived at an answer that was within a factor of 10.

See

<http://mathforum.org/workshops/sum96/interdisc/sheila2.html>.

Enrico Fermi Problem

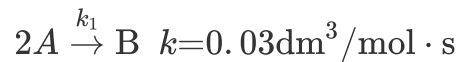
1. **EFP #1.** How many piano tuners are there in the city of Chicago? Show the steps in your reasoning.

1. Population of Chicago _____
2. Number of people per household _____
3. And so on, _____

An answer is given on the CRE Web site under Summary Notes for Chapter 1.

2. **EFP #2.** How many square meters of pizza were eaten by an undergraduate student body population of 20,000 during the Fall term 2016?
3. **EFP #3.** How many bathtubs of water will the average person drink in a lifetime?

P1-8A What is wrong with this solution? The irreversible liquid-phase second-order reaction ($-r = kC_A^2$)



is carried out in a CSTR. The entering concentration of A, C_{A0} , is 2 molar, and the exit concentration of A, C_A is 0.1 molar. The volumetric flow rate, v_0 , is constant at 3 dm³/s. What is the corresponding reactor volume?

Solution

1. Mole Balance

$$V = \frac{F_{A0} - F_A}{-r_A}$$

2. Rate Law (second order)

$$-r_A = kC_A^2$$

3. Combine

$$V = \frac{F_{A0} - F_A}{kC_A^2}$$

$$4. F_{A0} = v_0 C_{A0} = \frac{3\text{dm}^3}{\text{s}} \cdot \frac{2\text{molA}}{\text{dm}^3} = \frac{6\text{molA}}{\text{s}}$$

$$5. F_A = v_0 C_A = \frac{3\text{dm}^3}{\text{s}} \cdot \frac{0.1\text{molA}}{\text{dm}^3} = \frac{0.3\text{molA}}{\text{s}}$$

$$6. V = \frac{(6-0.3)\frac{\text{mol}}{\text{s}}}{\left(0.03\frac{\text{dm}^3}{\text{mol}\cdot\text{s}}\right)\left(2\frac{\text{mol}}{\text{dm}^3}\right)^2} = 47.5\text{dm}^3$$

If you like the **Puzzle Problems** in “What is wrong with the solutions”† you can find more for later chapters on the Web site under **Additional Material** for that chapter.

[†]**Puzzle Problems** for each chapter can be found on the CRE Web site under Expanded Material.

For more puzzles on what's "wrong with this solution," see additional material for each chapter on the CRE Web site home page, under "Expanded Material."



NOTE TO INSTRUCTORS: Additional problems (cf. those from the preceding editions) can be found in the solutions manual and on the CRE Web site. These problems could be photocopied and used to help reinforce the fundamental principles discussed in this chapter.

SUPPLEMENTARY READING

1. For further elaboration of the development of the general balance equation, see not only the Web site www.umich.edu/~elements/6e/index.html but also

R. M. FELDER and R. W. ROUSSEAU, *Elementary Principles of Chemical Processes*, 3rd ed. New York: Wiley, 2000, Chap. 4.

R. J. SANDERS, *The Anatomy of Skiing*. Denver, CO: Golden Bell Press, 1976.

2. A detailed explanation of a number of topics in this chapter can be found in the tutorials.

B. L. CRYNES and H. S. FOGLER, eds., *AIChE Modular Instruction Series E: Kinetics*, Vols. 1 and 2. New York: AIChE, 1981.

3. A discussion of some of the most important industrial processes is presented by

G. T. AUSTIN, *Shreve's Chemical Process Industries*, 5th ed.
New York: McGraw-Hill, 1984.

4. Short instructional videos (6–9 minutes) that correspond to the topics in this book can be found at <http://www.learncheme.com/>.
5. See the Web site, “Process Safety Across the Chemical Engineering Curriculum,” (<http://umich.edu/~safeche/index.html>).

2. Conversion and Reactor Sizing

Be more concerned with your character than with your reputation, because character is what you really are while reputation is merely what others think you are.

—John Wooden, former head coach, UCLA Bruins

Overview. In the first chapter, the general mole balance equation was derived and then applied to the four most common types of industrial reactors. A balance equation was developed for each reactor type and these equations are summarized in Table S1-1 in [Chapter 1](#). In [Chapter 2](#), we will show how to size and arrange these reactors *conceptually*, so that the reader may see the structure of chemical reaction engineering (CRE) design and will not get lost in the mathematical details.

In this chapter, we

- Define conversion
- Rewrite all balance equations for the four types of industrial reactors in [Chapter 1](#) in terms of the conversion, X
- Show how to size (i.e., determine the reactor volume) these reactors once the relationship between the reaction rate and conversion is known that is given, i.e., $-r_A = f(X)$
- Show how to compare CSTR and PFR sizes
- Show how to decide the best arrangements for reactors in series, a most important principle

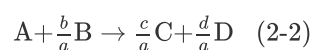
In addition to being able to determine CSTR and PFR sizes given the rate of reaction as a function of conversion, you will be able to calculate the overall conversion and reactor volumes for reactors arranged in series.

2.1 DEFINITION OF CONVERSION

Conversion helps us measure how far a reaction has progressed. In defining conversion, we choose one of the reactants as the basis of calculation and then relate the other species involved in the reaction to this basis. In virtually *all* instances, we *must* choose the limiting reactant as the basis of calculation. For single reactions, we can use conversion to develop the stoichiometric relationships and design equations by considering the general reaction



The uppercase letters represent chemical species, and the lowercase letters represent stoichiometric coefficients. We shall choose species A as our limiting reactant and, thus, our *basis of calculation*. The limiting reactant is the reactant that will be completely consumed first after the reactants have been mixed. We next divide the reaction expression through by the stoichiometric coefficient of the limiting reactant, that is, of species A, in order to arrange the reaction stoichiometry in the form



"A" is our basis of calculation

to put every quantity on a "*per mole of A*" basis, our limiting reactant.

Now we ask such questions as "How can we quantify how far a reaction (e.g., Equation (2-2)) proceeds to the right?" or "How many moles of C are formed for every mole of A consumed?" A convenient way to answer these questions is to define a parameter called *conversion*. The conversion X_A is the

number of moles of A that have reacted per mole of A fed to the system:

$$X_A = \frac{\text{Moles of A reacted}}{\text{Moles of A fed}}$$

Definition of X

Because we are defining conversion with respect to our basis of calculation (A in Equation (2-2)), we eliminate the subscript A for the sake of brevity and let $X \equiv X_A$. For *irreversible* reactions, the maximum conversion is 1.0, that is, complete conversion. For *reversible reactions*, the maximum conversion is the equilibrium conversion X_e (i.e., $X_{\max} = X_e$). We will take a closer look at equilibrium conversion in [Section 4.3](#).

2.2 BATCH REACTOR DESIGN EQUATIONS

In most batch reactors (BRs), the longer a reactant stays in the reactor, the more the reactant is converted to product until either equilibrium is reached or the reactant is exhausted. Consequently, in batch systems, the conversion X is a function of the time the reactants spend in the reactor. If N_{A0} is the number of moles of A initially present in the reactor (i.e., $t = 0$), then the total number of moles of A that have reacted (i.e., have been consumed) after a time t is $[N_{A0}X]$.

$$[\text{Moles of A reacted (consumed)}] = [\text{Moles of A fed}] \cdot \left[\frac{\text{Moles of A reacted}}{\text{Moles of A fed}} \right]$$

$$\left[\begin{array}{c} \text{Moles of A} \\ \text{reacted} \\ \text{(consumed)} \end{array} \right] = [N_{A0}] \cdot [X] \quad (2-3)$$

Now, the number of moles of A that remain in the reactor after a time t , N_A , can be expressed in terms of N_{A0} and X :

$$\begin{array}{rcl}
 \left[\begin{array}{c} \text{Moles of A} \\ \text{in reactor} \\ \text{at time } t \end{array} \right] & = & \left[\begin{array}{c} \text{Moles of A} \\ \text{initially fed} \\ \text{to reactor at} \\ t = 0 \end{array} \right] - \left[\begin{array}{c} \text{Moles of A that} \\ \text{have been} \\ \text{consumed by} \\ \text{chemical reaction} \end{array} \right] \\
 [N_A] & = & [N_{A0}] - [N_{A0}X]
 \end{array}$$

The number of moles of A in the reactor after a conversion X has been achieved is

$$N_A = N_{A0} - N_{A0}X = N_{A0}(1 - X) \quad (2-4)$$

Moles of A in the reactor at a time t

When no spatial variations in reaction rate exist, the mole balance on species A for a batch system is given by the following equation (cf. Equation (1-5)):

$$\frac{dN_A}{dt} = r_A V \quad (2-5)$$

This equation is valid whether or not the reactor volume is constant. In the general reaction, Equation (2-2), reactant A is disappearing; therefore, we multiply both sides of Equation (2-5) by -1 to obtain the mole balance for the batch reactor in the form

$$-\frac{dN_A}{dt} = (-r_A) V$$

The rate of disappearance of A, $-r_A$, in this reaction might be given by a rate law similar to Equation (1-2), such as $-r_A = kC_A C_B$.

For batch reactors, we are interested in determining how long to leave the reactants in the reactor to achieve a certain conversion X . To determine this length of time, we write the

mole balance, Equation (2-5), in terms of conversion by differentiating Equation (2-4) with respect to time, remembering that N_{A0} is the number of moles of A initially present in the reactor and is therefore a constant with respect to time.

$$\frac{dN_A}{dt} = 0 - N_{A0} \frac{dX}{dt}$$

Combining the above with Equation (2-5) yields

$$-N_{A0} \frac{dX}{dt} = r_A V$$

For a batch reactor, the design equation in differential form is

$$N_{A0} \frac{dX}{dt} = -r_A V \quad (2-6)$$

Batch reactor (BR) design equation

We call Equation (2-6) the differential form of the BR mole balance and it is often referred to as the **design equation** for a batch reactor because we have written the mole balance in terms of conversion. The differential forms of the batch reactor mole balances, Equations (2-5) and (2-6), are often used in the interpretation of reaction rate data (Chapter 7) and for reactors with heat effects (Chapters 11–13), respectively. Batch reactors are frequently used in industry for both gas-phase and liquid-phase reactions. The laboratory bomb calorimeter reactor is widely used for obtaining reaction rate data. Liquid-phase reactions are frequently carried out in batch reactors when small-scale production is desired or operating difficulties rule out the use of continuous-flow systems.

Uses of a BR

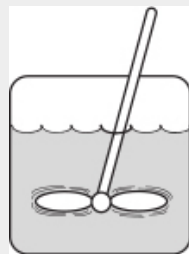
To determine the time to achieve a specified conversion X , we first separate the variables in Equation (2-6) as follows:

$$dt = N_{A0} \frac{dX}{-r_A V}$$

Batch time t to achieve a conversion X

Next, this equation is integrated with the limits that the reaction begins at time equals zero where there is no conversion initially (i.e., when $t = 0$, $X = 0$) and ends at time t when a conversion X is achieved (i.e., when $t = t$, then $X = X$). Carrying out the integration, we obtain the time t necessary to achieve a conversion X in a batch reactor

$$t = N_{A0} \int_0^X \frac{dX}{-r_A V} \quad (2-7)$$



Batch Reactor
Design Equation

The longer the reactants are left in the reactor, the greater the conversion will be. Equation (2-6) is the differential form of the design equation, and Equation (2-7) is the integral form of the design equation for a batch reactor.

2.3 DESIGN EQUATIONS FOR FLOW REACTORS

For a batch reactor, we saw that conversion increases with time spent in the reactor. For continuous-flow systems, this time usually increases with increasing reactor volume; for example, the bigger/longer the reactor, the more time it will take the reactants to flow completely through the reactor and thus, the more time to react. Consequently, the conversion X is a function of reactor volume V . If F_{A0} is the molar flow rate of species A fed to a system operated at steady state, the molar rate at which species A is reacting *within* the entire system will be $F_{A0}X$.

$$\begin{aligned} [F_{A0}] \cdot [X] &= \frac{\text{Moles of A fed}}{\text{time}} \cdot \frac{\text{Moles of A reacted}}{\text{Moles of A fed}} \\ [F_{A0}] \cdot [X] &= \frac{\text{Moles of A reacted}}{\text{time}} \end{aligned}$$

The molar flow rate of A leaving the system F_A *equals* the molar feed rate of A into the system F_{A0} *minus* the rate of reaction of A within the system ($F_{A0}X$). The preceding sentence can be expressed mathematically as

$$\begin{aligned} \left[\begin{array}{c} \text{Molar flow rate} \\ \text{at which A leaves} \\ \text{the system} \end{array} \right] &= \left[\begin{array}{c} \text{Molar flow rate} \\ \text{at which A is} \\ \text{fed to the system} \end{array} \right] - \left[\begin{array}{c} \text{Molar rate at} \\ \text{which A is} \\ \text{consumed within} \\ \text{the system} \end{array} \right] \\ [F_A] &= [F_{A0}] - [F_{A0}X] \end{aligned}$$

Rearranging gives

$$\boxed{F_A = F_{A0}(1 - X) \quad (2-8)}$$

The entering molar flow rate of species A, F_{A0} (mol/s), is just the product of the entering concentration, C_{A0} (mol/dm³), and the entering volumetric flow rate, v_0 (dm³/s).

$$\boxed{F_{A0} = C_{A0}v_0 \quad (2-9)}$$

For liquid systems, the volumetric flow rate, v , is constant and equal to v_0 , and C_{A0} is commonly given in terms of molarity, for example, $C_{A0} = 2 \text{ mol/dm}^3$.

Liquid phase

For gas systems, C_{A0} can be calculated from the entering mole fraction, y_{A0} , the temperature, T_0 , and pressure, P_0 , using the ideal gas law or some other gas law. For an ideal gas (see Appendix B):

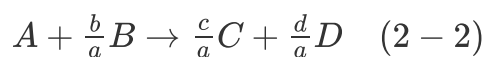
$$C_{A0} = \frac{P_{A0}}{RT_0} = \frac{y_{A0}P_0}{RT_0} \quad (2-10)$$

Gas phase

Now that we have a relationship [Equation (2-8)] between the molar flow rate and conversion, it is possible to express the design equations (i.e., mole balances) in terms of conversion for the *flow* reactors examined in Chapter 1.

2.3.1 CSTR (Also Known as a Backmix Reactor or a Vat)

Recall that the CSTR is modeled as being well mixed such that there are no spatial variations in the reactor. For the general reaction



the CSTR mole balance Equation (1-7) can be arranged to

$$V = \frac{F_{A0} - F_A}{-r_A} \quad (2-11)$$

We now substitute for F_A in terms of F_{A0} and X

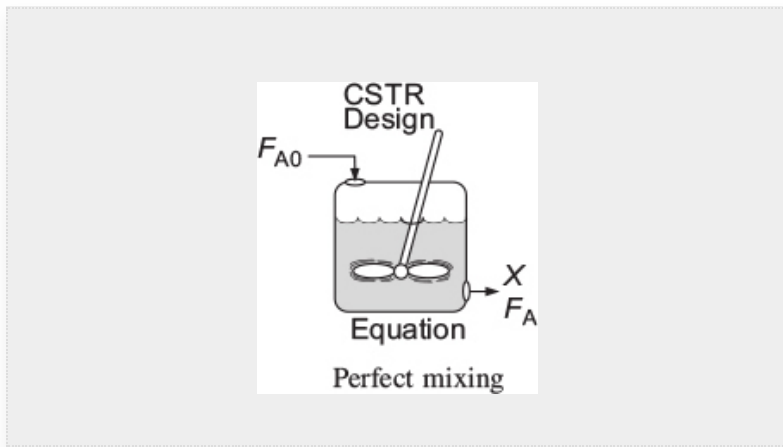
$$F_A = F_{A0} - F_{A0}X \quad (2-12)$$

and then substitute Equation (2-12) into (2-11)

$$V = \frac{F_{A0} - (F_{A0} - F_{A0}X)}{-r_A}$$

Simplifying, we see that the CSTR volume necessary to achieve a specified conversion X is

$$V = \frac{F_{A0}X}{(-r_A)_{\text{exit}}} \quad (2-13)$$



Because the reactor is *perfectly mixed*, the exit composition from the reactor is identical to the composition inside the reactor, and, therefore, the rate of reaction, $-r_A$, is evaluated at the exit conditions.

Evaluate $-r_A$ at the CSTR exit conditions!!

2.3.2 Tubular Flow Reactor (PFR)

We model the tubular reactor as having the fluid flowing in plug flow—that is, no radial gradients in concentration, temperature, or reaction rate.¹ As the reactants enter and flow axially down the reactor, they are consumed and the conversion increases along the length of the reactor. To

develop the PFR design equation, we first multiply both sides of the tubular reactor design equation given in Chapter 1, Equation (1-12), by -1 . We then express the mole balance equation for species A in the reaction as

¹ This constraint will be removed when we extend our analysis to nonideal (industrial) reactors in Chapters 16–18.

$$\frac{-dF_A}{dV} = -r_A \quad (2-14)$$

For a flow system, F_A has previously been given in terms of the entering molar flow rate F_{A0} and the conversion X

$$F_A = F_{A0} - F_{A0}X \quad (2-12)$$

Differentiating

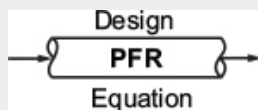
$$dF_A = -F_{A0} dX$$

and substituting into Equation (2-14) gives the differential form of the design equation for a plug-flow reactor (PFR)

$$F_{A0} \frac{dX}{dV} = -r_A \quad (2-15)$$

We now separate the variables and integrate with the limits $V = 0$ when $X = 0$ to obtain the plug-flow reactor volume necessary to achieve a specified conversion X

$$V = F_{A0} \int_0^X \frac{dX}{-r_A} \quad (2-16)$$



To carry out the integrations in the batch and plug-flow reactor design equations (2-7) and (2-16), as well as to evaluate the CSTR design equation (2-13), we need to know how the reaction rate $-r_A$ varies with the concentration (hence conversion) of the reacting species. This relationship between reaction rate and concentration is developed in Chapter 3.

2.3.3 Packed-Bed Reactor (PBR)

Packed-bed reactors are tubular reactors filled with catalyst particles. In PBRs, it is the weight of catalyst W that is important, rather than the reactor volume. The derivation of the differential and integral forms of the design equations for packed-bed reactors are analogous to those for a PFR (cf. Equations (2-15) and (2-16)). That is, substituting Equation (2-12) for F_A in Equation (1-15) gives

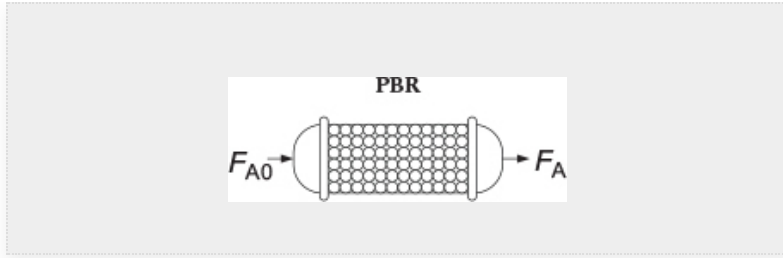
$$F_{A0} \frac{dX}{dW} = -r'_A \quad (2-17)$$

PBR design equation

The differential form of the design equation (i.e., Equation (2-17)) **must** be used when analyzing reactors that have a *pressure drop* along the length of the reactor. We discuss pressure drop in packed-bed reactors in Chapter 5.[†]

In the *absence* of pressure drop, that is, $\Delta P = 0$, we can integrate Equation (2-17) with limits $X = 0$ at $W = 0$, and when $W = W$ then $X = X$ to obtain

$$W = F_{A0} \int_0^X \frac{dX}{-r'_A} \quad (2-18)$$



Equation (2-18) can be used to determine the catalyst weight W (i.e., mass) necessary to achieve a conversion X when the total pressure remains constant.

2.4 SIZING CONTINUOUS-FLOW REACTORS

In this section, we are going to show how we can size CSTRs and PFRs (i.e., determine their reactor volumes) using the appropriate mole balance in terms of conversion and knowledge of the rate of reaction, $-r_A$, as a function of conversion, X (i.e., $-r_A = f(X)$). The rate of disappearance of A, $-r_A$, is almost always a function of the concentrations of the various species present (see Chapter 3). When only one reaction is occurring, each of the concentrations can be expressed as a function of the conversion X (see Chapter 4); consequently, $-r_A$ can be expressed as a function of X .

As an example, we shall choose a particularly simple functional dependence on concentration, that is, first-order.

$$-r_A = kC_A = kC_{A0}(1 - X)$$

Here, k is the specific reaction rate and is a function of temperature only, and C_{A0} is the entering concentration of A. We note in Equations (2-13) and (2-16) that the reactor volume is a function of the reciprocal of $-r_A$. For this first-order dependence, a plot of the reciprocal rate of reaction ($1/-r_A$) as a function of conversion yields a curve similar to the one shown in Figure 2-1, where

$$\frac{1}{-r_A} = \frac{1}{kC_{A0}} \left(\frac{1}{1-X} \right)$$

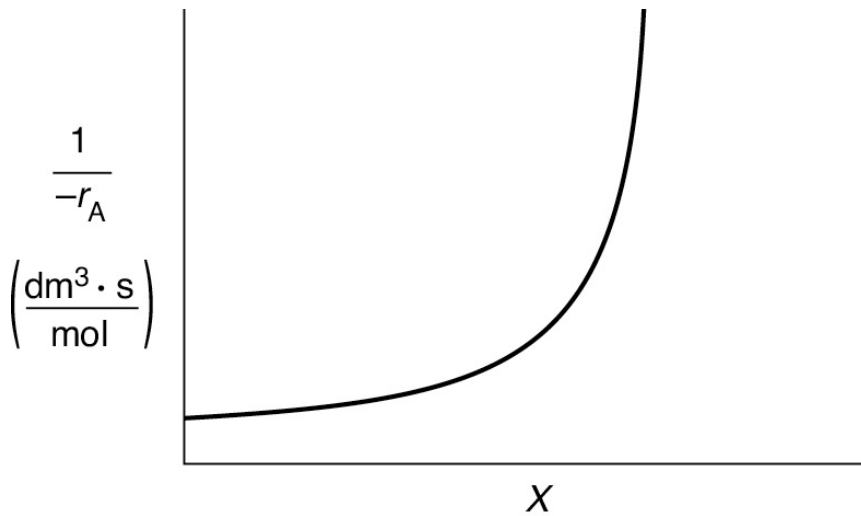


Figure 2-1 Typical curve of the reciprocal rate as a function of conversion.

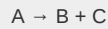
[†] Be sure to watch the YouTube video (<https://www.youtube.com/watch?v=S9mUAXmNqxs>).

We can use [Figure 2-1](#) to size CSTRs and PFRs for different entering flow rates. By *sizing* we mean either determine the reactor volume for a specified conversion *or* determine the conversion for a specified reactor volume. Before sizing flow reactors, let's consider some insights. If a reaction is carried out isothermally, the rate is usually greatest at the start of the reaction when the concentration of reactant is greatest (i.e., when there is negligible conversion [$X \equiv 0$]). Hence, the reciprocal rate ($1/-r_A$) will be small. Near the end of the reaction, when the reactant has been mostly used up and thus the concentration of A is small (i.e., the conversion is large), the reaction rate will be small. Consequently, the reciprocal rate ($1/-r_A$) is large.

For all irreversible reactions of greater than zero order (see [Chapter 3](#) for zero-order reactions), as we approach complete

conversion where all the limiting reactant is used up, that is, $X = 1$, the reciprocal rate approaches infinity as does the reactor volume, that is,

As $X \rightarrow 1$, $-r_A \rightarrow 0$, thus, $\frac{1}{-r_A} \rightarrow \infty$ and therefore $V \rightarrow \infty$

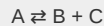


Consequently, we see that an *infinite* reactor volume is necessary to reach complete conversion, $X = 1.0$.

"To infinity and beyond"—Buzz Lightyear

For reversible reactions (e.g., $A \rightleftharpoons B$), the maximum conversion is the equilibrium conversion X_e . At equilibrium, the reaction rate is zero ($r_A \equiv 0$). Therefore,

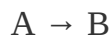
as $X \rightarrow X_e$, $-r_A \rightarrow 0$, thus, $\frac{1}{-r_A} \rightarrow \infty$ and therefore $V \rightarrow \infty$



and we see that an *infinite* reactor volume would also be necessary to obtain the exact equilibrium conversion, $X = X_e$. We will discuss X_e further in Chapter 4.

Examples of Reactor Design and Staging Given $-r_A = f(X)$

To illustrate the design of continuous-flow reactors (i.e., CSTRs and PFRs), we consider the irreversible isothermal gas-phase isomerization



Researchers at the Central Lab performed experiments to determine the rate of chemical reaction as a function of the conversion of reactant A and the results are shown in Table 2-1. The temperature was constant at 500 K (440°F), the total pressure was constant at 830 kPa (8.2 atm), and the initial charge to the reactor was pure A. The entering molar flow of reactant A is $F_{A0} = 0.4 \text{ mol/s}$.

TABLE 2-1 RAW DATA[†]

X	0	0.1	0.2	0.4	0.6	0.7	0.8
$-r_A \text{ (mol/m}^3 \cdot \text{s)}$	0.45	0.37	0.30	0.195	0.113	0.079	0.05

[†]Proprietary coded data courtesy of Jofostan Central Research Laboratory, Çölow, Jofostan, and published in *Jofostan Journal of Chemical Engineering Research*, Volume 21, page 73 (2023).

If we know $-r_A$ as a function of X , we can size any isothermal reaction system.

Recalling the CSTR and PFR design equations, (2-13) and (2-16), we see that the reactor volume varies directly with the molar flow rate F_{A0} and with the reciprocal of $-r_A$, $\left(\frac{1}{-r_A}\right)$, for example, $V = \left(\frac{F_{A0}}{-r_A}\right)X$. Consequently, to size reactors, we first convert the raw data in Table 2-1, which gives $-r_A$ as a function of X first to $\left(\frac{1}{-r_A}\right)$ as a function of X . Next, we multiply by the entering molar flow rate, F_{A0} , to obtain $\left(\frac{F_{A0}}{-r_A}\right)$ as a function of X as shown in Table 2-2 of the processed data for $F_{A0} = 0.4 \text{ mol/s}$.

TABLE 2-2 PROCESSED DATA

X	0.0	0.1	0.2	0.4	0.6	0.7	0.8
$-r_A \left(\frac{\text{mol}}{\text{m}^3 \cdot \text{s}} \right)$	0.45	0.37	0.30	0.195	0.113	0.079	0.05
$(1/-r_A) \left(\frac{\text{m}^3 \cdot \text{s}}{\text{mol}} \right)$	2.22	2.70	3.33	5.13	8.85	12.7	20
$(F_{A0}/-r_A)(\text{m}^3)$	0.89	1.08	1.33	2.05	3.54	5.06	8.0

We shall use the data in this table for the next five Example Problems.

To size reactors for different entering molar flow rates, F_{A0} , we would use rows 1 and 4, as shown by the arrows in Table 2-2 to construct the following figure:

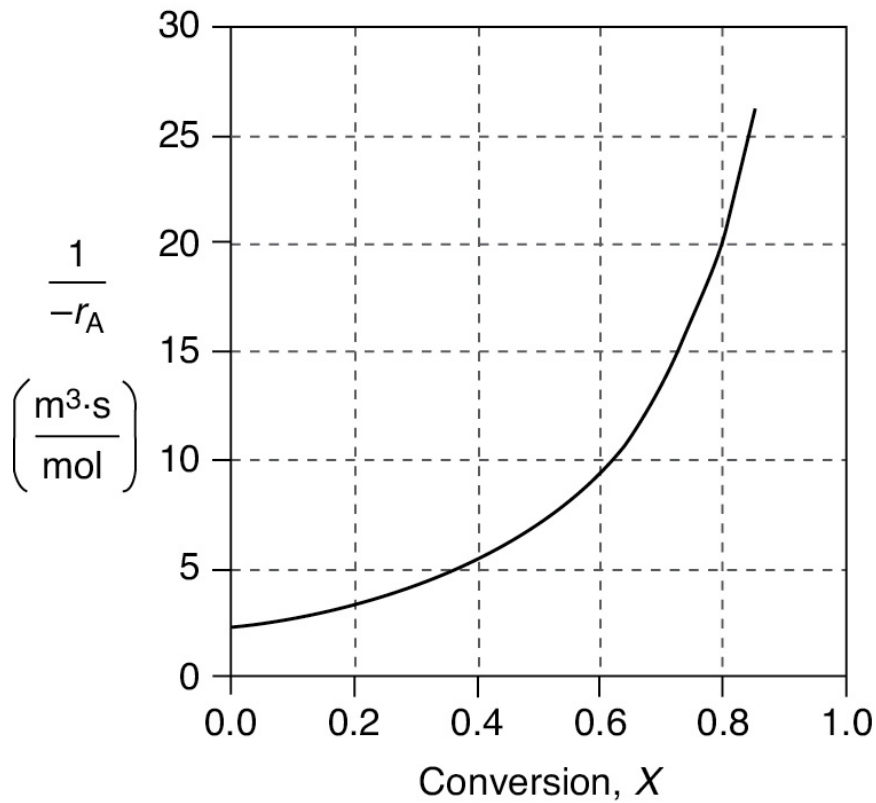


Figure 2-2(a) Levenspiel plot of processed data 1 in Table 2-2.

However, for a given F_{A0} , rather than using Figure 2-2(a) to size reactors, it is often more advantageous to plot $\left(\frac{F_{A0}}{-r_A}\right)$ as a function of X , which is called a Levenspiel plot.[†] We are now going to carry out a number of examples where we have specified the flow rate F_{A0} to be 0.4 mol A/s.

Plotting $\left(\frac{F_{A0}}{-r_A}\right)$ as a function of X using the data in Table 2-2 we obtain the plot shown in Figure 2-2(b).

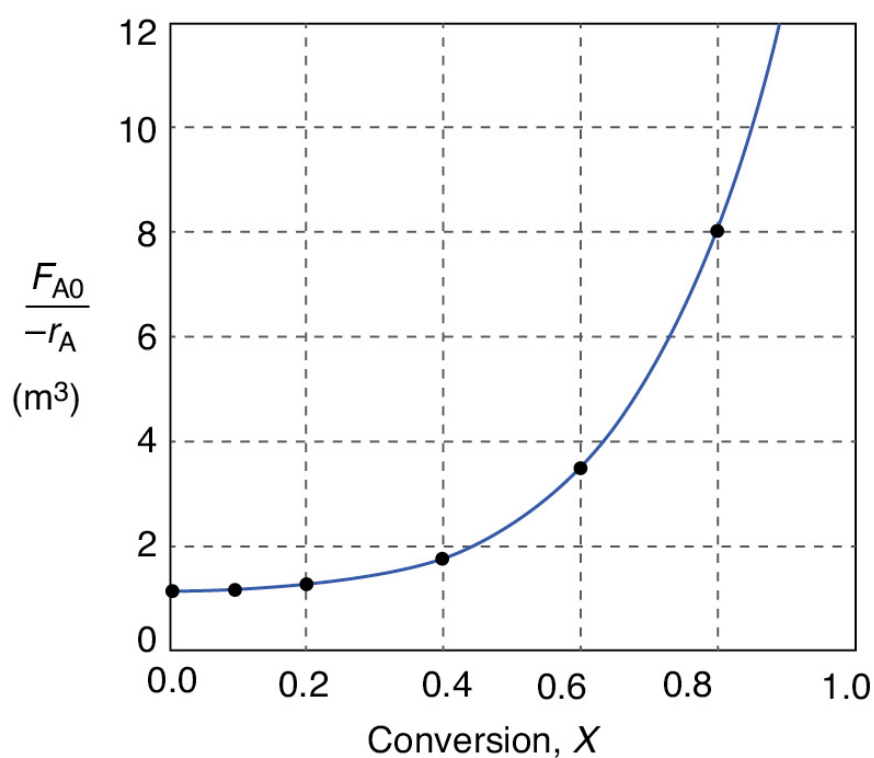


Figure 2-2(b) Levenspiel plot of processed data 2 in Table 2-2.

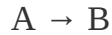
Levenspiel plot

We are now going to use the Levenspiel plot of the processed data (Figure 2-2(b)) to size a CSTR and a PFR.

†After Professor Octave Levenspiel (1/1/1926–3/5/2017), Oregon State University, Corvallis, OR.

Example 2-1 Sizing a CSTR

The reaction described by the data in Table 2-2



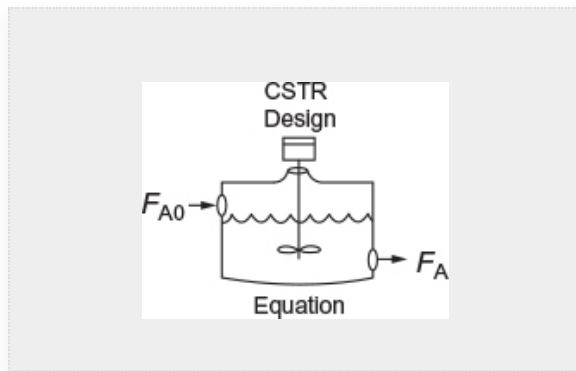
is to be carried out in a CSTR. Species A enters the reactor at a molar flow rate of $F_{A0} = 0.4 \frac{\text{mol}}{\text{s}}$, which is the flow rate used to construct the Levenspiel plot in Figure 2-2(b).

1. Using the data in either Table 2-2 or Figure 2-2(b), calculate the volume necessary to achieve 80% conversion in a CSTR.
2. Shade the area in Figure 2-2(b) that would give the CSTR volume necessary to achieve 80% conversion.

Solutions

1. Equation (2-13) gives the volume of a CSTR as a function of F_{A0} , X , and $-r_A$

$$V = \frac{F_{A0}X}{(-r_A)_{exit}} \quad (2-13)$$



In a CSTR, the composition, temperature, and conversion of the effluent stream are identical to that of the fluid within the reactor, because perfect mixing is assumed. Therefore, we need to find the value of $-r_A$ (or reciprocal thereof) at $X = 0.8$. From either Table 2-2 or Figure 2-2(a), we see that when $X = 0.8$, then

$$\left(\frac{1}{-r_A} \right)_{X=0.8} = 20 \frac{\text{m}^3 \cdot \text{s}}{\text{mol}}$$

Substitution into Equation (2-13) for an entering molar flow rate, F_{A0} , of 0.4 mol A/s and $X = 0.8$ gives

$$V = 0.4 \frac{\text{mol}}{\text{s}} \left(\frac{20 \text{ m}^3 \cdot \text{s}}{\text{mol}} \right) (0.8) = 6.4 \text{ m}^3 \quad (\text{E2} - 1.1)$$

$$V = 6.4 \text{ m}^3 = 6400 \text{ dm}^3 = 6400 \text{ liters} \quad \underline{\text{Answer}}$$

2. Shade the area in Figure 2-2(b) that yields the CSTR volume to achieve 80% conversion. Rearranging Equation (2-13) gives

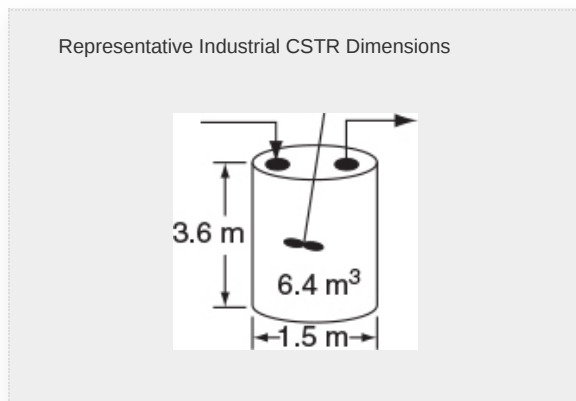
$$V = \left[\frac{F_{A0}}{-r_A} \right] X \quad (2 - 13)$$

In Figure E2-1.1, the volume is equal to the area of a rectangle with a height ($F_{A0}/-r_A = 8 \text{ m}^3$) and a base ($X = 0.8$). This rectangle is shaded in the figure.

$$V = \left[\frac{F_{A0}}{-r_A} \right]_{X=0.8} (0.8) \quad (\text{E2} - 1.2)$$

$V = \text{Levenspiel rectangle area} = \text{height} \times \text{width}$

$$V = [8 \text{ m}^3][0.8] = 6.4 \text{ m}^3 = 6400 \text{ dm}^3 = 6400 \text{ L} \quad \underline{\text{Answer}}$$



The CSTR volume necessary to achieve 80% conversion is 6.4 m^3 when operated at 500 K, 830 kPa (8.2 atm), and with an entering molar flow rate of A of 0.4 mol/s. This volume corresponds to a reactor about 1.5 m in diameter and 3.6 m high. It's a large CSTR, but this is a gas-phase reaction, and CSTRs are normally not used for gas-phase reactions. CSTRs are used primarily for liquid-phase reactions. Oops!

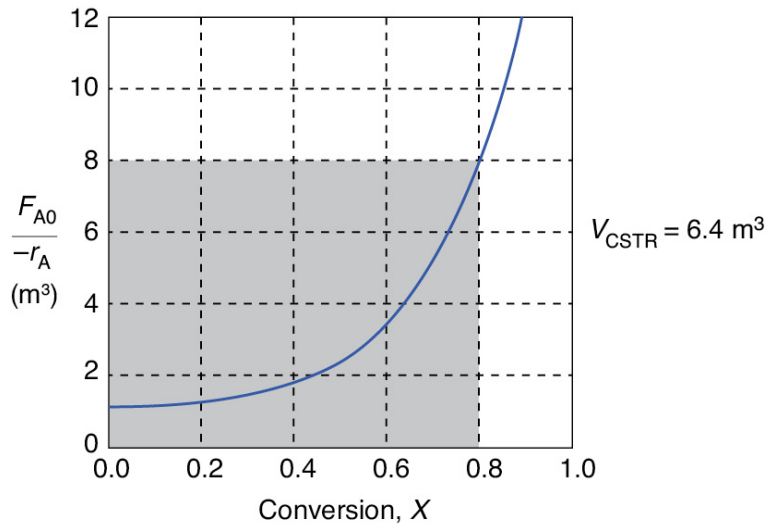


Figure E2-1.1 Levenspiel CSTR plot.

Plots of $(F_{A0}/-r_A)$ versus X are often referred to as Levenspiel plots (after Prof. Octave Levenspiel).

Analysis: Given the conversion, the rate of reaction as a function of conversion along with the molar flow of the species A, we saw how to calculate the volume of a CSTR. From the data and information given, we calculated the volume to be 6.4 m^3 for 80% conversion. We showed how to carry out this calculation using the design equation (2-13) and also using a Levenspiel plot.

Example 2–2 Sizing a PFR

The reaction described by the data in [Tables 2-1](#) and [2-2](#) is to be carried out in a PFR. The entering molar flow rate of A is again, $F_{A0} = 0.4 \text{ mol/s}$.

1. First, use one of the integration formulas given in [Appendix A.4](#) to determine the PFR reactor volume necessary to achieve 80% conversion.
2. Next, shade the area in [Figure 2-2\(b\)](#) that would give the PFR volume necessary to achieve 80% conversion.
3. Finally, make a qualitative sketch of the conversion, X , and the rate of reaction, $-r_A$, down the length (volume) of the reactor.

Solution

We start by repeating rows 1 and 4 of [Table 2-2](#) to produce the results shown in [Table 2-3](#)

TABLE 2-3 PROCESSED DATA 2

X	0.0	0.1	0.2	0.4	0.6	0.7	0.8
$(F_{A0}/-r_A)(\text{m}^3)$	0.89	1.08	1.33	2.05	3.54	5.06	8.0

1. **(a) Numerically evaluate PFR volume.** For the PFR, the differential form of the mole balance is

$$F_{A0} \frac{dX}{dV} = -r_A \quad (2-15)$$

Rearranging and integrating gives

$$V = F_{A0} \int_0^{0.8} \frac{dX}{-r_A} = \int_0^{0.8} \frac{F_{A0}}{-r_A} dX \quad (2-16)$$

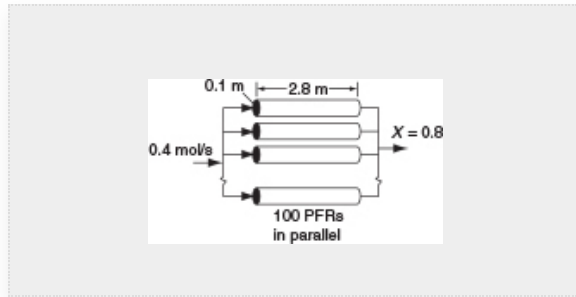
We shall use the *five-point quadrature* formula ([Equation \(A-23\)](#)) given in [Appendix A.4](#) to numerically evaluate [Equation \(2-16\)](#). The five-point formula with a final conversion of 0.8 gives four equal segments between $X = 0$ and $X = 0.8$, with a segment length of $\Delta X = \frac{0.8}{4} = 0.2$. The function inside the integral is evaluated at $X = 0$, $X = 0.2$, $X = 0.4$, $X = 0.6$, and $X = 0.8$.

$$V = \frac{\Delta X}{3} \left[\frac{F_{A0}}{-r_A(X=0)} + \frac{4F_{A0}}{-r_A(X=0.2)} + \frac{2F_{A0}}{-r_A(X=0.4)} + \frac{4F_{A0}}{-r_A(X=0.6)} + \frac{F_{A0}}{-r_A(X=0.8)} \right] \quad (\text{E2-2.1})$$

Using values of $[F_{A0}/(-r_A)]$ corresponding to the different conversions in Table 2-3 yields

$$V = \left(\frac{0.2}{3} \right) [0.89 + 4(1.33) + 2(2.05) + 4(3.54 + 8.0)] \text{ m}^3 = \left(\frac{0.2}{3} \right) (32.47 \text{ m}^3)$$

$$V = 2.165 \text{ m}^3 = 2165 \text{ dm}^3$$



The PFR reactor volume necessary to achieve 80% conversion is 2165 dm^3 . This volume could be achieved by using a bank of 100 PFRs that are each 0.1 m in diameter with a length of 2.8 m (e.g., see margin figure or Figures 1-8(a) and (b)).

Note: As we proceed through later chapters and have analytical formulas for $-r_A$, we will use integration tables or software packages (e.g., Polymath, rather than quadrature formulas, such as Equation (E2-2.1)).

2. The PFR volume, that is, the integral in Equation (2-16), can also be evaluated from the area under the curve of a plot of $(F_{A0}/-r_A)$ versus X .

$$V = \int_0^{0.8} \frac{F_{A0}}{-r_A} dX = \text{Area under the curve between } X = 0 \text{ and } X = 0.8$$

(see shaded area in Figure E2-2.1)

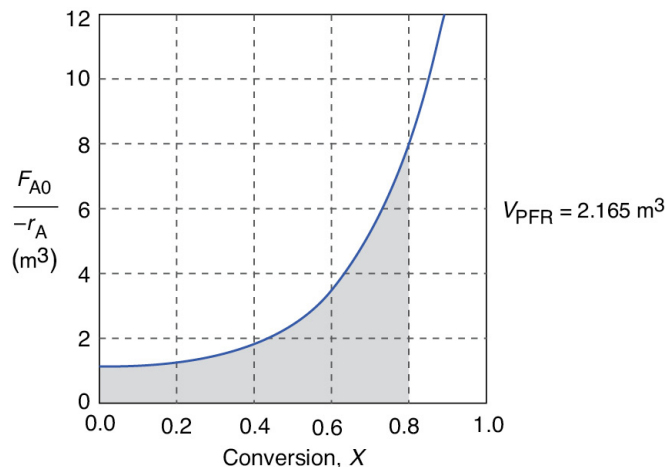


Figure E2-2.1 Levenspiel PFR plot.

PFR

The area under the curve will give the tubular reactor volume necessary to achieve the specified conversion of A. For 80% conversion, the shaded area is roughly equal to 2165 dm^3 (2.165 m^3).

3. Sketch the profiles of $-r_A$ and X down the length of the reactor.

We know that as we proceed down the reactor, the conversion increases as more and more reactant is converted to product. Consequently, as the reactant is consumed, the concentration of reactant decreases, as does the rate of disappearance of A for isothermal reactions.

1. For $X = 0.2$, we calculate the corresponding reactor volume using Simpson's rule (given in [Appendix A.4](#) as Equation (A-21)) with increment $\Delta X = 0.1$ and the data in rows 1 and 4 in [Table 2-2](#).

$$\begin{aligned} V &= F_{A0} \int_0^{0.2} \frac{dX}{-r_A} = \frac{\Delta X}{3} \left[\frac{F_{A0}}{-r_A(X=0)} + \frac{4F_{A0}}{-r_A(X=0.1)} + \frac{F_{A0}}{-r_A(X=0.2)} \right] \quad (\text{E2} - 2.2) \\ &= \left(\frac{0.1}{3} [0.89 + 4(1.08) + 1.33] \right) \text{m}^3 = \frac{0.1}{3} (6.54 \text{m}^3) = 0.218 \text{m}^3 = 218 \text{m}^3 \\ &= 218 \text{ m}^3 \end{aligned}$$

This volume (218 m^3) is the volume at which $X = 0.2$.

From [Table 2-2](#), we see the corresponding rate of reaction at $X = 0.2$ is $-r_A = 0.3 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$.

Therefore at $X = 0.2$, then $-r_A = 0.3 \text{ mol/m}^3 \cdot \text{s}$ and $V = 218 \text{ dm}^3$.

2. For $X = 0.4$, we can again use [Table 2-3](#) and Simpson's rule with $\Delta X = 0.2$ to find the reactor volume necessary for a conversion of 40%.

$$\begin{aligned} V &= \frac{\Delta X}{3} \left[\frac{F_{A0}}{-r_A(X=0)} + \frac{4F_{A0}}{-r_A(X=0.2)} + \frac{F_{A0}}{-r_A(X=0.4)} \right] \\ &= \left(\frac{0.2}{3} [0.89 + 4(1.33)] + 2.05 \right) \text{m}^3 = 0.551 \text{m}^3 \\ &= 551 \text{ dm}^3 \end{aligned}$$

From [Table 2-2](#) we see that at $X = 0.4$, $-r_A = 0.195 \text{ mol m}^3 \cdot \text{s}$ and $V = 551 \text{ dm}^3$.

We can continue in this manner to arrive at [Table E2-2.1](#).

TABLE E2-2.1 CONVERSION AND REACTION RATE PROFILES

X	0	0.2	0.4	0.6	0.8
$-r_A \left(\frac{\text{mol}}{\text{m}^3 \cdot \text{s}} \right)$	0.45	0.30	0.195	0.113	0.05
$V \text{ (dm}^3\text{)}$	0	218	551	1093	2165

The data in Table E2-2.1 are plotted in Figures E2-2.2(a) and (b).

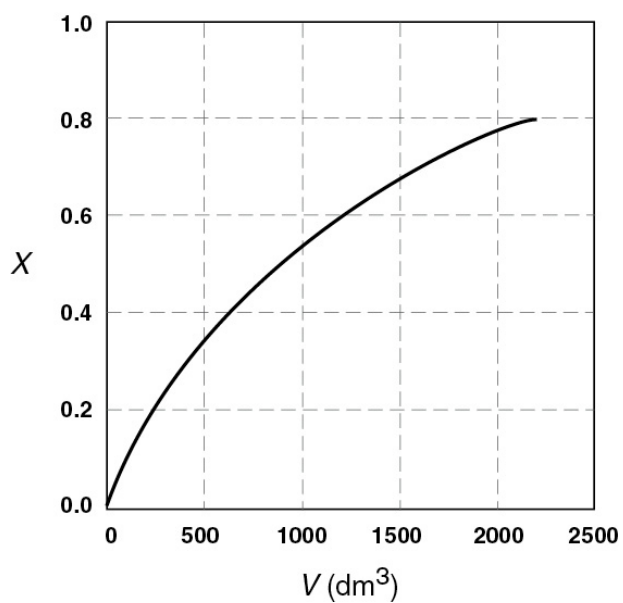


Figure E2-2.2(a) Conversion profile.

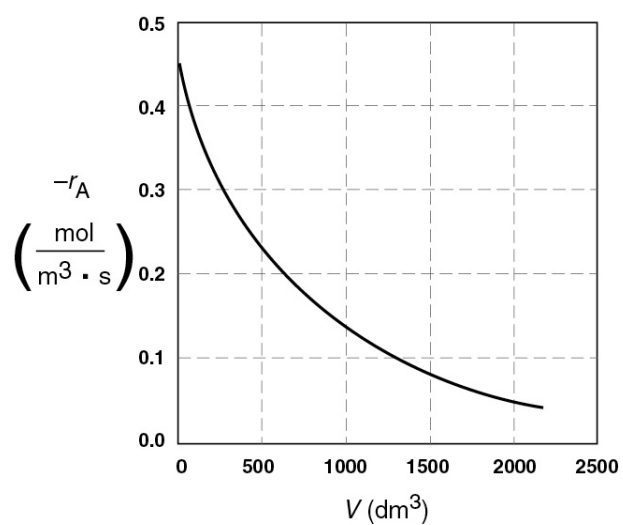


Figure E2-2.2(b) Reaction rate profile.

For isothermal reactions, the conversion increases and the rate decreases as we move down the PFR.

Analysis: One observes that for *most* all isothermal reactions the reaction rate, $-r_A$, decreases as we move down the reactor while the conversion increases. These plots are typical for reactors operated isothermally.

Example 2-3 Comparing CSTR and PFR Sizes

Compare the volumes of a CSTR and a PFR required for the same conversion using the data in [Figure 2-2\(b\)](#). Which reactor would require the smaller volume to achieve a conversion of 80%: a CSTR or a PFR? The entering molar flow rate and the feed conditions are the same in both cases.

Solution

We will again use the data in [Table 2-3](#).

TABLE 2-3 PROCESSED DATA 2

X	0	0.00	0.10	0.20	0.40	0.60	0.70	0.8
$(F_{A0}/-r_A)$ (m ³)		0.8	1.0	1.3	2.0	3.5	5.0	8.
		9	8	3	5	4	6	0

The CSTR volume was 6.4 m³ and the PFR volume was 2.165 m³. When we combine [Figures E2-1.1](#) and [E2-2.1](#) on the same graph, [Figure 2-3.1\(a\)](#), we see that the crosshatched area above the curve is the difference in the CSTR and PFR reactor volumes. [Figure E2-3.1\(b\)](#) shows the rate of reaction, $-r_A$, as a function of conversion. We note that at 80% conversion the rate is approximately one-tenth the initial rate.

For isothermal reactions *greater* than zero order (see [Chapter 3](#)), the CSTR volume will always be greater

than the PFR volume for the same conversion and reaction conditions (temperature, flow rate, etc.).

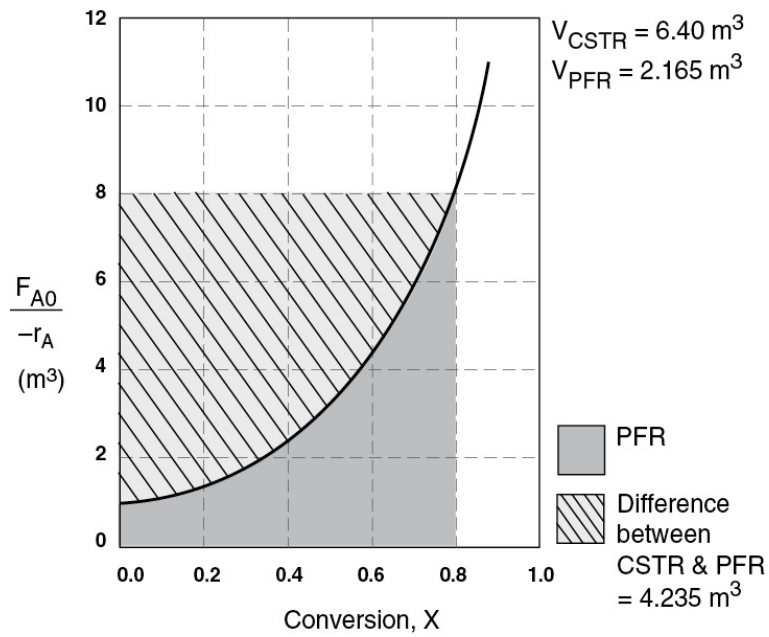


Figure E2-3.1(a) Comparison of CSTR and PFR reactor sizes for $X = 0.8$.

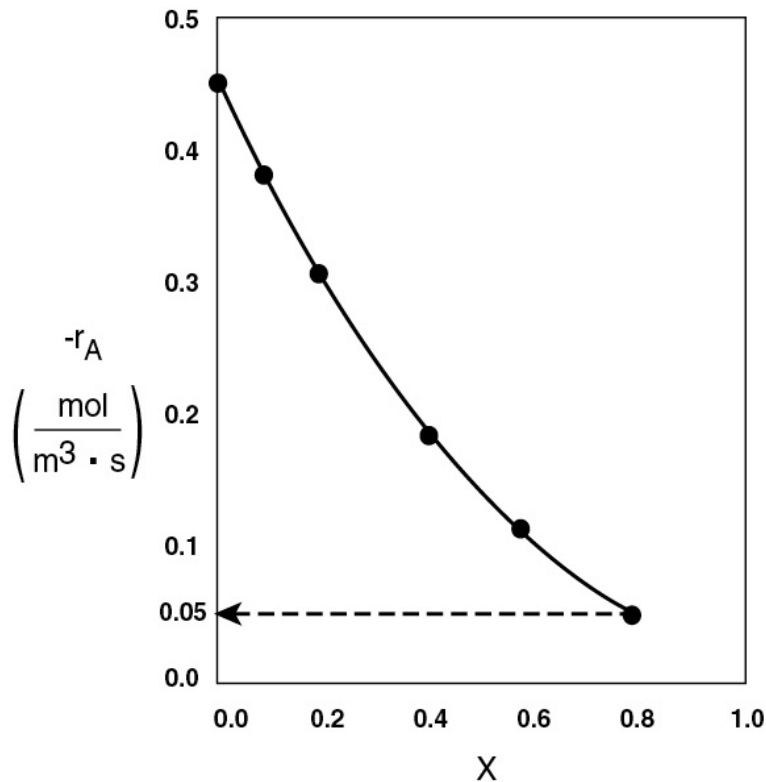


Figure E2-3.1(b) $-r_A$ as a function of X obtained from Table 2-2.1.

Analysis: We see that the reason the isothermal CSTR volume is usually greater than the PFR volume is that the CSTR is always operating at the lowest reaction rate (e.g., $-r_A = 0.05 \text{ mol m}^3 \cdot \text{s}$ in Figure E2-3.1(b)). The PFR, on the other hand, starts at a high rate at the entrance and gradually decreases to the exit rate, thereby requiring less volume because the volume is inversely proportional to the rate. However, there are exceptions such as autocatalytic reactions, product-inhibited reactions, and nonisothermal exothermic reactions; these trends will not always be the case, as we will see in Chapters 9 and 11.

2.5 REACTORS IN SERIES

Many times, reactors are connected in series so that the exit stream of one reactor is the feed stream for another reactor. When this arrangement is used, it is often possible to speed calculations by defining conversion in terms of location at a point downstream rather than with respect to any single reactor. That is, the conversion X is the *total number of moles* of A that have reacted up to that point per mole of A fed to the *first* reactor.

For reactors in series

$$X_i = \frac{\text{Total moles of A reacted up to point } i}{\text{Moles of A fed to the first reactor}}$$

Only valid for **NO** side streams!!

However, this definition can *only* be used when the feed stream only enters the first reactor in the series and there are *no* side streams either fed or withdrawn. The molar flow rate of A at point i is equal to the moles of A fed to the first reactor, minus all the moles of A reacted up to point i .



$$F_{Ai} = F_{A0} - F_{A0}X_i$$

$$F_{Ai} = F_{A0} - F_{A0}X_i$$

For the reactors shown in Figure 2-3, X_1 at point $i = 1$ is the conversion achieved in the PFR, X_2 at point $i = 2$ is the total conversion achieved at this point in the PFR and the CSTR, and X_3 is the total conversion achieved by all three reactors.

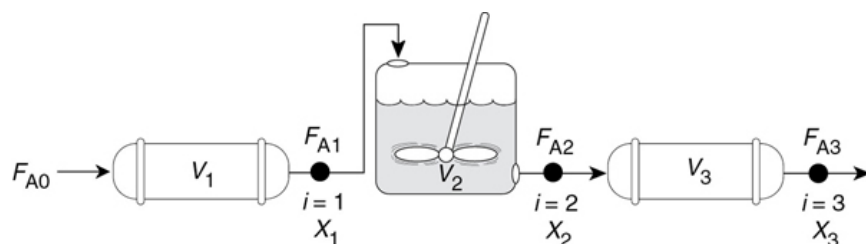


Figure 2-3 Reactors in series.

To demonstrate these ideas, let us consider three different schemes of reactors in series: two CSTRs, two PFRs, and then a combination of PFRs and CSTRs in series. To size these reactors, we shall use the impeccable data in Table 2-1 from Jofostan Central Research laboratories that gives the reaction rate at different conversions.

2.5.1 CSTRs in Series

The first scheme to be considered is the two CSTRs in series shown in Figure 2-4.

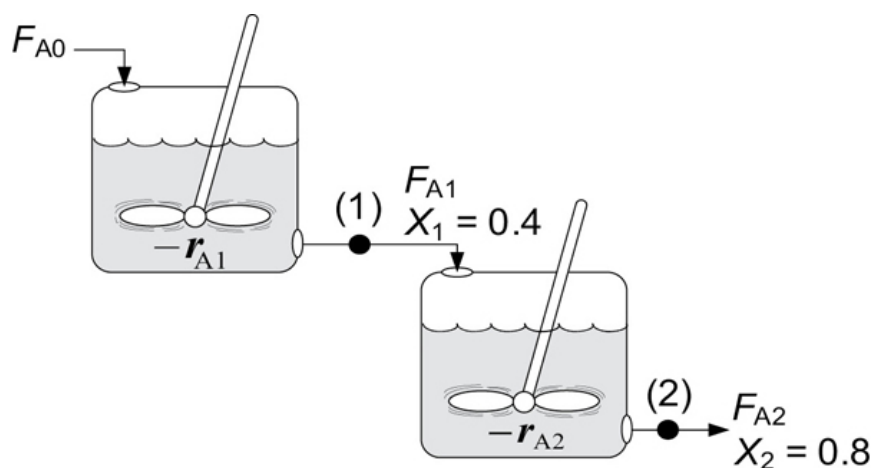


Figure 2-4 Two CSTRs in series.

For the first reactor, the rate of disappearance of A is $-r_{A1}$ at conversion X_1 .

A mole balance on reactor 1 gives

$$\text{In} - \text{Out} + \text{Generation} = 0$$

$$\text{Reactor 1: } F_{A0} - F_{A1} + r_{A1}V_1 = 0 \quad (2-19)$$

The molar flow rate of A at point 1 is

$$F_{A1} = F_{A0} - F_{A0}X_1 \quad (2-20)$$

Combining Equations (2-19) and (2-20), and rearranging

$$V_1 = \frac{F_{A0}X_1}{-r_A} \quad (2-21)$$

Reactor 1

In the second reactor, the rate of disappearance of A, $-r_{A2}$, is evaluated at the conversion of the exit stream of reactor 2, X_2 .

A steady-state mole balance on the second reactor is

$$\text{In} - \text{Out} + \text{Generation} = 0$$

$$\text{Reactor 2: } F_{A1} - F_{A2} + r_{A2}V_2 = 0 \quad (2-22)$$

The molar flow rate of A at point 2 is

$$F_{A2} = F_{A0} - F_{A0}X_2 \quad (2-23)$$

combining Equations (2-22) and (2-23) and rearranging

$$V_2 = \frac{F_{A1} - F_{A2}}{-r_{A2}} = \frac{(F_{A0} - F_{A0}X_1) - (F_{A0} - F_{A0}X_2)}{-r_{A2}}$$

$$V_2 = \frac{F_{A0}}{-r_{A2}}(X_2 - X_1) \quad (2-24)$$

Reactor 2

For the second CSTR, recall that $-r_{A2}$ is evaluated at X_2 and then use $(X_2 - X_1)$ to calculate V_2 .

In the examples that follow, we shall again use the molar flow rate of A used in Example 2-1 (i.e., $F_{A0} = 0.4 \text{ mol A/s}$) and the reaction conditions given in Table 2-3 in Example 2-3 processed data 2.

Example 2–4 Comparing Volumes for CSTRs in Series

For the two CSTRs in series, 40% conversion is achieved in the first reactor. What is the volume of each of the two reactors necessary to achieve 80% overall conversion of the entering species A? (See Table 2-3.)

TABLE 2-3 PROCESSED DATA 2

X	0.0	0.1	0.2	0.4	0.6	0.7	0.8
$(F_{A0}/-r_A)(\text{m}^3)$	0.89	1.08	1.33	2.05	3.54	5.06	8.0

Solution

For Reactor 1, we observe from either Table 2-3 or Figure 2-2(b) that when $X = 0.4$, then

$$\left(\frac{F_{A0}}{-r_{A1}}\right)_{X=0.4} = 2.05 \text{ m}^3$$

Then, using Equation (2-13)

$$V_1 = \left(\frac{F_{A0}}{-r_{A1}}\right)_{X_1} X_1 = (2.05)(0.4) = 0.82 \text{ m}^3 = 820 \text{ dm}^3$$

$$V_1 = 820 \text{ dm}^3 \text{ (liters)} \quad \underline{\text{Answer}}$$

For Reactor 2, when $X_2 = 0.8$, then

$$\left(\frac{F_{A0}}{-r_A}\right)_{X=0.8} = 8.0 \text{ m}^3$$

Using Equation (2-24)

$$V_2 = \left(\frac{F_{A0}}{-r_{A2}}\right)(X_2 - X_1) \quad (2-24)$$

$$V_2 = (8.0 \text{ m}^3)(0.8 - 0.4) = 3.2 \text{ m}^3 = 3200 \text{ dm}^3$$

$$V_2 = 3200 \text{ dm}^3 \text{ (liters)} \quad \underline{\text{Answer}}$$

To achieve the same overall conversion, the total volume for two CSTRs in series is less than that required for one CSTR.

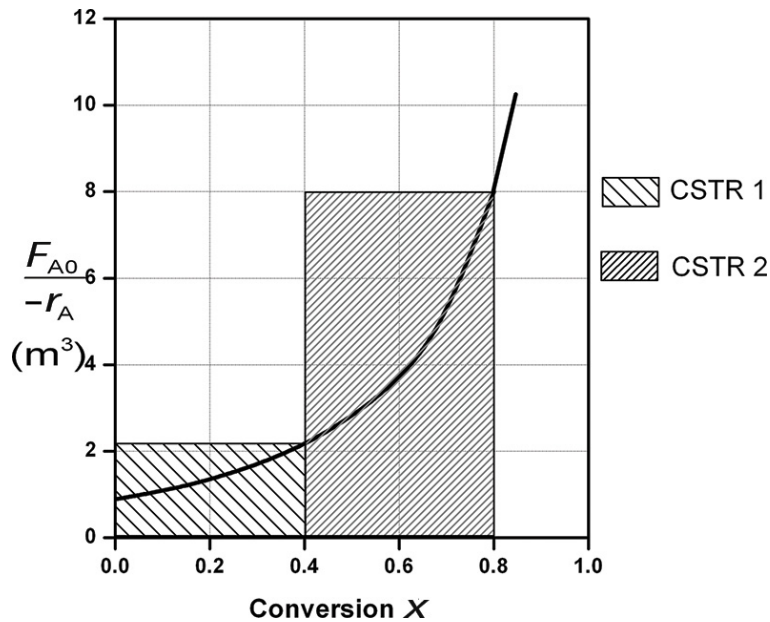


Figure E2-4.1 Two CSTRs in series.

The shaded areas in [Figure E2-4.1](#) could also have been used to determine volumes of CSTR 1 and CSTR 2.

Note again that for CSTRs in series, the rate $-r_{A1}$ is evaluated at a conversion of 0.4 and rate $-r_{A2}$ is evaluated at a conversion of 0.8. The total volume for these two reactors in series is

$$V = V_1 + V_2 = 0.82 \text{ m}^3 + 3.2 \text{ m}^3 = 4.02 \text{ m}^3 = 4020 \text{ dm}^3 \quad \underline{\text{Answer}}$$

By comparison, the volume necessary to achieve 80% conversion in **one** CSTR is

$$V = \left(\frac{F_{A0}}{-r_{A1}} \right) X = (8.0)(0.8) = 6.4 \text{ m}^3 = 6400 \text{ dm}^3$$

Answer

We need only $-r_A = f(X)$ and F_{A0} to size reactors.

Notice in Example 2-4 that the sum of the two CSTR reactor volumes (4.02 m^3) in series is less than the volume of one CSTR (6.4 m^3) to achieve the same overall conversion.

Analysis: When we have reactors in series, we can speed our analysis and calculations by defining an overall conversion at a point in the series, rather than the conversion of each individual reactor. In this example, we saw that 40% was achieved at point 1, the exit to the first reactor, and that a total of 80% conversion was achieved by the time we exit the second reactor. Using two CSTRs in series will give a smaller total volume than one CSTR to achieve the same conversion.

Approximating a PFR by a Large Number of CSTRs in Series

Consider approximating a PFR with a number of small, equal-volume CSTRs of V_i in series (Figure 2-5). We want to compare the total volume of all these CSTRs in series with the volume of one plug-flow reactor for the same conversion, say 80%.

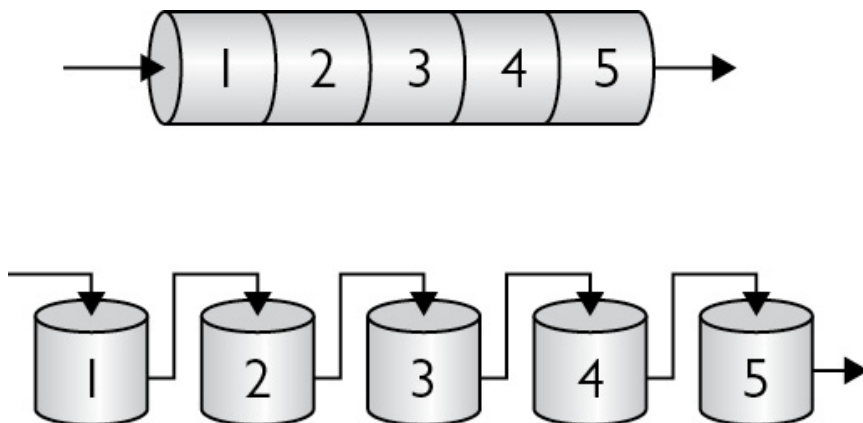


Figure 2-5 Modeling a PFR with CSTRs in series.

Useful Concept!

The fact that we can model a PFR with a large number of CSTRs is an important result.

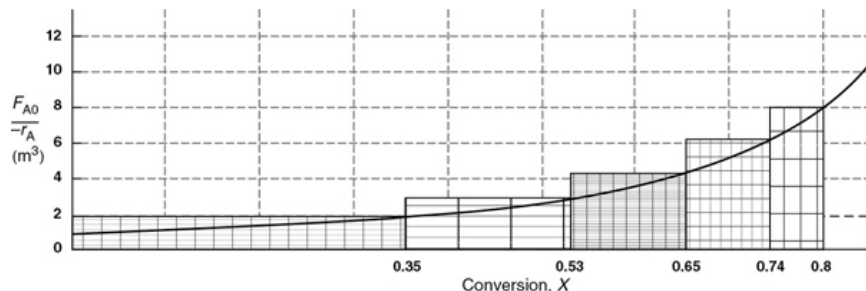


Figure 2-6 Levenspiel plot showing comparison of CSTRs in series with one PFR.

From [Figure 2-6](#), we note a very important observation! The total volume to achieve 80% conversion for five CSTRs of equal volume in series is “*roughly*” the same as the volume of a PFR. As we make the volume of each CSTR smaller and increase the number of CSTRs, the total volume of the CSTRs in series and the volume of the PFR will become identical. *That is, we can model a PFR with a large number of CSTRs in series.* This concept of using many CSTRs in series to model a

PFR will be used later in a number of situations, such as modeling catalyst decay in packed-bed reactors or transient heat effects in PFRs.

2.5.2 PFRs in Series

We saw that two CSTRs in series gave a smaller total volume than a single CSTR to achieve the same conversion. This case does not hold true for the two plug-flow reactors connected in series shown in Figure 2-7.

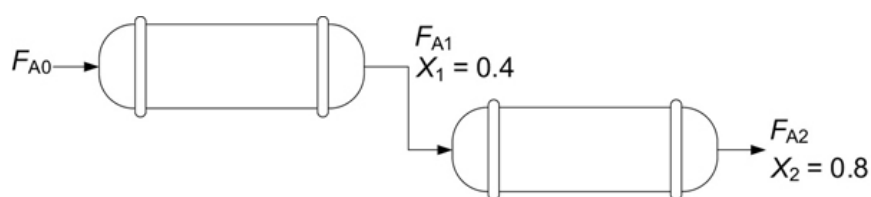


Figure 2-7 Two PFRs in series.

We can see from Figure 2-8 and from the following equation

$$\int_0^{X_2} F_{A0} \frac{dX}{-r_A} \equiv \int_0^{X_1} F_{A0} \frac{dX}{-r_A} + \int_{X_1}^{X_2} F_{A0} \frac{dX}{-r_A}$$

PFRs in series

that it is immaterial whether you place two plug-flow reactors in series or have one continuous plug-flow reactor; the total reactor volume required to achieve the same conversion is identical!

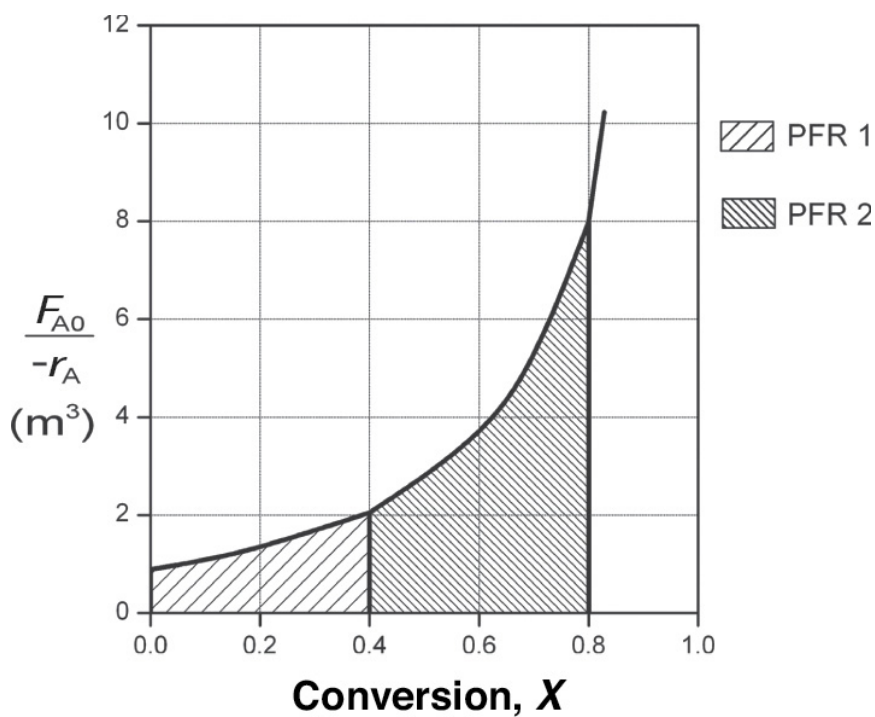


Figure 2-8 Levenspiel plot for two PFRs in series.

The overall conversion of two PFRs in series is the same as one PFR with the same total volume.

2.5.3 Combinations of CSTRs and PFRs in Series

The final sequences we shall consider in this chapter are combinations of CSTRs and PFRs in series. An industrial example of reactors in series is shown in the photo in [Figure 2-9](#) where two CSTRs in series are followed by a PFR. This sequence is used to dimerize propylene (A) into isohexanes (B), for example,

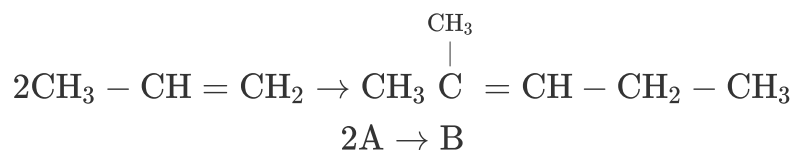




Figure 2-9 Dimersol G (an organometallic catalyst) unit (two CSTRs and one tubular reactor in series) to dimerize propylene into isohexanes. Institut Français du Pétrole process. Photo courtesy of Editions Technip (Institut Français du Pétrole).

Not sure whether the size of these CSTRs is in the *Guinness Book of World Records*.

A schematic of the industrial reactor system in [Figure 2-9](#) is shown in [Figure 2-10](#).

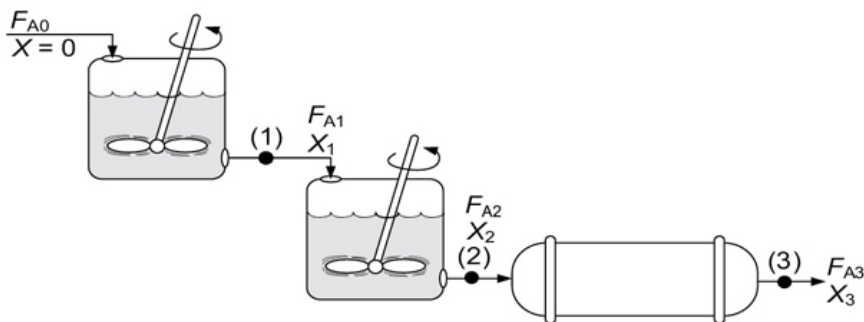


Figure 2-10 Schematic of a real system.

For the sake of illustration, let's assume that the reaction carried out in the reactors in [Figure 2-10](#) follows the same

$\left(\frac{F_{A0}}{-r_A}\right)$ versus X curve given by [Table 2-3](#).

The volumes of the first two CSTRs in series (see [Example 2-4](#)) are:

$$\text{Reactor 1: } V_1 = \frac{F_{A0}X_1}{-r_{A1}} \quad (2-13)$$

$$\text{Reactor 2: } V_2 = \frac{F_{A0}(X_2 - X_1)}{-r_{A2}} \quad (2-14)$$

In this series arrangement, $-r_{A2}$ is evaluated at X_2 for the second CSTR.

Starting with the differential form of the PFR design equation

$$F_{A0} \frac{dX}{dV} = -r_A \quad (2-15)$$

rearranging and integrating between limits, when $V = 0$, then $X = X_2$, and when $V = V_3$, then $X = X_3$ we obtain

$$\text{Reactor 3: } V_3 = \int_{X_2}^{X_3} \frac{F_{A0}}{-r_A} dX \quad (2-25)$$

The corresponding reactor volumes for each of the three reactors can be found from the shaded areas in [Figure 2-11](#).

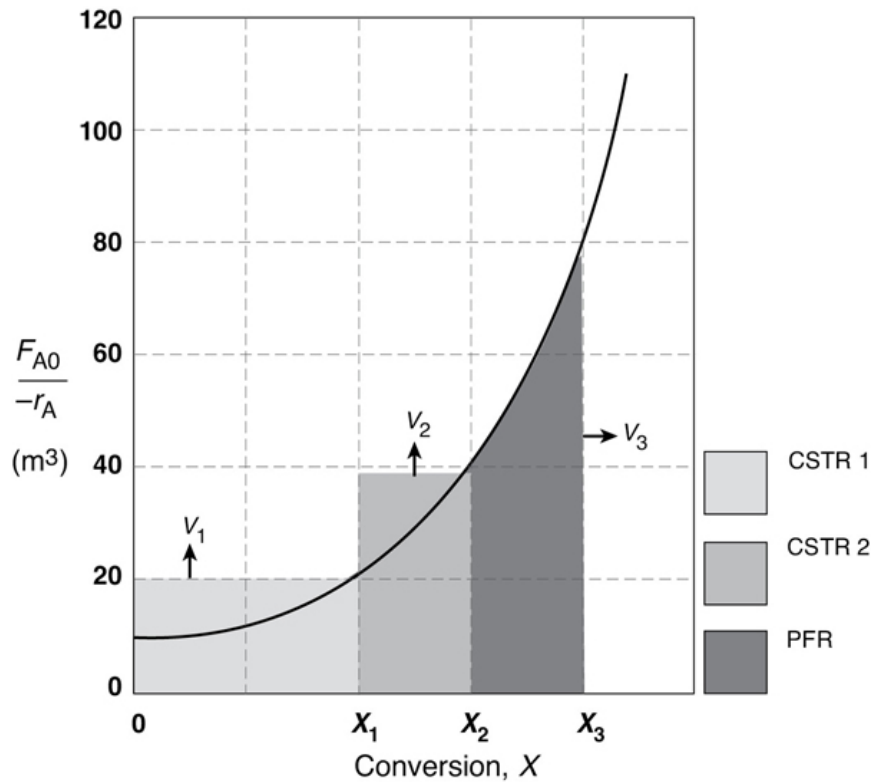
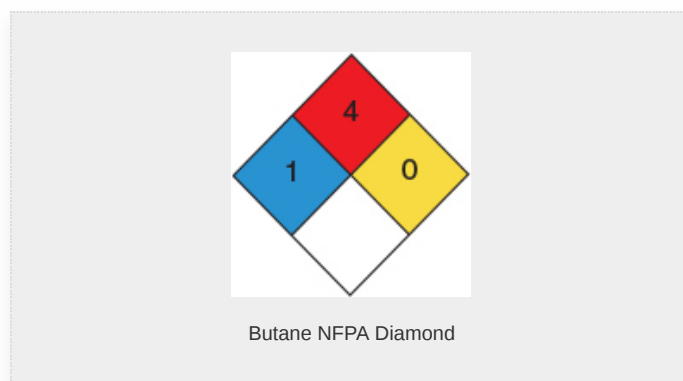


Figure 2-11 Levenspiel plot to determine the reactor volumes V_1 , V_2 , and V_3 .

The $(F_{A0}/-r_A)$ versus X curves we have been using in the previous examples are typical of those found in *isothermal* reaction systems. We will now consider a real reaction system that is carried out *adiabatically*. Isothermal reaction systems are discussed in [Chapter 5](#) and adiabatic systems in [Chapter 11](#), where we will see that for adiabatic exothermic reactions the temperature increases with increasing conversion.

Example 2–5 An Adiabatic Liquid-Phase Isomerization

The isomerization of butane



was carried out adiabatically in the liquid phase. The data for this reversible reaction are given in [Table E2-5.1](#). (Example 11.3 shows how the data in [Table E2-5.1](#) were generated.)

TABLE E2-5.1 RAW DATA

X	0.0	0.2	0.4	0.6	0.65
$-r_A(\text{kmol/m}^3 \cdot \text{h})$	39	53	59	38	25

Don't worry how we got this data or why the $(1/-r_A)$ looks the way it does; we will see how to construct this table in [Chapter 11, Example 11-3](#). It is *real data* for a *real reaction* carried out adiabatically, and the reactor scheme shown below in [Figure E2-5.1](#) is used.

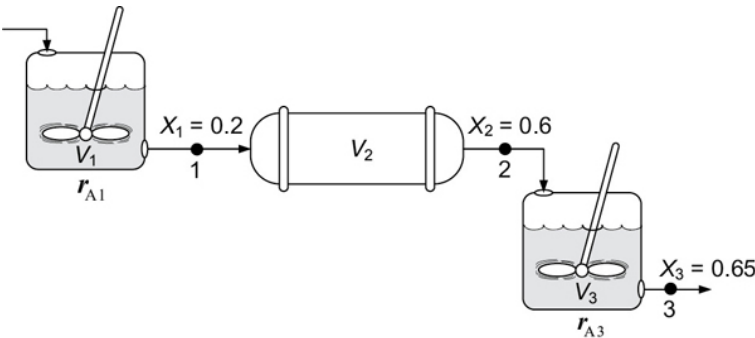


Figure E2-5.1 Reactors in series.

Real Data for a Real Reaction

Calculate the volume of each of the reactors for an entering molar flow rate of n-butane of 50 kmol/hr, that is, $F_{A0} = 50 \text{ kmol/h}$.

Solution

Taking the reciprocal of $-r_A$ and multiplying by F_{A0} , we obtain Table E2-5.2.

For example, at

$$X = 0 : \frac{F_{A0}}{-r_A} = \frac{50 \text{ kmol/h}}{39 \text{ kmol/h} \cdot \text{m}^3} = 1.28 \text{ m}^3$$

TABLE E2-5.2 PROCESSED DATA[†]

X	0.0	0.2	0.4	0.6	0.65
$-r_A \text{ (kmol/m}^3 \cdot \text{h)}$	39	53	59	38	25
$[F_{A0}/-r_A] \text{ (m}^3\text{)}$	1.28	0.94	0.85	1.32	2.0

[†]Data from Table E11-3.1.

1. For the first CSTR,

when $X = 0.2$, then $\frac{F_{A0}}{-r_A} = 0.94 \text{ m}^3$

$$V_1 = \frac{F_{A0}}{-r_A} X_1 = (0.94 \text{ m}^3)(0.2) = 0.188 \text{ m}^3 \quad (\text{E2-5.1})$$

$$V_1 = 0.188 \text{ m}^3 = 188 \text{ dm}^3 \quad (\text{E2-5.2})$$

2. For the PFR,

$$V_2 = \int_{0.2}^{0.6} \left(\frac{F_{A0}}{-r_A} \right) dX$$

Using Simpson's three-point formula with $\Delta X = (0.6 - 0.2)/2 = 0.2$, and $X_1 = 0.2$, $X_2 = 0.4$, and $X_3 = 0.6$

$$V_2 = \int_{0.2}^{0.6} \frac{F_{A0}}{-r_A} dX = \frac{\Delta X}{3} \left[\left(\frac{F_{A0}}{-r_A} \right)_{X=0.2} + 4 \left(\frac{F_{A0}}{-r_A} \right)_{X=0.4} + \left(\frac{F_{A0}}{-r_A} \right)_{X=0.6} \right]$$

$$= \frac{0.2}{3} [0.94 + 4(0.85) + 1.32] \text{ m}^3 \quad (\text{E2-5.3})$$

$$V_2 = 0.38 \text{ m}^3 = 380 \text{ dm}^3 \quad (\text{E2-5.4})$$

3. For the last reactor and the second CSTR, mole balance on A for the CSTR:

$$\text{In} - \text{Out} + \text{Generation} = 0$$

$$F_{A2} - F_{A3} + r_{A3} V_3 = 0 \quad (\text{E2-5.5})$$

Rearranging

$$V_3 = \frac{F_{A2} - F_{A3}}{-r_{A3}} \quad (\text{E2-5.6})$$

$$F_{A2} = F_{A0} - F_{A0} X_2$$

$$F_{A3} = F_{A0} - F_{A0} X_3$$

$$V_3 = \frac{(F_{A0} - F_{A0} X_2) - (F_{A0} - F_{A0} X_3)}{-r_{A3}}$$

Simplifying

$$V_3 = \left(\frac{F_{A0}}{-r_{A3}} \right) (X_3 - X_2) \quad (\text{E2-5.7})$$

We find from Table E2-5.2 that at $X_3 = 0.65$, then

$$\frac{F_{A0}}{-r_{A3}} = 2.0 \text{ m}^3$$

$$V_3 = 2 \text{ m}^3 (0.65 - 0.6) = 0.1 \text{ m}^3$$

$$V_3 = 0.1 \text{ m}^3 = 100 \text{ dm}^3 \quad (\text{E2-5.8})$$

A Levenspiel plot of $(F_{A0}/-r_A)$ versus X is shown in Figure E2-5.2.

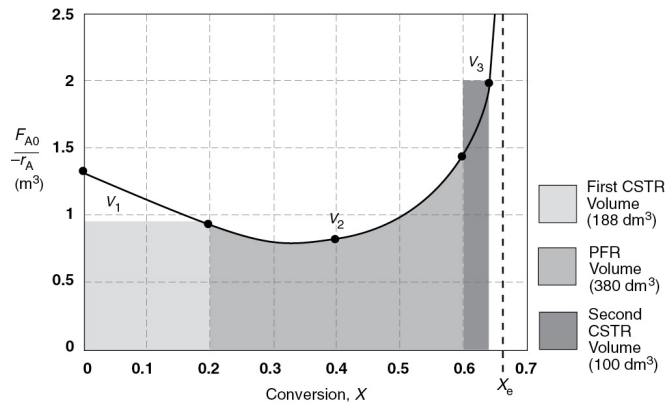


Figure E2-5.2 Levenspiel plot for adiabatic reactors in series.

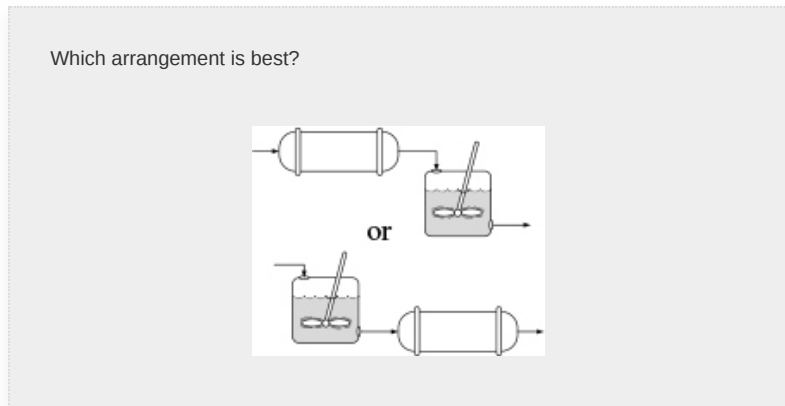
For this adiabatic reaction, the three reactors in series resulted in an overall conversion of 65%. The maximum conversion we can achieve is the equilibrium conversion, which is 68%, and is shown by the dashed line in Figure E2-5.2. Recall that at equilibrium, the rate of reaction is zero and an infinite reactor volume is required to reach equilibrium ($V - \frac{1}{-r_A} \sim \frac{1}{0} = \infty$).

Analysis: For exothermic reactions that are not carried out isothermally, the rate usually increases at the start of the reaction because reaction temperature increases. However, as the reaction proceeds the rate eventually decreases as the conversion increases because the reactants are consumed. These two competing effects give the bowed shape of the curve in Figure E2-5.2, which will be discussed in detail in Chapters 11 and 12. Under these circumstances, we saw that a CSTR will require a smaller volume than a PFR at low conversions.

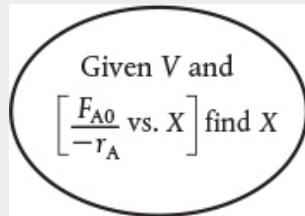
2.5.4 Comparing the CSTR and PFR Volumes and Reactor Sequencing

If we look at Figure E2-5.2, the area under the curve (PFR volume) between $X = 0$ and $X = 0.2$, we see that the PFR area is greater than the rectangular area corresponding to the CSTR volume, that is, $V_{\text{PFR}} > V_{\text{CSTR}}$. However, if we compare the

areas under the curve between $X = 0.6$ and $X = 0.65$, we see that the area under the curve (PFR volume) is smaller than the rectangular area corresponding to the CSTR volume, that is, $V_{\text{CSTR}} > V_{\text{PFR}}$. This result often occurs when the reaction is carried out adiabatically, which is discussed when we look at heat effects in Chapter 11.



In the *sequencing of reactors*, one is often asked, “Which reactor should go first to give the highest overall conversion? Should it be a PFR followed by a CSTR, or two CSTRs, then a PFR, or ...?” The answer is **“It depends.”** It depends not only on the shape of the Levenspiel plot ($F_{A0}/-r_A$) versus X , but also on the relative reactor sizes. As an exercise, examine Figure E2-5.2 to learn if there is a better way to arrange the two CSTRs and one PFR. Suppose you were given a Levenspiel plot of ($F_{A0}/-r_A$) versus X for three reactors in series, along with their reactor volumes $V_{\text{CSTR1}} = 3 \text{ m}^3$, $V_{\text{CSTR2}} = 2 \text{ m}^3$, and $V_{\text{PFR}} = 1.2 \text{ m}^3$, and were asked to find the highest possible conversion X . What would you do? The methods we used to calculate reactor volumes all apply, except the procedure is reversed and a *trial-and-error solution* is needed to find the exit overall conversion from each reactor (see Problem P2-5B).



Given V and $\left[\frac{F_{A0}}{-r_A} \text{ vs. } X \right]$ find X

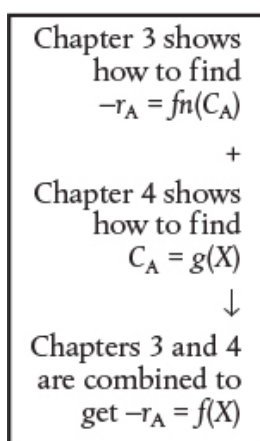
The previous examples show that *if* we know the molar flow rate to the reactor and the reaction rate as a function of conversion, *then* we can calculate the reactor volume necessary to achieve a specified conversion. The reaction rate does not depend on conversion alone, however. It is also affected by the initial concentrations of the reactants, the temperature, and the pressure. Consequently, the experimental data obtained in the laboratory and presented in [Table 2-1](#) as $-r_A$ as a function of X are useful *only* in the design of full-scale reactors that are to be operated at the *identical conditions* as the laboratory experiments (temperature, pressure, and initial reactant concentrations). However, such circumstances are **seldom** encountered and we must revert to the methods we describe in [Chapters 3 and 4](#) to obtain $-r_A$ as a function of X .

It is important to remember that if the rate of reaction is available or can be obtained solely as a function of conversion, $-r_A = f(X)$, or if it can be generated by some intermediate calculations, one can design a variety of reactors and combinations of reactors.

Only need $-r_A = f(X)$ to size flow reactors

Ordinarily, laboratory data are used to formulate a rate law, and then the reaction rate–conversion functional dependence is determined using the rate law. The preceding sections show

that with the reaction rate–conversion relationship, that is, $-r_A = f(X)$, different reactor schemes can readily be sized. In Chapters 3 and 4, we show how we obtain this relationship between reaction rate and conversion from rate law and reaction stoichiometry.



2.6 SOME FURTHER DEFINITIONS

Before proceeding to Chapter 3, some terms and equations commonly used in reaction engineering need to be defined. We also consider the special case of the plug-flow design equation when the volumetric flow rate is constant.

2.6.1 Space Time

The space time tau, τ , is obtained by dividing the reactor volume by the volumetric flow rate entering the reactor

$$\tau \equiv \frac{V}{v_0} \quad (2-26)$$

τ is an important quantity!

The *space time* is the time necessary to process one reactor volume of fluid based on entrance conditions. For example,

consider the tubular reactor shown in Figure 2-12, which is 20 m long and 0.2 m^3 in volume. The dashed line in Figure 2-12 represents 0.2 m^3 of fluid directly upstream of the reactor. The time it takes for this upstream fluid volume to enter the reactor completely is called the *space time tau*. It is also called the *holding time* or *mean residence time*.

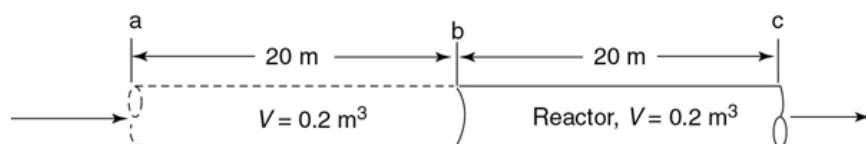
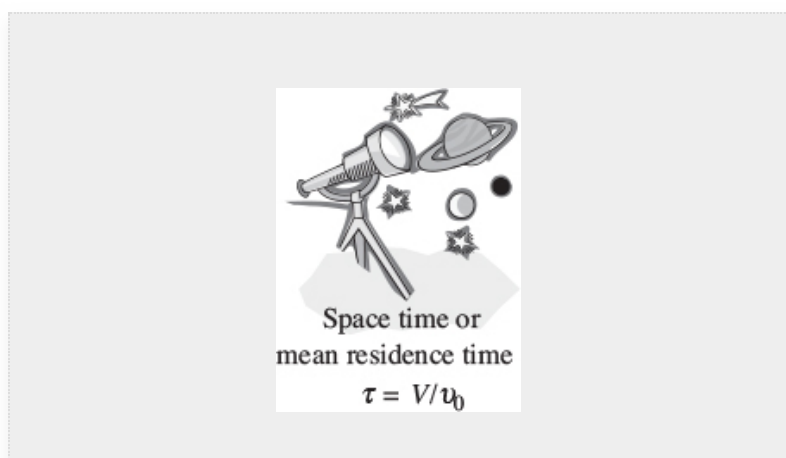


Figure 2-12 Tubular reactor showing identical volume upstream.



For example, if the reactor volume is 0.2 m^3 and the inlet volumetric flow rate is $0.01 \text{ m}^3/\text{s}$, it would take the upstream equivalent reactor volume ($V = 0.2 \text{ m}^3$), shown by the dashed lines, a time τ equal to

$$\tau = \frac{0.2 \text{ m}^3}{0.01 \text{ m}^3/\text{s}} = 20 \text{ s}$$

to enter the reactor ($V = 0.2 \text{ m}^3$). In other words, it would take 20 s for the fluid molecules at point **a** to move to point **b**, which corresponds to a space time of 20 s. We can substitute for $F_{A0} = u_0 C_{A0}$ in Equations (2-13) and (2-16) and then

divide both sides by to write our mole balance in the following forms:

For a PFR $\tau_p = \left(\frac{V_p}{v_0}\right) = C_{A0} \int_0^X \frac{dX}{-r_A}$

and

For a CSTR $\tau_{CSTR} = \left(\frac{V_{CSTR}}{v_0}\right) = \frac{C_{A0}}{-r_A} X$

For plug flow, the space time is equal to the mean residence time in the reactor, t_m (see Chapter 16). This time is the average time that the molecules spend in the reactor. A range of typical processing times in terms of the space time (residence time) for industrial reactors is shown in Table 2-4.

TABLE 2-4 TYPICAL SPACE TIME FOR INDUSTRIAL REACTORS²

Reactor Type	Mean Residence Time Range	Production Capacity
Batch	15 min to 20 h	Few kg/day to 100,000 tons/year
CSTR	10 min to 4 h	10 to 3,000,000 tons/year
Tubular	0.5 s to 1 h	50 to 5,000,000 tons/year

² P. Trambouze, H. Landeghem, and J. P. Wauquier, *Chemical Reactors*, Paris: Editions Technip, 1988; Houston: Gulf Publishing Company, 1988, p. 154.

Practical guidelines

Table 2-5 shows an order of magnitude of the space times for six industrial reactions and associated reactors.

TABLE 2-5 SAMPLE INDUSTRIAL SPACE TIMES³

	Reaction	Reactor	Temperature	Pressure atm	Space Time
(1)	$C_2H_6 \rightarrow C_2H_4 + H_2$	PFR [†]	860°C	2	1 s
(2)	$CH_3CH_2OH + HCH_3COOH \rightarrow$ $CH_3CH_2COOCH_3 + H_2O$	CSTR	100°C	1	2 h
(3)	Catalytic cracking	PBR	490°C	20	$1\text{ s} < \tau < 400\text{ s}$
(4)	$C_6H_5CH_2CH_3 \rightarrow C_6H_5CH = CH_2 + H_2$	PBR	600°C	1	0.2 s
(5)	$CO + H_2O \rightarrow CO_2 + H_2$	PBR	300°C	26	4.5 s
(6)	$C_6H_6 + HNO_3 \rightarrow$ $C_6H_5NO_2 + H_2O$	CSTR	50°C	1	20 min

[†]The reactor is tubular but the flow may or may not be ideal plug flow.

Typical industrial reaction space times

Table 2-6 gives typical sizes for batch and CSTR reactors (along with the comparable size of a familiar object) and the costs associated with those sizes. All reactors are glass lined and the prices include heating/cooling jacket, motor, mixer, and baffles. The reactors can be operated at temperatures between 20°F and 450°F, and at pressures up to 100 psi.



TABLE 2-6 REPRESENTATIVE PFAUDLER CSTR/BATCH
REACTOR SIZES AND PRICES[†]

<i>Volume</i>	<i>Price</i>
20 dm ³ (Waste Basket)	\$30,000
200 dm ³ (Garbage Can)	\$40,000
2000 dm ³ (Jacuzzi)	\$75,000
30000 dm ³ (Gasoline Tanker)	\$300,000

†Doesn't include instrumentation costs.



2.6.2 Space Velocity

The space velocity (SV) is another term used by reaction engineers and is defined as

$$SV \equiv \frac{v_0}{V} \quad SV = \frac{1}{\tau} \quad (2 - 27)$$

³ Walas, S. M. Chemical Reactor Data, *Chemical Engineering*, 79 (October 14, 1985).

The space velocity might be regarded at first sight as the reciprocal of the space time. However, there can be a difference in the two quantities' definitions. For the space time, the entering volumetric flow rate is measured at the

entrance conditions, but for the space velocity, other conditions are often used. The two space velocities commonly used in industry are the *liquid-hourly* and *gas-hourly space velocities*, LHSV and GHSV, respectively. The entering volumetric flow rate, v_0 , in the LHSV is frequently measured as that of a liquid feed rate at 60°F or 75°F, even though the feed to the reactor may be a vapor at some higher temperature. Strange but true.

$$\text{LHSV} = \frac{v_0|_{\text{liquid}}}{V} \quad (2-28)$$

Slight differences in space velocities

The gas volumetric flow rate, v_0 , in the GHSV is normally reported at standard temperature and pressure (STP).

$$\text{GHSV} = \frac{v_0|_{\text{STP}}}{V} \quad (2-29)$$

Example 2–6 Reactor Space Times and Space Velocities

Calculate the space time, τ , and space velocities for the reactor in Examples 2-1 and 2-3 for an entering volumetric flow rate of $2 \text{ dm}^3/\text{s}$.

Solution

The entering volumetric flow rate is $2 \text{ dm}^3/\text{s}$ ($0.002 \text{ m}^3/\text{s}$).

From Example 2-1, the CSTR volume was 6.4 m^3 and the corresponding space time, τ , and space velocity, SV are

$$\tau = \frac{V}{v_0} = \frac{6.4 \text{ m}^3}{0.002 \text{ m}^3/\text{s}} = 3200 \text{ s} = 0.89 \text{ h}$$

It takes 0.89 h to put 6.4 m^3 into the reactor and the corresponding space velocity, SV , is

$$SV = \frac{1}{\tau} = \frac{1}{0.89 \text{ h}} = 1.125 \text{ h}^{-1}$$

From Example 2-3, the PFR volume was 2.165 m^3 , and the corresponding space time and space velocity are

$$\tau = \frac{V}{v_0} = \frac{2.165 \text{ m}^3}{0.002 \text{ m}^3/\text{s}} = 1083 \text{ s} = 0.30 \text{ h}$$

$$SV = \frac{1}{\tau} = \frac{1}{0.30 \text{ h}} = 3.3 \text{ h}^{-1}$$

Analysis: This example gives an *important industrial concept*. These space times are the times for each of the reactors to take the volume of fluid equivalent to one reactor volume and put it into the reactor.

Summary

In these last examples we have seen that in the design of reactors that are to be operated at conditions (e.g., temperature and initial concentration) identical to those at which the reaction rate–conversion data $-r_A = f(X)$ were obtained, we can size (determine the reactor volume) both CSTRs and PFRs alone or in various combinations. In principle, it may be possible to scale up a laboratory-bench or pilot-plant reaction system solely from knowledge of $-r_A$ as a function of X or C_A . However, for most reactor systems in industry, a scale-up process cannot be achieved in this manner because knowledge of $-r_A$ solely as a function of X is seldom, if ever, available under identical conditions. By combining the information in [Chapters 3 and 4](#), we shall see how we can obtain $-r_A = f(X)$ from information obtained either in the laboratory or from the literature. This relationship will be developed in a two-step process. In Step 1, we will find the rate law that gives the rate as a function of concentration ([Table 3-1](#)) and in Step 2, we will find the concentrations as a function of conversion ([Figure 4-3](#)). Combining Steps 1 and 2 in [Chapters 3 and 4](#), we obtain $-r_A = f(X)$. We can then use the methods developed in this chapter, along with integral and numerical methods, to size reactors.

Coming attractions in [Chapters 3 and 4](#)

2.7 AND NOW... A WORD FROM OUR SPONSOR—SAFETY 2 (AWFOS—S2 THE NFPA DIAMOND)

In this AWFOS—S, we describe the National Fire Protection Agency (NFPA) Diamond which quickly identifies risks of hazardous materials. This identification is extremely important to first responders in an emergency. Each color in the diamond represents a different type of hazard, while the numbers in the

hazard refer to a degree of concern one should have about the material. The different types of hazards and levels of concern of the NFPA diamond are shown in Figure 2-13.



Figure 2-13 Components of each color of the NFPA Diamond. (Image: Dmitry Kovalchuk/Shutterstock)

A tutorial on how to fill in the numbers in the diamond for the insecticide dichlorodiphenyltrichloroethane (DDT) using the CAMEO Chemicals Website

(<https://cameochemicals.noaa.gov>) is given in the NFPA

Diamond tutorial on the safety Website

(<http://umich.edu/~safeche/nfpa.html>,

<http://umich.edu/~safeche/assets/pdf/CAMEO.pdf>). The NFPA

Diamond for the chemical DDT discussed in Example 1-1,

DDT, is shown in Figure 2-14.



Figure 2-14 NFPA Diamond Levels of Concern for DDT. (Image: Idea.s/Shutterstock)

We see that the number two in the red (top-most) diamond indicates DDT has a flash point below 200°F, the zero in the yellow (far-right) diamond indicates it is stable, the blank in the white (bottom-most) diamond indicates no specific hazard, and the two in the blue (far-left) diamond indicates DDT is hazardous to one's health.

The following photographs show two examples of how the NFPA Diamond is used in industry.



Figure 2-15 NFPA Diamond in Action. (Photos: left, Gado Images/Getty; right, TFoxFoto/Shutterstock)

The NFPA Diamond along with its companion GHS Diamond (see AWFOS-S3) is shown on the *Process Safety Across the Chemical Engineering Curriculum* Web site. For tutorials and NFPA data sheets see

NFPA Diamond Tutorial: https://cse.wvu.edu/files/safety-tutorials/Gen_Chem_Tutorial/HTML/GCST_10.htm

CAMEO Chemicals Tutorial:

<http://umich.edu/~safeche/assets/pdf/CAMEO.pdf>

Quick Card:

https://www.nfpa.org/Assets/files/AboutTheCodes/704/NFPA704_HC2012_QCard.pdf

Data Sheets:

<https://cameochemicals.noaa.gov/chemical/694>
<https://cameochemicals.noaa.gov/chemical/4145>

FAQs:

https://www.nfpa.org/Assets/files/AboutTheCodes/704/704_FAQs.pdf

The CRE Algorithm

- Mole Balance, Ch 1
- Rate Law, Ch 3
- Stoichiometry, Ch 4
- Combine, Ch 5
- Evaluate, Ch 5
- Energy Balance, Ch 11

Closure

In this chapter, we have shown that if you are given the rate of reaction as a function of conversion, that is, $-r_A = f(X)$, you will be able to size CSTRs and PFRs, and arrange the order of a given set of reactors to determine the maximum overall conversion. After completing this chapter, the reader should be able to:

1. Define the parameter *conversion* and rewrite the mole balances in terms of conversion
2. Show that by expressing $-r_A$ as a function of conversion X , a number of reactors and reaction systems can be sized or a conversion calculated from a given reactor size
3. Arrange reactors in series to achieve the maximum conversion for a given Levenspiel plot

SUMMARY

1. The conversion X is the moles of A reacted per mole of A fed.

For batch systems:

$$X = \frac{N_{A0} - N_A}{N_{A0}} \quad (\text{S2-1})$$

For flow systems:

$$X = \frac{F_{A0} - F_A}{F_{A0}} \quad (\text{S2-2})$$

For reactors in series with no side streams, the conversion at point i is

$$X_i = \frac{\text{Total moles of A reacted up to Point } i}{\text{Moles A fed to the first reactor}} \quad (\text{S2-3})$$

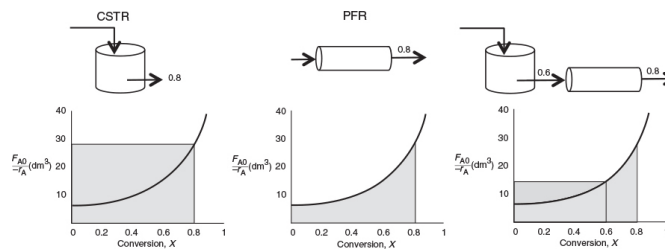
2. The differential and integral forms of the reactor design equations (i.e., GMBEs) are shown in Table S2-1.

TABLE S2-1 MOLE BALANCE FOR BR, CSTR, PFR, AND PBR
TERMS OF CONVERSION

	Differential Form	Algebraic Form	Integral Form
Batch	$N_{A0} \frac{dX}{dt} = -r_A V$		$t = N_{A0} \int_0^X \frac{dX}{-r_A V}$
CSTR		$V = \frac{F_{A0}(X_{out} - X_{in})}{(-r_A)_{out}}$	
"Fluidized" CSTR		$W = \frac{F_{A0}(X_{out} - X_{in})}{(-r'_A)_{out}}$	
PFR	$F_{A0} \frac{dX}{dV} = -r_A$		$V = F_{A0} \int_{X_{in}}^{X_{out}} \frac{dX}{-r_A}$
PBR	$F_{A0} \frac{dX}{dW} = -r'_A$		$W = F_{A0} \int_{X_{in}}^{X_{out}} \frac{dX}{-r'_A}$

3. If the rate of disappearance of A is given as a function of conversion, the following graphical techniques can be used to size a CSTR and a plug-flow reactor.

1. Graphical Integration Using Levenspiel Plots



The PFR integral could also be evaluated by

2. Numerical Integration

See [Appendix A.4](#) for quadrature formulas such as the five-point quadrature formula with $\Delta X = 0.8/4$ of five equally spaced points, $X_1 = 0$, $X_2 = 0.2$, $X_3 = 0.4$, $X_4 = 0.6$, and $X_5 = 0.8$.

4. Space time, τ , and space velocity, SV , are given by

$$\tau = \frac{V}{v_0} \quad (\text{S2-4})$$

$$SV = \frac{v_0}{V} \quad (\text{at STP for gas-phase reaction}) \quad (\text{S2-5})$$

CRE WEB SITE MATERIALS

(<http://www.umich.edu/~elements/6e/02chap/obj.html>)

Useful Links

Living Example Problems

Polymath, Python, Matlab and Wolfram

Extra Help

Multiple Resources extra problems, screencasts and lecture notes

Additional Materials

New Technical Material, Detailed Derivations and Web Modules

Professional Reference Shelf

Material important to the practicing engineer that is not necessarily covered in all CRE courses.

YouTube Videos

Humorous videos covering topics varying from example problems to light hearted breaks from studying

Evaluation

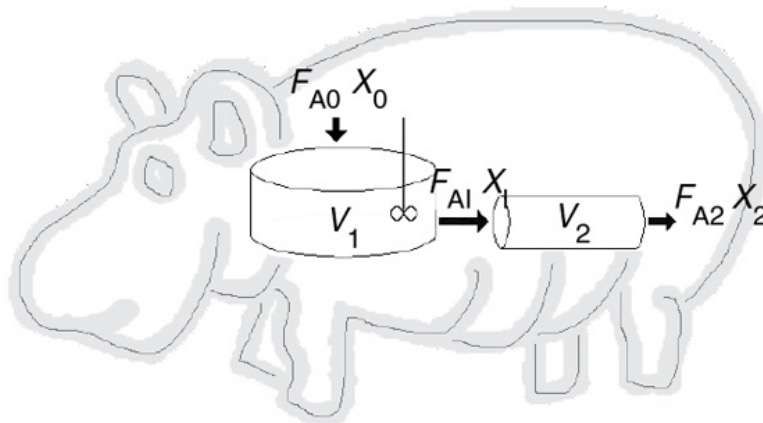
Self Tests

Interactive problems with solutions to provide extra practice of concepts

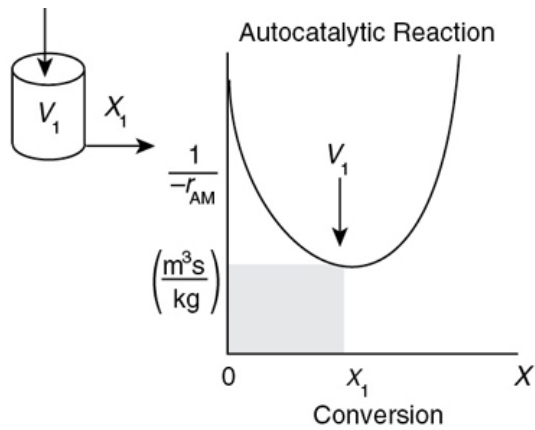
Clicker Questions

Interactive multiple choice questions to help assess your understanding of the material

Web Module Hippopotamus Digestive System



(http://umich.edu/~elements/6e/web_mod/hippo/index.htm)

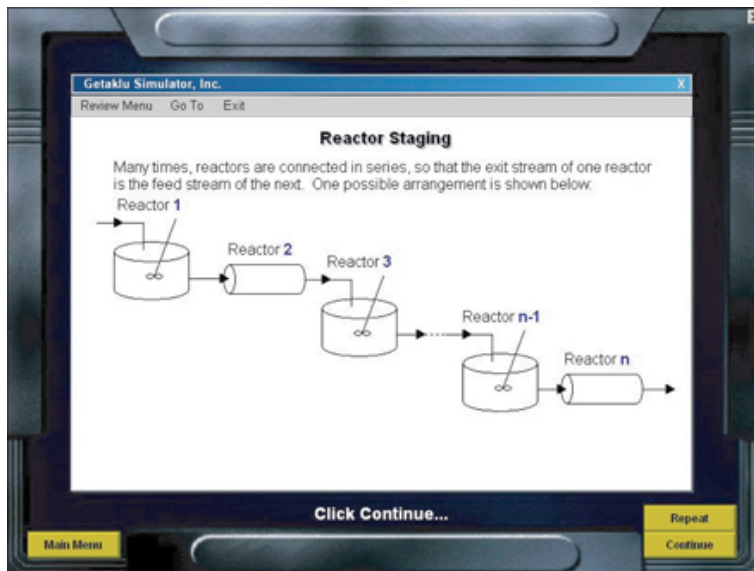


Levenspiel Plot for Autocatalytic Digestion in a CSTR

Interactive Computer Games

Reactor Staging

(<http://umich.edu/~elements/6e/icm/staging.html>)



QUESTIONS AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$A = \bullet \quad B = \blacksquare \quad C = \blacklozenge \quad D = \blacklozenge\blacklozenge$$

Questions

Q2-1_A QBR (Questions Before Reading). Will or could there ever be a case where the CSTR volume is represented by something other than a square or rectangle on a Levenspiel plot?

Q2-2_A i>clicker. Go to the Web site http://www.umich.edu/~elements/6e/02chap/iclicker_ch2_q1.html and view at least five i>clicker questions. Choose one that could be used as is, or a variation thereof, to be included on the next exam. You also could consider the opposite case: explaining why the question should *not* be on the next exam. In either case, explain your reasoning.

Q2-3 (a) Without referring back, make a list of the most important items you learned in this chapter.

(b) Overall, what do you believe were the three major purposes of the chapter?

Q2-4 Go to the Web site www.engr.ncsu.edu/learningstyles/ilsweb.html. Take the Inventory of Learning Style test, and record your learning style according to the Soloman/Felder inventory, and then use Appendix I.2 to suggest two ways to facilitate your learning style in each of the four categories.

Global/Sequential_____

Active/Reflective_____

Visual/Verbal_____

Sensing/Intuitive_____

Q2-5_A Go to the Chapter 2 Video Screencasts Web page (<http://www.umich.edu/~elements/6e/02chap/learn-cheme-videos.html>).

1. View one or more of the screencast 5- to 6-minute videos and write a two-sentence evaluation.
2. What did the speaker do well and what could be improved?

Q2-6_A AWFOS-S2

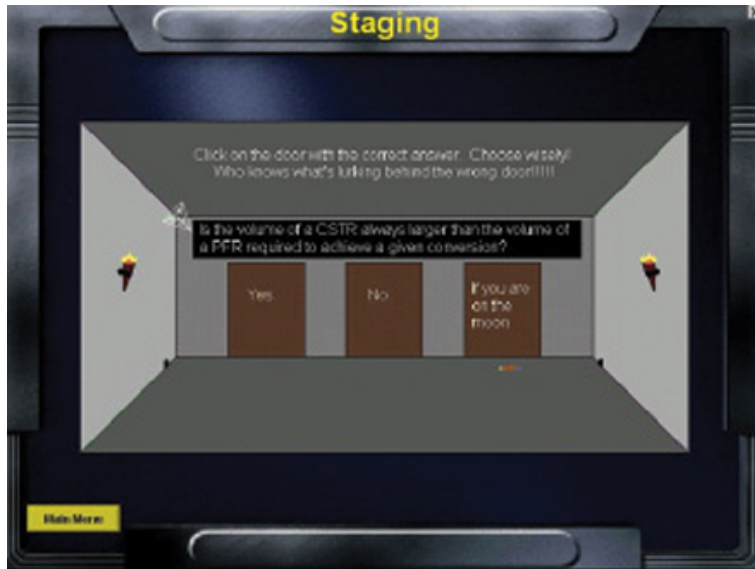
1. What is the NFPA diamond and why is it important?
2. Go to Wikipedia and search ethylene oxide to find the NFPA diamond numbers.
3. Draw the NFPA diamond for the chemicals propylene, isohexane, and isobutane that we discussed in [Figure 2-6](#), and [Example 2-5](#).

Interactive Computer Games

P2-1_A **ICG Staging.** Download the Interactive Computer Game (ICG) from the CRE Web site, <http://www.umich.edu/~elements/6e/icm/staging.html>. Play this game and then record your performance number, which indicates your mastery of the material. Your professor has the key to decode your performance number. *Note:* To play this game you *must* have Windows 2000 or a later version.

Write the ICG Reactor Staging Performance here #

_____.



Problems

Before solving the problems, state or sketch qualitatively the expected results or trends.

P2-2_A

1. Revisit the data in *Table 2-1 Raw Data* and calculate the batch reactor (BR) times to achieve 10%, 50%, and 80% conversion when 100 moles of A are charged to a 400 dm³ reactor.
2. Revisit **Examples 2-1** through **2-3**. How would your answers change if the flow rate, F_{A0} , were cut in half? If it were doubled? What conversion can be achieved in a 4.5 m³ PFR and in a 4.5 m³ CSTR?
3. Revisit **Example 2-2**. Being a company about to go bankrupt, you can only afford a 2.5 m³ CSTR. What conversion can you achieve?
4. Revisit **Example 2-3**. What conversion could you achieve if you could convince your boss, Dr. Pennypincher, to spend more money to buy a 1.0 m³ PFR to attach to a 2.40 CSTR?
5. Revisit **Example 2-4**. How would your answers change if the two CSTRs (one 0.82 m³ and the other 3.2 m³) were placed in parallel with the flow, F_{A0} , divided equally between the reactors?
6. Revisit **Example 2-5**. (1) What is the worst possible way to arrange the two CSTRs and one PFR? (2) What would be the reactor volumes if the two intermediate conversions were changed to 20% and 50%, respectively? (3) What would be the conversions, X_1 , X_2 , and X_3 , if all the reactors had the same volume of 100 dm³ and were placed in the same order?

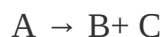
7. Revisit **Example 2-6**. If the term $C_{A0} \int_0^X \frac{dX}{-r_A}$ is 2 seconds for 80% conversion, how much fluid (m^3/min) can you process in a 3 m^3 reactor?

P2-3_B You have two CSTRs and two PFRs, each with a volume of 1.6 m^3 . Use **Figure 2-2(b)** on page 45 to calculate the conversion for each of the reactors in the following arrangements.

- Two CSTRs in series. (**Ans:** $X_1 = 0.435$, $X_2 = 0.66$)
- Two PFRs in series.
- Two CSTRs in parallel with the feed, F_{A0} , divided equally between the two reactors.
- Two PFRs in parallel with the feed divided equally between the two reactors.
- A PFR followed by a CSTR.
- (f)** A CSTR followed by a PFR. (**Ans:** $X_{\text{CSTR}} = 0.435$, $X_{\text{PFR}} = 0.71$)
- A PFR followed by two CSTRs. Is this a good arrangement or is there a better one?
- Caution: Part (h)** is a C level problem. A CSTR and a PFR in parallel with the flow equally divided. Calculate the overall conversion, X_{ov}

$$X_{\text{ov}} = \frac{F_{A0} - F_{\text{ACSTR}} - F_{\text{APFR}}}{F_{A0}}, \text{ with } F_{\text{ACSTR}} = \frac{F_{A0}}{2} - \frac{F_{A0}}{2} X_{\text{CSTR}}, \text{ and } F_{\text{APFR}} = \frac{F_{A0}}{2} (1 - X_{\text{PFR}})$$

P2-4_B The exothermic reaction of stillbene (A) to form the economically important tropophene (B) and methane (C), that is,



was carried out adiabatically and the following data recorded:

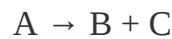
X	0	0.2	0.4	0.45	0.5	0.6	0.8	0.9
$-r_A$ ($\text{mol}/\text{dm}^3 \cdot \text{min}$)	1.0	1.67	5.0	5.0	5.0	5.0	1.25	0.91

The entering molar flow rate of A was $300 \text{ mol}/\text{min}$.

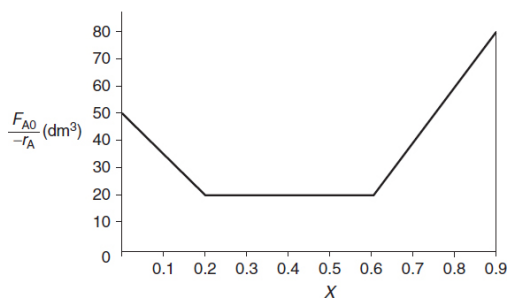
- Calculate the batch reactor (BR) times to achieve 40% and 80% conversion when 400 moles of A are charged to a 400 dm^3 reactor.
- What are the PFR and CSTR volumes necessary to achieve 40% conversion? ($V_{\text{PFR}} = 72 \text{ dm}^3$, $V_{\text{CSTR}} = 24 \text{ dm}^3$)
- Over what range of conversions would the CSTR and PFR reactor volumes be identical?

- What is the maximum conversion that can be achieved in a 105-dm³ CSTR?
- What conversion can be achieved if a 72-dm³ PFR is followed in series by a 24-dm³ CSTR?
- What conversion can be achieved if a 24-dm³ CSTR is followed in a series by a 72-dm³ PFR?
- Plot the conversion and rate of reaction as a function of PFR reactor volume up to a volume of 100 dm³.

P2-5B The financially important reaction to produce the valuable product B (not the real name) was carried out in Jesse Pinkman's garage (see *Breaking Bad* Season 3, Episode 7). This Breaking Bad, fly-by-night company, is on a shoestring budget and has very little money to purchase equipment. Fortunately, cousin Bernie has a reactor surplus company and you can get reactors from Bernie. The reaction



takes place in the liquid phase. Below is the Levenspiel plot for this reaction. You have up to \$10,000 to use to purchase reactors from those given below.

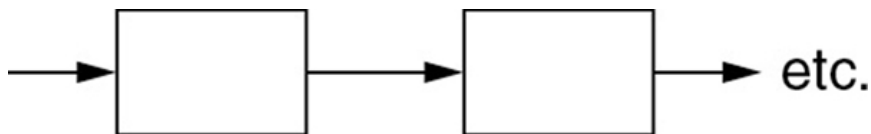


Cousin Bernie's Reactors

Reactor Type	Number	Volume (dm ³)	Cost
CSTR	2	2	\$1,000
CSTR	1	4	\$2,000
PFR	2	4	\$2,000
CSTR	2	6	\$4,000
CSTR	3	12	\$8,000
PFR	2	12	\$6,000

What reactors do you choose, how do you arrange them, and what is the highest conversion you can get for \$10,000? Approximately what is the corresponding highest conversion with your arrangement of reactors?

Scheme and sketch your reactor volumes.



P2-6_B Read the Web Module “Chemical Reaction Engineering of Hippopotamus Stomach” on the CRE Web site (http://www.umich.edu/~elements/6e/web_mod/hippo/index.htm).



1. Write five sentences summarizing what you learned from the Web Module.
2. Work problems (1) and (2) in the Hippo Web Module.
3. The hippo has picked up a river fungus, and now the effective volume of the CSTR stomach compartment is only 0.2 m^3 . The hippo needs 30% conversion to survive. Will the hippo survive?
4. The hippo had to have surgery to remove a blockage. Unfortunately, the surgeon, Dr. No, accidentally reversed the CSTR and the PFR during the operation. **Oops!!** What will be the conversion with the new digestive arrangement? Can the hippo survive?

P2-7_B OEQ (Old Exam Question). The adiabatic exothermic irreversible gas-phase reaction



is to be carried out in a flow reactor for an equimolar feed of A and B. A Levenspiel plot for this reaction is shown in Figure P2-7_B.

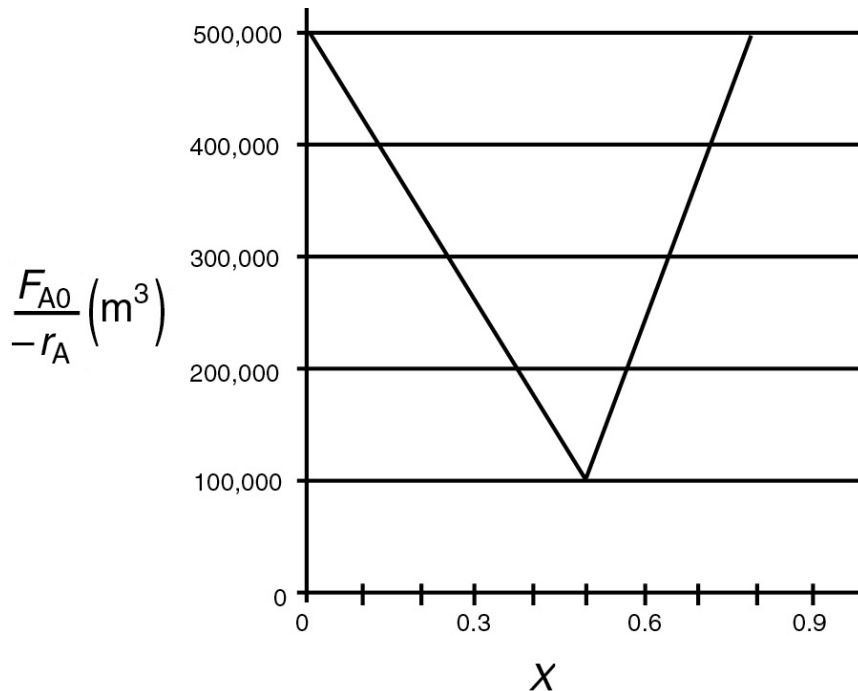


Figure P2-7_B Levenspiel plot.

1. What PFR volume is necessary to achieve 50% conversion?
2. What CSTR volume is necessary to achieve 50% conversion?
3. What is the volume of a second CSTR added in series to the first CSTR (**Part b**) necessary to achieve an overall conversion of 80%? (**Ans:** $V_{\text{CSTR}} = 1.5 \times 10^5 \text{ m}^3$)
4. What PFR volume must be added to the first CSTR (**Part b**) to raise the conversion to 80%?
5. What conversion can be achieved in a $6 \times 10^4 \text{ m}^3$ CSTR? In a $6 \times 10^4 \text{ m}^3$ PFR?
6. Think critically (cf. Introduction, Section H, page xxix) to critique the answers (numbers) to this problem.

P2-8_A Estimate the reactor volumes of the two CSTRs and the PFR shown in the photo in [Figure 2-9](#). *Hint:* Use the dimensions of the door as a scale.

P2-9_D Don't calculate anything. Just go home and relax.

P2-10_C **OEQ (Old Exam Question).** The curve shown in [Figure 2-1](#) is typical of a reaction carried out isothermally, and the curve shown in [Figure P2-10_C](#) (see [Example 11-3](#)) is typical of a gas–solid catalytic exothermic reaction carried out adiabatically.

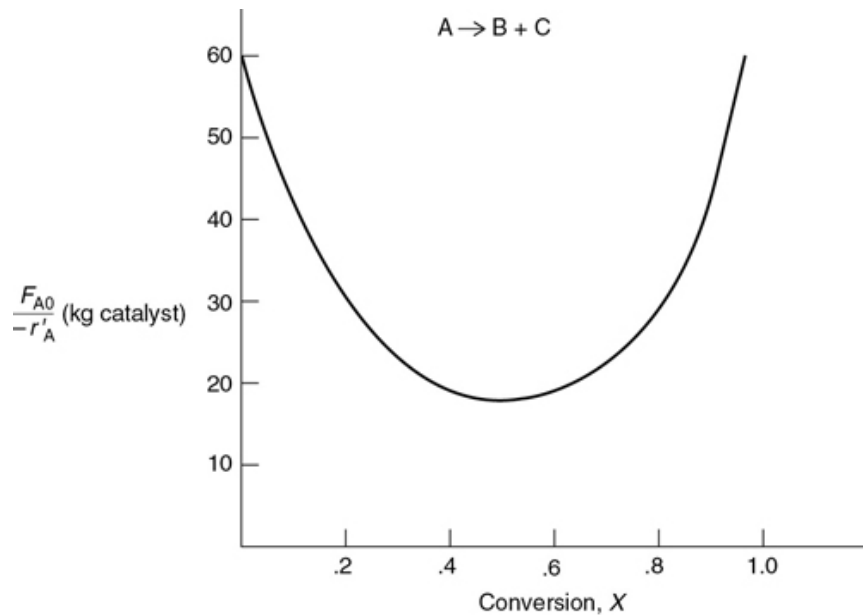
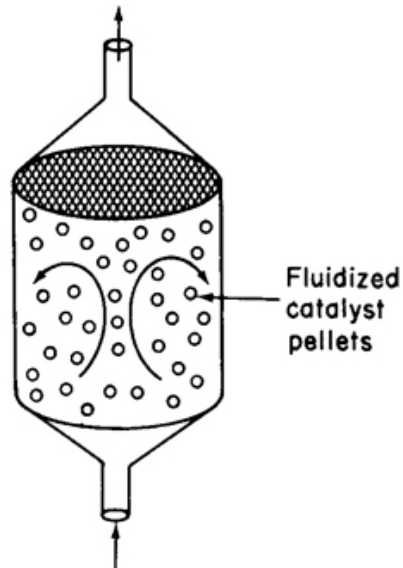


Figure P2-10C Levenspiel plot for an adiabatic exothermic heterogeneous reaction.

1. Assuming that you have a fluidized CSTR and a PBR containing equal weights of catalyst, how should they be arranged for this adiabatic reaction? Use the smallest amount of catalyst weight to achieve 80% conversion of A.
2. What is the catalyst weight necessary to achieve 80% conversion in a fluidized CSTR? (**Ans:** $W = 23.2$ kg of catalyst)
3. What fluidized CSTR weight is necessary to achieve 40% conversion?
4. What PBR weight is necessary to achieve 80% conversion?
5. What PBR weight is necessary to achieve 40% conversion?
6. Plot the rate of reaction and conversion as a function of PBR catalyst weight, W .

Additional information: $F_{A0} = 2$ mol/s.



P2-11 The experiments on reaction $A \rightarrow B$ were carried out and the conversion-rate data is given in Table P2-11.

TABLE P2-11 CONVERSION-RATE DATA

X	0	0.2	0.4	0.6	0.8
$-r_A$ (mol/m ³)	4	3	2.2	1.5	1.0

1. What are the batch reactor times to achieve 10%, 50%, and 80% for the reactor $A \rightarrow B$ when the initial concentration is 2 molar?
 2. Plot the reaction rate, $-r_A$, as a function of time up to a time necessary to achieve 80% conversion.
- Additional Homework Problems can be found on the CRE Web site under [Chapter 2](#) A. EXERCISES hot button.

SUPPLEMENTARY READING

Further discussion of the proper staging of reactors in series for various rate laws, in which a plot of $(=1/r_A)$ versus X is given, *may or may not* be presented in

THORNTON W. BURGESS, *The Adventures of Poor Mrs. Quack*, New York: Dover Publications, Inc., 1917.

CHESTER L. KARRASS, *Effective Negotiating: Workbook and Discussion Guide*, Beverly Hills, CA: Karrass Ltd., 2004.

OCTAVE LEVENSPIEL, *Chemical Reaction Engineering*, 3rd ed. New York: Wiley, 1999, Chapter 6, pp. 139–156.

3. Rate Laws

Success is measured not so much by the position one has reached in life, as by the obstacles one has overcome while trying to succeed.

—Booker T. Washington

Overview. In [Chapter 2](#), we showed that if we knew the rate of reaction as a function of conversion, $-r_A = f(X)$, we could calculate reactor volumes necessary to achieve a specified conversion for flow systems and the time to achieve a given conversion in a batch system. Unfortunately, one is seldom, if ever, given $-r_A = f(X)$ directly from raw data. Not to fear, using the material in [Chapters 3 and 4](#), we will show how to obtain the rate of reaction as a function of conversion. This relationship between reaction rate and conversion will be obtained in two steps.

- In *Step 1*, described in this chapter, [Chapter 3](#), we define the rate law, which relates the rate of reaction to temperature and to the concentrations of the reacting species, $-r_A = [k_A(T)][f_n(C_A, C_B, \dots)]$.
- In *Step 2*, which will be described in [Chapter 4](#), we define concentrations for flow and batch systems and develop stoichiometric tables that one can use to write concentrations as a function of conversion, $C_A = h(X)$.
- *Combining Steps 1 and 2*, we see that one can then write the rate as a function of conversion, that is, $-r_A = f(X)$, and use the techniques in [Chapter 2](#) to design reaction systems.

After completing this chapter, you will be able to:

- Relate the rates of reaction of species in a reaction to each other
- Write the rate law in terms of concentrations
- Use the Arrhenius Equation to find the rate constant as a function of temperature
- Describe the energy barrier height (activation energy) and the fraction of molecular collisions that have the energy to pass over the barrier and react

3.1 BASIC DEFINITIONS

A **homogeneous reaction** is one that involves only one phase. A **heterogeneous reaction** involves more than one phase, and the reaction usually occurs at the interface between the phases. An **irreversible reaction** is one that proceeds in only one direction and continues in that direction until one of the reactants is exhausted. A **reversible reaction**, on the other hand, can proceed in either direction, depending on the temperature and on the concentrations of reactants and products relative to the corresponding equilibrium concentrations. An irreversible reaction behaves as if no equilibrium condition exists. Strictly speaking, no chemical reaction is completely irreversible. However, for many reactions, the equilibrium point lies so far to the product side that these reactions are treated as irreversible reactions.

Types of reactions

The **molecularity** of a reaction is the number of atoms, ions, or molecules involved (colliding) in a reaction step. The terms *unimolecular*, *bimolecular*, and *termolecular* refer to reactions involving, respectively, one, two, and three atoms (or molecules) interacting or colliding in any one reaction step. The most common example of a *unimolecular* reaction is radioactive decay, such as the spontaneous emission of an alpha particle from uranium-238 to give thorium and helium

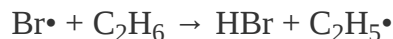


The rate of disappearance of uranium (U) is given by the rate law

$$-r_{\text{U}} = kC_{\text{U}}$$

The only true bimolecular reactions are those that involve the collision with free radicals (i.e., unpaired electrons, e.g., $\text{Br}\cdot$),

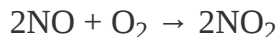
such as



with the rate of disappearance of bromine given by the rate law

$$-r_{\text{Br}\cdot} = kC_{\text{Br}\cdot}C_{\text{C}_2\text{H}_6}$$

The probability of a *termolecular* reaction, where three molecules collide all at once, is almost nonexistent, and in most instances the reaction pathway follows a series of *bimolecular* reactions, as in the case of the reaction



The reaction pathway for this “Hall of Fame” reaction is quite interesting and is discussed in Problem P9-5A and also in [Chapter 9](#) where similar reactions that form active intermediate complexes in their reaction pathways are given.

In discussing **rates of chemical reactions**, we have three rates to consider:

- Relative Rates
- Rate Laws
- Net Rates

Relative rates tell us how fast one species is disappearing or appearing relative to the other species in the given reaction.

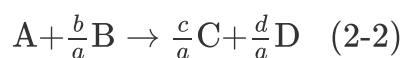
Rate laws are the algebraic equations that give the rate of reaction as a function of the reacting species concentrations and of temperature in a specific reaction.

Net rates of formation of a given species (e.g., A) is the sum of the rate of reactions of A in all the reactions in which A is either a reactant or product in the system.

A thorough discussion of net rates is given in Table 8-2 in Chapter 8, where we discuss multiple reactions.

3.1.1 Relative Rates of Reaction

The relative rates of reaction of the various species involved in a reaction can be obtained from the ratio of the stoichiometric coefficients.[†] For Reaction (2-2),



Reaction stoichiometry

we see that for every mole of A that is consumed, c/a moles of C appear. In other words,

Rate of formation of C = $\frac{c}{a} \times$ (Rate of disappearance of A)

$$r_C = \frac{c}{a}(-r_A) = -\frac{c}{a}r_A$$

Similarly, the relationship between the rates of formation of C and D is

$$r_C = \frac{c}{d}r_D$$

The relationship can be expressed directly from the stoichiometry of the reaction



for which

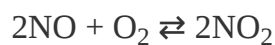
$$\boxed{\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d}} \quad (3-1)$$

or

$$\boxed{\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d}}$$

Useful Neumonics

For example, in the reaction



we have

$$\frac{r_{\text{NO}}}{-2} = \frac{r_{\text{O}_2}}{-1} = \frac{r_{\text{NO}_2}}{2}$$

If NO_2 is being formed at a rate of $4 \text{ mol/m}^3/\text{s}$, that is,

$$r_{\text{NO}_2} = 4 \text{ mol/m}^3/\text{s}$$

[†]Tutorial Video: <https://www.youtube.com/watch?v=wYqQCojggyM>

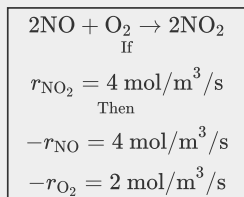
then the rate of formation of NO is

$$r_{\text{NO}} = \frac{-2}{2} r_{\text{NO}_2} = -4 \text{ mol/m}^3/\text{s}$$

the rate of disappearance of NO is

$$-r_{\text{NO}} = 4 \text{ mol/m}^3/\text{s}$$

Summary



and the rate of disappearance of oxygen, O_2 , is

$$-r_{\text{O}_2} = \frac{-1}{-2} r_{\text{NO}_2} = 2 \text{ mol/m}^3/\text{s}$$

3.2 THE RATE LAW

To understand the rate of reaction, we need to describe three molecular concepts. In **Concept 1: Law of Mass Action**, we use rate laws to relate the rate of reaction to the concentrations of the reacting species. **Concept 2: Potential Energy Surfaces** and **Concept 3: The Energy Needed for Crossing the Barriers** help us explain the effect of temperature on the rate of reaction.

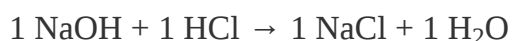
In the chemical reactions considered in the following paragraphs, we take as the basis of calculation a species A, which is one of the reactants that is disappearing as a result of the reaction. The limiting reactant is usually chosen as our basis for calculation. The rate of disappearance of A, $-r_A$, depends on temperature and concentration. For many irreversible reactions, it can be written as the product of a *reaction rate constant*, k_A , and a function of the concentrations (activities) of the various species involved in the reaction:

$$-r_A = [\kappa_A(T)] [\text{fn}(C_A, C_B, \dots)] \quad (3-2)$$

Concept 1: Law of Mass Action. The rate of reaction increases with increasing concentration of reactants which

leads to a corresponding increase in the number of molecular collisions. The rate law for bimolecular collisions is derived in the collision theory section of the *Professional Reference Shelf R3.1* (<http://www.umich.edu/~elements/6e/03chap/prof.html>). A schematic of the reaction of **A** and **B** molecules colliding and reacting is shown in Figure R3.1 on page 108.

The algebraic equation that relates the rate of reaction $-r_A$ to the species concentrations is called the kinetic expression or **rate law**.[†] The specific rate of reaction (also called the rate constant), k_A , like the reaction rate, $-r_A$, always refers to a particular species in the reaction and normally should be subscripted with respect to that species. However, for reactions in which the stoichiometric coefficient is 1 for all species involved in the reaction, for example,



The rate law gives the relationship between reaction rate and concentration.

we shall delete the subscript on the specific reaction rate, (e.g., A in k_A), to let

$$k = k_{\text{NaOH}} = k_{\text{HCl}} = k_{\text{NaCl}} = k_{\text{H}_2\text{O}}$$

[†]Tutorial Video: <https://www.youtube.com/watch?v=6mAqX31RRJU>

3.2.1 Power Law Models and Elementary Rate Laws

The dependence of the reaction rate, $-r_A$, on the concentrations of the species present, $\text{fn}(C_j)$, is almost without exception determined by experimental observation. Although the functional dependence on concentration may be postulated from theory, experiments are necessary to confirm the proposed form. One of the most common general forms of this dependence is the *power-law model*. Here the rate law is the

product of concentrations of the individual reacting species, each of which is raised to a power, for example,

$$-r_A = k_A C_A^\alpha C_B^\beta \quad (3-3)$$



The exponents of the concentrations in Equation (3-3) lead to the concept of *reaction order*. The **order of a reaction** refers to the powers to which the concentrations are raised in the kinetic rate law.[†] In Equation (3-3), the reaction is **α order with respect to reactant A**, and **β order with respect to reactant B**. The overall order of the reaction, **n** , is

$$n = \alpha + \beta$$

Overall reaction order

The units of $-r_A$ are always in terms of concentration per unit time, while the units of the specific reaction rate, k_A , will vary with the order of the reaction. Consider a reaction involving only one reactant, such as



with an overall reaction order n . The units of rate, $-r_A$, and the specific reaction rate, k are

$$\{-r_A\} = [\text{concentration/time}]$$

$$\text{and } \left\{ k \right\} = \frac{[\text{concentration}]^{1-n}}{\text{time}}$$

Generally, the overall reaction order can be deduced from the units of the specific reaction-rate constant k . For example, the rate laws corresponding to a zero-, first-, second-, and third-order reaction, together with typical units for the corresponding rate constants, are

Zero-order ($n = 0$):

$$-r_A = k_A:$$

$$\{k\} = \text{mol/dm}^3/\text{s} \quad (3-4)$$

[†] Strictly speaking, the reaction rates should be written in terms of the activities, a_i , ($a_i = \gamma_i C_i$, where γ_i is the activity coefficient). Kline and Fogler, *JCIS*, 82, 93 (1981); *ibid.*, p. 103; and *Ind. Eng. Chem Fundamentals* 20, 155 (1981).

$$-r_A = k'_A a_A^\alpha a_B^\beta$$

However, for many reacting systems, the activity coefficients, γ_i , do not change appreciably during the course of the reaction, and they are absorbed into the specific reaction-rate constant, k_A

$$-r_A = k'_A a_A^\alpha a_B^\beta = k'_A (\gamma_A C_A)^\alpha (\gamma_B C_B)^\beta = \overbrace{\left(k'_A \gamma_A^\alpha \gamma_B^\beta \right)}^{k_A} C_A^\alpha C_B^\beta = k_A C_A^\alpha C_B^\beta$$

First order ($n = 1$):

$$\begin{aligned} -r_A &= k_A C_A : \\ \{k\} &= \text{s}^{-1} \quad (3-5) \end{aligned}$$

Second order ($n = 2$):

$$\begin{aligned} -r_A &= k_A C_A^2 : \\ \{k\} &= \text{dm}^3/\text{mol/s} \quad (3-6) \end{aligned}$$

Third order ($n = 3$):

$$-r_A = k_A C_A^3 :$$

$$\{k\} = (\text{dm}^3/\text{mol})^2/\text{s} \quad (3-7)$$

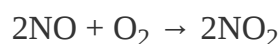
An *elementary reaction* is one that involves a single reaction step, such as the bimolecular reaction between an oxygen free radical and methanol molecule:

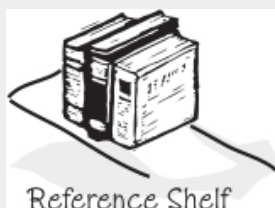


The stoichiometric coefficients in this reaction are *identical* to the powers in the rate law. Consequently, the rate law for the disappearance of molecular oxygen is

$$-r_{\text{O}\cdot} = k_{\text{O}\cdot} C_{\text{CH}_3\text{OH}}$$

The reaction is first order in an oxygen free radical and first order in methanol; therefore, we say that both the reaction and the rate law are *elementary*. This form of the rate law can be derived from *Collision Theory*, as shown in the *Professional Reference Shelf R3.1* on the CRE Web site (www.umich.edu/~elements/6e/index.html). There are many reactions where the stoichiometric coefficients in the reaction are identical to the reaction orders, but the reactions are not elementary, owing to such things as pathways involving active intermediates and series reactions. For these reactions that are not elementary but whose stoichiometric coefficients are identical to the reaction orders in the rate law, we say the reaction *follows an elementary rate law*. For example, the oxidation reaction of nitric oxide discussed earlier





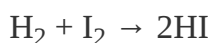
Collision theory

is not really an elementary reaction, but *follows* an elementary rate law, that is, second order in NO and first order in O₂, therefore,

$$-r_{\text{NO}} = k_{\text{NO}} C_{\text{NO}}^2 C_{\text{O}_2}$$

Note: The rate constant, k , is defined with respect to NO.

Another nonelementary reaction that *follows* an elementary rate law is the gas-phase reaction between hydrogen and iodine



and is first order in H₂ and first order in I₂, with

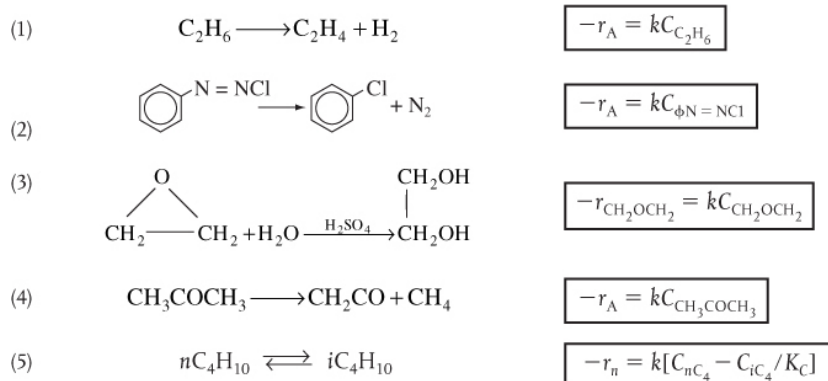
$$\rightarrow r_{\text{H}_2} = k_{\text{H}_2} C_{\text{H}_2} C_{\text{I}_2}$$

In summary, for many reactions involving multiple steps and pathways, the powers in the rate laws surprisingly agree with the stoichiometric coefficients. Consequently, to facilitate describing this class of reactions, we say that a reaction *follows an elementary rate law* when the reaction orders are identical to the stoichiometric coefficients of the reacting species for the **reaction as written**. It is important to

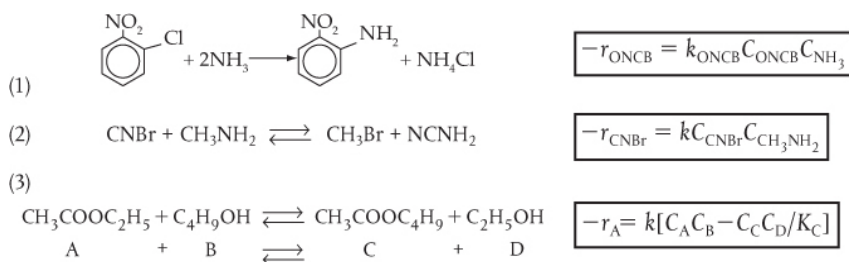
remember that the rate laws **are determined by experimental observation!** Chapter 7 describes how these and other rate laws can be developed from experimental data. They are a function of the reaction chemistry and not the type of reactor in which the reactions occur. Table 3-1 gives examples of rate laws for a number of reactions. By saying a reaction follows an elementary rate law as written gives us a quick way to look at the reaction stoichiometry and then write the mathematical form of the rate law. The values of specific reaction rates for these and a number of other reactions can be found in the *Database* found in the footnote below.

TABLE 3-1 EXAMPLES OF REACTION-RATE LAWS

A. First-Order Rate Laws

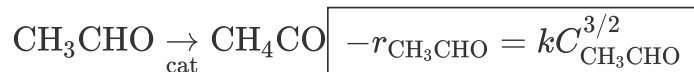


B. Second-Order Rate Laws

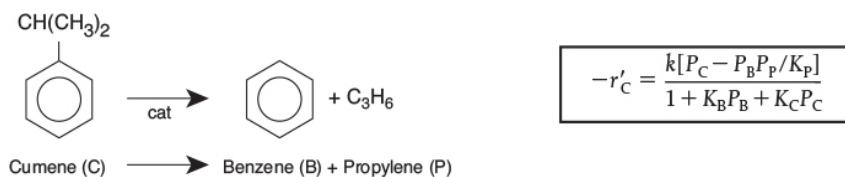


C. Nonelementary Rate Laws

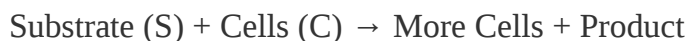
(1) Homogeneous



(2) Heterogeneous

**D. Enzymatic Reactions (Urea (U) + Urease (E))**

$$\boxed{-r_U = \frac{kC_U}{K_M + C_U}}$$

E. Biomass Reactions

$$\boxed{-r_S = \frac{kC_S C_C}{K_S + C_S}}$$

Note: The rate constants, k , and activation energies for a number of the reactions in these examples are given in the Databases in Appendix E. For more rate laws with specific reaction rates, see

<http://www.umich.edu/~elements/6e/03chap/summary-example3.html>.

The rate constants and the reaction orders for a large number of gas- and liquid-phase reactions can be found in the National Bureau of Standards' circulars and supplements.¹ Also consult the journals listed at the end of Chapter 1.

Where do you find rate laws?

We note in [Table 3-1](#) that Reaction Number (3) in the *First-Order Rate Laws* and Reaction Number (1) in the *Second-Order Rate Laws* do not follow elementary reaction-rate laws. We know this because the reaction orders are not the same as the stoichiometric coefficients for the reactions as they are written.[†]

¹ Kinetic data for a larger number of reactions can be obtained on CD-ROMs provided by *National Institute of Standards and Technology (NIST)*. Standard Reference Data 221/A320 Gaithersburg, MD 20899; phone: (301) 975-2208. Additional sources are *Tables of Chemical Kinetics: Homogeneous Reactions*, National Bureau of Standards Circular 510 (Sept. 28, 1951); Suppl. 1 (Nov. 14, 1956); Suppl. 2 (Aug. 5, 1960); Suppl. 3 (Sept. 15, 1961) (Washington, DC: U.S. Government Printing Office). *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, Evaluate No. 10, JPL Publication 92-20 (Pasadena, CA: Jet Propulsion Laboratories, Aug. 15, 1992).

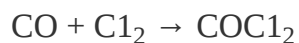
[†] Just as an aside, Prof. Dr. Sven Köttlov, a prominent resident of Riça, Jofostan, was once pulled over by police, questioned, and detained for breaking a reaction-rate law. #Seriously? He insisted that it was second order when experiments clearly showed it was first order.

Very important references. You should also look in the other literature *before* going to the lab.

3.2.2 Nonelementary Rate Laws

A large number of both homogeneous and heterogeneous reactions do not follow simple rate laws. Examples of reactions that don't follow simple elementary rate laws will now be discussed.

Homogeneous Reactions. The overall order of a reaction does not have to be an integer, nor does the order have to be an integer with respect to any individual component. As an example, consider the gas-phase synthesis of phosgene,

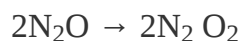


in which the experiments showed that the kinetic *rate law* is

$$-r_{\text{CO}} = kC_{\text{CO}}C_{\text{Cl}_2}^{3/2}$$

This reaction is first order with respect to carbon monoxide, three-halves order with respect to chlorine, and five-halves order overall.

Sometimes reactions have complex rate expressions that cannot be separated into solely temperature-dependent and concentration-dependent portions. In the decomposition of nitrous oxide,



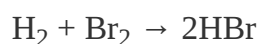
the kinetic *rate law* is

$$-r_{\text{N}_2\text{O}} = \frac{k_{\text{N}_2\text{O}}C_{\text{N}_2\text{O}}}{1+k'C_{\text{O}_2}}$$

Both $k_{\text{N}_2\text{O}}$ and k' are strongly temperature dependent. When a rate expression such as the one given above occurs, we *cannot* state an overall reaction order. Here, we can only speak of reaction orders under certain limiting conditions. *For example*, at very low concentrations of oxygen, the second term in the denominator would be negligible with respect to 1 ($1 \gg k'C_{\text{O}_2}$), and the reaction would be “apparent” first order with respect to nitrous oxide and first order overall. However, if the concentration of oxygen were large enough so that the number 1 in the denominator were insignificant in comparison with the second term, $k'C_{\text{O}_2}$ ($k'C_{\text{O}_2} \gg 1$), the *apparent* reaction order would be -1 with respect to oxygen and first order with respect to nitrous oxide, giving an overall *apparent* zero order. Rate laws of this type are very common for liquid and gaseous reactions promoted by solid catalysts (see [Chapter 10](#)). They

also occur in homogeneous reaction systems with reactive intermediates (see [Chapter 9](#)).

It is interesting to note that although the reaction orders often correspond to the stoichiometric coefficients, as evidenced for the reaction between hydrogen and iodine, just discussed, to form HI, the rate law for the reaction between hydrogen and another halogen, bromine, is quite complex. This non-elementary reaction



proceeds by a free-radical mechanism, and its reaction-rate law is

$$-r_{\text{Br}_2} = \frac{k_{\text{Br}_2} C_{\text{H}_2} C_{\text{Br}_2}^{1/2}}{k' + C_{\text{HBr}}/C_{\text{Br}_2}} \quad (3-8)$$

Apparent First-Order Reactions. Because the law of mass action in collision theory shows that two molecules must collide giving a second-order dependence on the rate, you are probably wondering how rate laws such as Equation (3-8) as well as the rate law for first-order reactions come about. An example of first-order reaction not involving radioactive decay is the decomposition of ethanol to form ethylene and hydrogen.



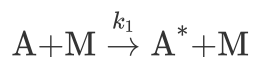
$$-r_{\text{C}_2\text{H}_6} = kC_{\text{C}_2\text{H}_6}$$

In terms of symbols



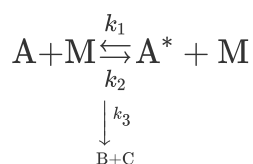
$$-r_{\text{A}} = kC_{\text{A}}$$

Rate laws of this form usually involve a number of elementary reactions and at least one active intermediate. An *active intermediate is a high-energy molecule that reacts virtually as fast as it is formed. As a result*, it is present in very small concentrations. Active intermediates (e.g., A*) can be formed by collision or interaction with other molecules (M) such as inerts or reactants



Here, the activation occurs when translational kinetic energy is transferred into energy stored in internal degrees of freedom, particularly vibrational degrees of freedom.² An unstable molecule (i.e., active intermediate) is not formed solely as a consequence of the molecule moving at a high velocity (high-translational kinetic energy). The translational kinetic energy must be absorbed into the chemical bonds where high-amplitude oscillations will lead to bond ruptures, molecular rearrangement, and decomposition. In the absence of photochemical effects or similar phenomena, the transfer of translational energy to vibrational energy to produce an active intermediate can occur only as a consequence of molecular collision or interaction. Collision theory is discussed in the *Professional Reference Shelf* on the CRE Web site for [Chapter 3](#).

As will be shown in [Chapter 9](#), the molecule A becomes activated to A* by collision with another molecule M. The activated molecule can become deactivated by collision with another molecule or the activated molecule can decompose to B and C.



Using this mechanism, we show in Equation (9-10) in Section 9.1.1 that at high concentrations of M, the rate law for this mechanism becomes

$$-r_A = \frac{k_1 k_3}{k_2} C_A = k_A C_A$$

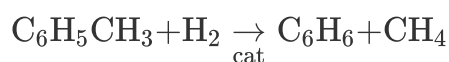
and at low concentration of M, the rate law becomes

$$-r_A = \frac{k_1 k_3 C_A C_M}{k_2 C_M + k_3} \approx k_3 C_A C_M$$

² W. J. Moore, *Physical Chemistry*, Reading, MA: Longman Publishing Group, 1998.

In Chapter 9, we will discuss reaction mechanisms and pathways that lead to nonelementary rate laws, such as the rate of formation of HBr shown in Equation (3-8).

Heterogeneous Reactions. Historically, it has been the practice in many gas–solid catalyzed reactions to write the rate law in terms of partial pressures rather than concentrations. In heterogeneous catalysis it is the *weight of catalyst* that is important, rather than the reactor volume. Consequently, we use $-r'_A$ in order to write the rate law in terms of (mol per kg of catalyst per time) in order to design PBRs. An example of a heterogeneous reaction and corresponding rate law is the hydrodemethylation of toluene (T) to form benzene (B) and methane (M) carried out over a solid catalyst



The rate of disappearance of toluene per mass of catalyst, $-r'_T$, that is, (mol/mass/time) follows Langmuir-Hinshelwood kinetics (discussed in Section 10.4.2), and the rate law was found experimentally to be

$$-r'_T = \frac{k' P_{\text{H}_2} P_T}{1 + K_B P_B + K_T P_T}$$

where the prime in $-r'_T$ denotes typical units are in per kilogram of catalyst (mol/kg-cat/s), P_T , P_{H_2} , and P_B are partial pressures of toluene, hydrogen, and benzene in (kPa, bar or atm), and K_B and K_T are the adsorption constants for benzene and toluene respectively, with units of kPa^{-1} (bar^{-1} or atm^{-1}). The specific reaction rate k has units of

$$\{k'\} = \frac{\text{mol toluene}}{\text{kg-cat} \cdot \text{s} \cdot \text{kPa}^2}$$

You will find that almost all heterogeneous catalytic reactions will have a term such as $(1 + K_A P_A + \dots)$ or $(1 + K_A P_A + \dots)^2$ in the denominator of the rate law (cf. [Chapter 10](#)).

To express the rate of reaction in terms of concentration rather than partial pressure, we simply substitute for P_i using the ideal gas law

$$\boxed{P_i = C_i RT} \quad (3-9)$$

The rate of reaction per unit weight (i.e., mass) catalyst, $-r'_A$ (e.g., $-r'_T$), and the rate of reaction per unit volume, $-r_A$, are related through the bulk density ρ_b (mass of solid/volume) of the *catalyst particles* in the fluid media:

$$\boxed{-r_A = (\rho_b) (-r'_A)}$$

$$\frac{\text{moles}}{\text{time} \cdot \text{volume}} = \left(\frac{\text{mass}}{\text{volume}} \right) \left(\frac{\text{moles}}{\text{time} \cdot \text{mass}} \right)$$

Relating rate per unit volume and rate by per unit mass of catalyst

In “fluidized” catalytic beds, the bulk density, ρ_b , is normally a function of the volumetric flow rate through the bed.

Consequently, using the above equations for P_i and $-r'_T$, we can write the rate law for the hydromethylation of toluene in terms of concentration and in (mole/dm³) and the rate, $-r_T$ in terms of reactor volume, that is,

$$-r_T = \frac{\overbrace{[\rho_b k' (RT)^2]}^k C_{H_2} C_T}{1 + K_B RT C_B + K_T RT C_T} \left(\frac{\text{mol}}{\text{dm}^3 \cdot s} \right)$$

$$\{k\} = \left(\frac{\text{dm}^3}{\text{mol} \cdot s} \right)$$

or as we will see in Equation (S4-14) in Chapter 4, we can leave it in terms of partial pressures.

In summary, reaction orders **cannot** be deduced from reaction stoichiometry. Even though a number of reactions follow elementary rate laws, at least as many reactions do not. One **must** determine the reaction order from the literature or from experiments.

3.2.3 Reversible Reactions

All rate laws for reversible reactions *must* reduce to the thermodynamic relationship relating the reacting species concentrations at equilibrium. At equilibrium, the net rate of reaction is identically zero for all species (i.e., $-r_A \equiv 0$). That is, for the general reaction



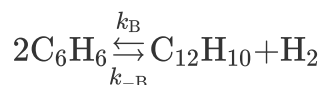
the concentrations at equilibrium are related by the thermodynamic relationship for the equilibrium constant K_C (see Appendix C).

$$K_C = \frac{C_{Ce}^c C_{De}^d}{C_{Ae}^a C_{Be}^b} \quad (3-10)$$

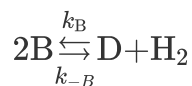
Thermodynamic equilibrium relationship

The units of the thermodynamic concentration equilibrium constant, K_C , are $(\text{mol/dm}^3)^{d+c-b-a}$.

To illustrate how to write rate laws for reversible reactions, we will use the combination of two benzene molecules to form one molecule of hydrogen and one of diphenyl. In this discussion, we shall consider this gas-phase reaction to be *elementary* as written and *reversible*

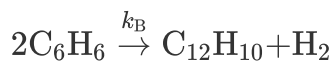


or, symbolically,



The forward and reverse specific reaction-rate constants, k_B and k_{-B} , respectively, will **be defined with respect to benzene**.

Benzene (B) is being depleted by the forward reaction



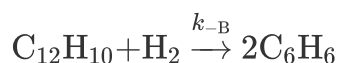
in which the rate of disappearance of benzene is

$$-r_{\text{B, forward}} = k_B C_B^2$$

If we multiply both sides of this equation by -1 , we obtain the expression for the rate of formation of benzene for the forward reaction

$$r_{\text{B, forward}} = -k_B C_B^2 \quad (3-11)$$

For the reverse reaction between diphenyl (D) and hydrogen (H_2),



the rate of formation of benzene is given as

$$r_{\text{B, reverse}} = k_{-B} C_{\text{D}} C_{\text{H}_2} \quad (3-12)$$

The specific reaction rate constant, k_i , must be defined with respect to a particular species.

Again, both the rate constants k_{B} and k_{-B} are *defined with respect to benzene!!!*

The net rate of formation of benzene is the sum of the rates of formation from the forward reaction [i.e., Equation (3-11)] and the reverse reaction (i.e., Equation (3-12))

$$r_{\text{B}} \equiv r_{\text{B, net}} \equiv r_{\text{B, forward}} + r_{\text{B, reverse}}$$

$$r_{\text{B}} = -k_{\text{B}} C_{\text{B}}^2 + k_{-B} C_{\text{D}} C_{\text{H}_2} \quad (3-13)$$

Net rate

Multiplying both sides of Equation (3-13) by -1 , and then factoring out k_{B} , we obtain the rate law for the rate of disappearance of benzene, $-r_{\text{B}}$

$$-r_{\text{B}} = k_{\text{B}} C_{\text{B}}^2 - k_{-B} C_{\text{D}} C_{\text{H}_2} = k_{\text{B}} \left(C_{\text{B}}^2 - \frac{k_{-B}}{k_{\text{B}}} C_{\text{D}} C_{\text{H}_2} \right)$$

$$\text{Elementary reversible } A \rightleftharpoons B \quad -r_A = k \left(C_A - \frac{C_B}{K_C} \right)$$

Replacing the ratio of the reverse to forward rate law constants by the reciprocal of the concentration equilibrium constant, K_C , we obtain

$$-r_B = k_B \left(C_B^2 - \frac{C_D C_{H_2}}{K_C} \right) \quad (3-14)$$

where

$$\frac{k_B}{k_{-B}} = K_C = \text{Concentration equilibrium constant}$$

The equilibrium constant decreases with increasing temperature for exothermic reactions and increases with increasing temperature for endothermic reactions.

Let's write the rate of formation of diphenyl, r_D , in terms of the concentrations of hydrogen, H_2 , diphenyl, D , and benzene, B . The rate of formation of diphenyl, r_D , **must** have the same functional dependence on the reacting species concentrations as does the rate of disappearance of benzene, $-r_B$. The rate of formation of diphenyl is

$$r_D = k_D \left(C_B^2 - \frac{C_D C_{H_2}}{K_C} \right) \quad (3-15)$$

Using the relationship given by Equation (3-1) for the general reaction

Relative rates

$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d} \quad (3-1)$$

we can obtain the relationship between the various specific reaction rates, k_B , k_D

$$\frac{r_D}{1} = \frac{r_B}{-2} = \frac{-k_B [C_B^2 - C_D C_{H_2} / K_C]}{-2} = \frac{k_B}{2} \left[C_B^2 - \frac{C_D C_{H_2}}{K_C} \right] \quad (3-16)$$

Comparing Equations (3-15) and (3-16), we see the relationship between the specific reaction rate with respect to diphenyl, k_D , and the specific reaction rate with respect to benzene, k_B , is

$$k_D = \frac{k_B}{2}$$

Consequently, as previously stated, we must define the rate constant, k , with respect to a particular species.

Finally, we need to check to see whether the rate law given by Equation (3-14) is thermodynamically consistent at equilibrium. Applying Equation (3-10) (and Equation (C-2) in Appendix C) to the diphenyl reaction and substituting the appropriate species concentration and exponents, thermodynamics tells us that

$$K_C = \frac{C_{De} C_{H_2e}}{C_{Be}^2} \quad (3-17)$$

Now let's look at the rate law. At equilibrium, $-r_B \equiv 0$, and the rate law given by Equation (3-14) becomes

$$-r_B \equiv 0 = k_B \left[C_{Be}^2 - \frac{C_{De} C_{H_2e}}{K_C} \right]$$

At equilibrium, the rate law must reduce to an equation consistent with thermodynamic equilibrium.

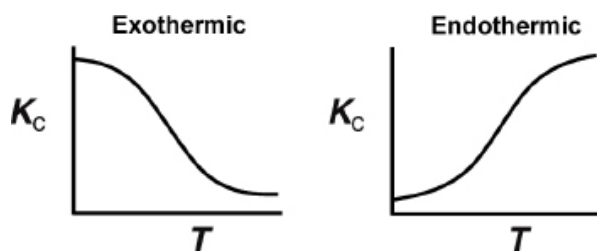
Rearranging, we obtain, as expected, the equilibrium expression

$$K_C = \frac{C_{\text{De}} C_{\text{H}_2\text{e}}}{C_{\text{Be}}^2}$$

that is identical to Equation (3-17) obtained from thermodynamics.

From Appendix C, Equation (C-9), we know that when there is no change in the total number of moles and the heat capacity term, $\Delta C_p = 0$, the temperature dependence of the concentration equilibrium constant is

$$K_C(T) = K_C(T_1) \exp \left[\frac{\Delta H_{\text{Rx}}^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (\text{C-9})$$



Therefore, if we know the equilibrium constant at one temperature, T_1 (i.e., $K_C(T_1)$), and the heat of reaction, $\Delta H_{\text{Rx}}^\circ$, we can calculate the equilibrium constant at any other temperature T . For endothermic reactions, the equilibrium constant, K_C , increases with increasing temperature; for exothermic reactions, K_C decreases with increasing temperature. A further discussion of the equilibrium constant and its thermodynamic relationship is given in Appendix C. For large values of the equilibrium constant, K_C , the reaction behaves as if it were irreversible.

3.3 THE REACTION-RATE CONSTANT

Concept 1, the law of mass action was discussed in Section 3.2 along with the dependence of the reaction rate on concentration. In this section, we investigate the reaction-rate constant, k , and its temperature dependence using **Concept 2, potential energy surfaces and energy barriers**, and **Concept 3, the energy needed to cross over these barriers**.

3.3.1 The Rate Constant k and Its Temperature Dependence

The reaction-rate constant k is not truly a constant; it is merely independent of the concentrations of the species involved in the reaction. The quantity k is referred to as either the **specific reaction rate or the rate constant**. It is almost always strongly dependent on temperature. It also depends on whether or not a catalyst is present, and in gas-phase reactions, it may be a function of total pressure. In liquid systems, it can also be a function of other parameters, such as ionic strength and choice of solvent. These other variables normally exhibit much less of an effect on the specific reaction rate than does temperature, with the exception of supercritical solvents, such as supercritical water. Consequently, for the purposes of the material presented here, it will be assumed that k_A depends *only on* temperature. This assumption is valid in most laboratory and industrial reactions, and seems to work quite well.

It was the great Nobel Prize-winning Swedish chemist Svante Arrhenius (1859–1927) who first suggested that the temperature dependence of the specific reaction rate, k_A , could be correlated by an equation of the type

$$k_A(T) = Ae^{-E/RT} \quad (3-18)$$

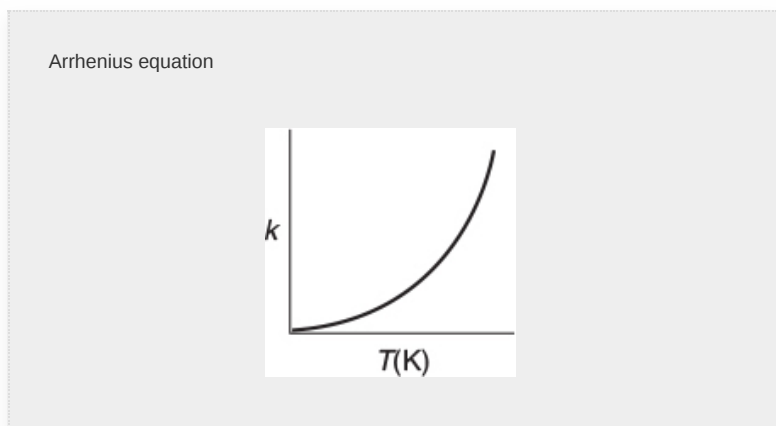
where A = pre-exponential factor or frequency factor

E = activation energy, J/mol or cal/mol

R = gas constant = 8.314 J/mol · K = 1.987 cal/mol · K

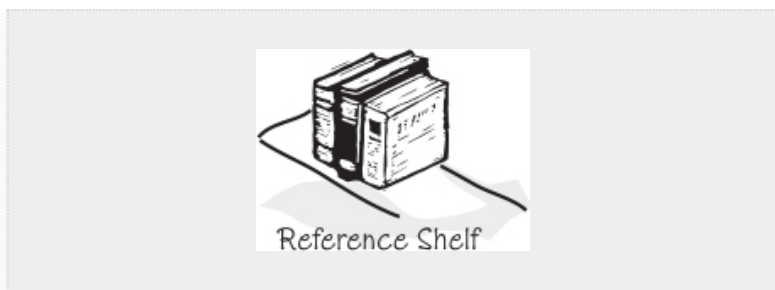
T = absolute temperature, K

(<http://www.umich.edu/~elements/6e/03chap/summary.html>)



Equation (3-18), known as the *Arrhenius equation*, has been verified empirically to give the correct temperature behavior of most reaction-rate constants within experimental accuracy over fairly large temperature ranges. The Arrhenius equation is “derived” in section R3.1, *Collision Theory*, on the CRE Web site (<http://www.umich.edu/~elements/6e/03chap/prof-collision.html>). One can view the activation energy in terms of collision theory (Professional Reference Shelf R3.1).

By increasing the temperature, we increase the kinetic energy of the reactant molecules. This kinetic energy can in turn be transferred through molecular collisions to internal energy to increase the stretching and bending of the bonds, causing the molecules to reach an activated state, vulnerable to bond breaking and reaction.



3.3.2 Interpretation of the Activation Energy

Why is there an activation energy? If the reactants are free radicals that essentially react immediately on collision, there usually isn't an activation energy. However, for most atoms and molecules undergoing reaction, there is an activation energy. A couple of the reasons are that in order to react

1. The molecules need energy to distort or stretch their bonds so that they break and now can form new bonds.
2. The molecules need energy to overcome the steric and electron repulsive forces as they come close together.

The activation energy can be thought of as a barrier to energy transfer (from kinetic energy to potential energy) between reacting molecules that must be overcome. The activation energy is the minimum increase in potential energy of the reactants that must be provided to transform the reactants into products. This increase can be provided by the kinetic energy of the colliding molecules.

In addition to the concentrations of the reacting species, there are two other factors that affect the rate of reaction:

- The height of the potential energy barrier, that is, activation energy
- The fraction of molecular collisions that have sufficient energy to cross over the barrier (i.e., react when the molecules collide)

If we have a small barrier height, the molecules colliding will need only low kinetic energies to cross over the barrier. For

reactions of molecules with small barrier heights occurring at room temperatures, a greater fraction of molecules will have this energy at low temperatures. However, for larger barrier heights, we require higher temperatures where a higher fraction of colliding molecules will have the necessary energy to cross over the barrier and react. We will discuss each of these concepts separately in Concept 2 and Concept 3.

Concept 2. Potential Energy Surfaces and Energy Barriers.

One way to view the barrier to a reaction is through the use of potential energy surfaces and the reaction coordinates. These coordinates denote the minimum potential energy of the system as a function of the progress along the reaction path as we go from reactants to an intermediate to products. For the exothermic reaction



the potential energy surface and the reaction coordinate are shown in Figures 3-1 and 3-2. Here E_A , E_{AB} , E_{BC} , and E_C are the potential surface energies of the reactants (A and BC) and products (AB and C), while E_{ABC} is the energy of the complex A-B-C at the top of the barrier shown in Figure 3-2(a).

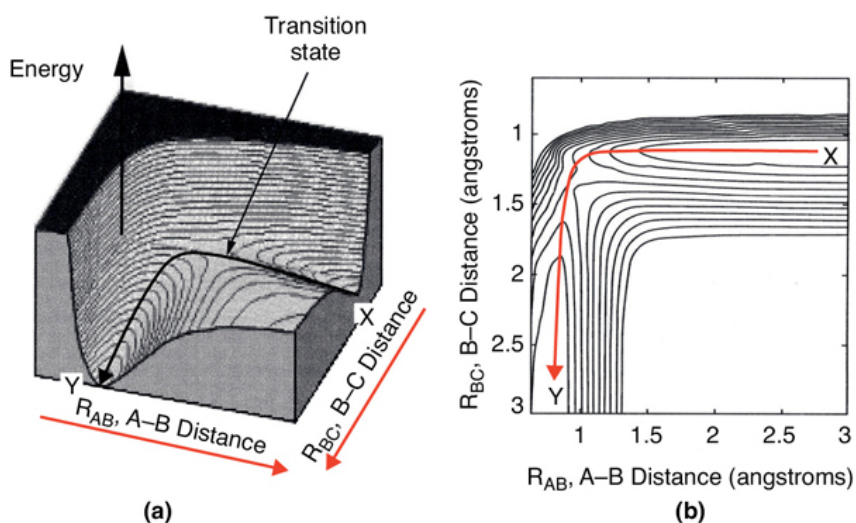


Figure 3-1 A potential energy surface for the $\text{H} + \text{CH}_3\text{OH} \rightarrow \text{H}_2 + \text{CH}_2\text{OH}$ from the calculations of Blowers and Masel. The lines in the figure are contours of constant energy. The lines are spaced 5 kcal/mol. Richard I. Masel, *Chemical Kinetics and Catalysis*, p. 370, Fig. 7.6 (Wiley, 2001).

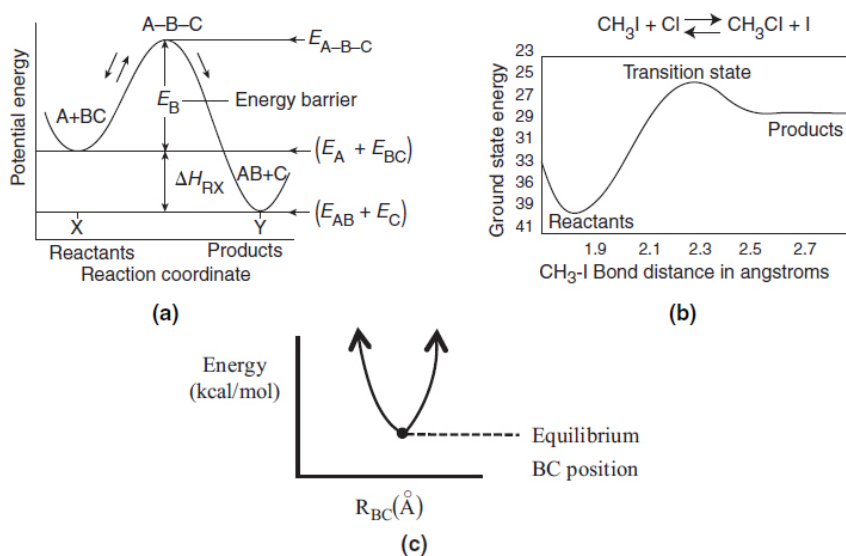


Figure 3-2 Progress along reaction path. **(a)** Symbolic reaction; **(b)** Calculated from computational software on the CRE Web site, Chapter 3 Web Module on Molecular Modeling. **(c)** Side view at point X in Figure 3-1(b), showing the valley.

Figure 3-1(a) shows a 3D plot of the potential energy surface, which is analogous to a mountain pass where we start out in a valley and then climb up to pass over the top of the pass, that is, the *col* or *saddle point*, and proceed down into the next valley. Figure 3-1(b) shows a contour plot of the pass and valleys and the reaction coordinate as we pass over the col from valley to valley.

Energy changes as we move within the potential energy surfaces.

At point X in Figure 3-1(b), species A and BC are far apart and are not interacting, and R_{BC} is just the equilibrium bond length between B and C. Consequently, the potential energy is just the BC bond energy. Here, species A and BC are in their minimum potential energy in the valley and the steep rise up from the valley to the col from point X would correspond to increases in the potential energy as A comes close to BC.[†]

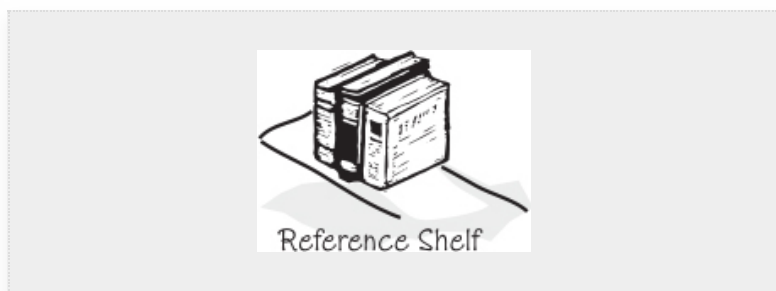
Figure 3-2(c) illustrates when the BC bond is stretched from its equilibrium position at point X, the potential energy increases up one side of the valley hill (R_{BC} increases). The potential energy is now greater because of the attractive forces trying to bring the B–C distance back to its equilibrium position. If the BC bond is compressed at point X from its equilibrium position, the repulsive forces cause the potential energy to increase on the other side of the valley hill, that is, R_{BC} decreases at point X. At the end of the reaction, point Y, the products AB and C are far apart on the valley floor and the potential energy is just the equilibrium AB bond energy. The sides of the valley at point Y represent the cases where AB is either compressed or stretched causing the corresponding increases in potential energy at point Y and can be described in an analogous manner to BC at point X.

We want the minimum energy path across the barrier for converting the kinetic energy of the molecules into potential energy. This path is shown by the curve $X \rightarrow Y$ in Figure 3-1 and also by Figure 3-2(a). As we move along the A–B distance axis in Figure 3-2(a), A comes closer to BC, such that A begins to bond with BC and push B and C apart. Consequently, the potential energy of the reaction pair (A and BC) continues to increase until we arrive at the top of the energy barrier, which is the transition state. In the transition state, the molecular distances between A and B and between B and C are close. As a result, the potential energy of the three

atoms (molecules) is high. As we proceed further along the arc length of the reaction coordinate depicted in [Figure 3-1\(a\)](#), the AB bond strengthens and the BC bond weakens and C moves away from AB and the energy of the reacting pair decreases until we arrive at the valley floor where AB is far apart from C. The reaction coordinate in [Figure 3-2\(a\)](#) quantifies how far the reaction has progressed. The commercial software available to carry out calculations for the transition state for the real reaction

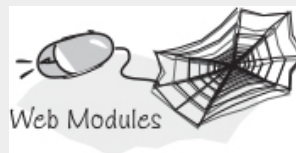


shown in [Figure 3-2\(b\)](#) is discussed in the Web Module *Molecular Modeling in Chemical Reaction Engineering* on the CRE Web site (http://www.umich.edu/~elements/6e/web_mod/quantum/index.htm). In addition to Spartan software, which was used to calculate [Figure 3-2\(b\)](#), the software packages, Gaussian 16, IQMol, Q-Chem, and GAMES could be used.



We next discuss the pathway over the barrier shown along the line Y–X. We see that for the reaction to occur, the reactants must overcome the minimum energy barrier, E_B , shown in [Figure 3-2\(a\)](#). The energy barrier, E_B , is related to the activation energy, E . The energy barrier height, E_B , can be calculated from differences in the energies of formation of the transition-state molecule and the energy of formation of the reactants; that is,

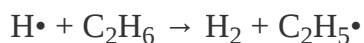
$$E_B = E_{A-B-C}^{\circ} - (E_A^{\circ} + E_{B-C}^{\circ})$$



The energy of formation of the reactants can be found in the literature or calculated from quantum mechanics, while the energy of formation of the transition state can also be calculated from quantum mechanics using a number of software packages, such as Gaussian (<http://www.gaussian.com/>) and Dacapo (<https://wiki.fysik.dtu.dk/dacapo>). The activation energy, E , is often approximated by the barrier height, E_B , which is a good approximation in the absence of quantum mechanical tunneling.

[†] LearnChemE CU video Reaction Coordinate (<https://www.youtube.com/watch?v=...>)

Now that we have the general idea for a reaction coordinate, let's consider another real reaction system



The energy–reaction coordinate diagram for the reaction between a hydrogen atom and an ethane molecule is shown in [Figure 3-3](#) where the bond distortions, breaking, and forming are identified. This figure shows schematically how the hydrogen molecule, H_2 , moves into $\text{CH}_3\text{--CH}_3$ molecule, distorting the C--H bond and pushing the C--H bond off the

methyl hydrogen to arrive at the transition state. As one continues along the reaction coordinate, the methyl hydrogen moves out of the C–H bond into the H–H bond to form the products CH_3CH_2 and H_2 .

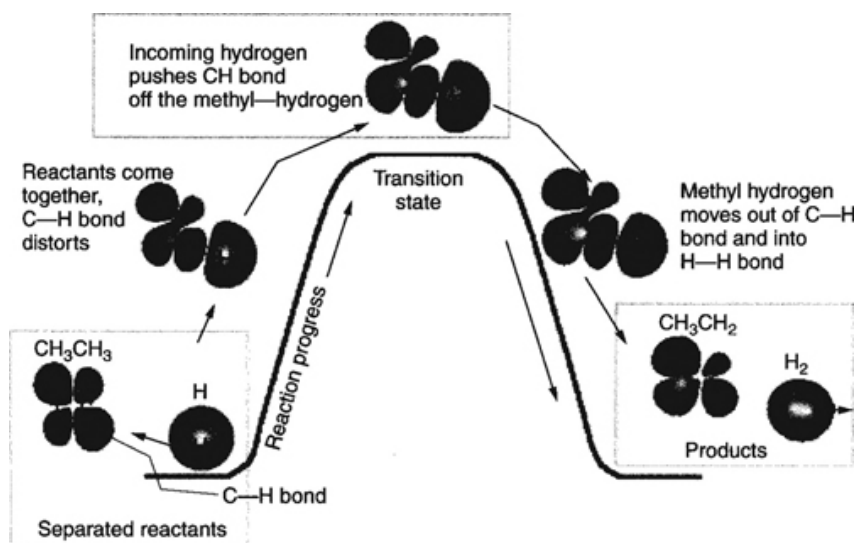
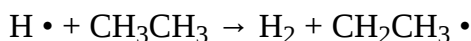


Figure 3-3 A diagram of the orbital distortions during the reaction



The diagram shows only the interaction with the energy state of ethane (the C–H bond). Other molecular orbitals of the ethane molecule also distort. Courtesy of Richard I. Masel, *Chemical Kinetics and Catalysis*, p. 594 (Wiley, 2001).

Concept 3. Fraction of Molecular Collisions That Have Sufficient Energy to React. Now that we have established the concept of a barrier height, we need to know what fraction of molecular collisions have sufficient energy to cross over the barrier and react. To discuss this issue, we consider reactions in the gas phase where the reacting molecules will not have only a single velocity, U , but a distribution of velocities, $f(U, T)$. Some will have high velocities and some will have low velocities as they move around and collide. These velocities

are not defined with respect to a fixed coordinate system; these velocities are defined with respect to the other reactant molecules. The Maxwell Boltzmann distribution of relative velocities is given by the probability function, $f(U, T)$

$$f(U, T) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left[\frac{-mU^2}{2k_B T} \right] U^2$$

k_B = Boltzmann's constant = 3.29×10^{-24} cal/molecule/K

m = Reduced mass, g

U = Relative velocity, m/s

T = Absolute Temperature, K

e = Energy kcal/molecule

E = Kinetic energy kcal/mol

We usually interpret $f(U, T)$ with dU , that is,

$f(U, T) dU$ = fraction of reactant molecules with velocities between U and $(U + dU)$.

Rather than using velocities to discuss the fraction of molecules with sufficient energy to cross the barrier, we convert these velocities to energies using the equation for kinetic energy in making this conversion

$$e = \frac{1}{2} m U^2$$

Using this relationship we substitute, the Maxwell Boltzmann probability distribution of collisions with energy e (cal/molecule) at temperature T is

$$f(e, T) = 2\pi \left(\frac{1}{\pi k_B T} \right)^{3/2} e^{1/2} \exp \left[\frac{-e}{k_B T} \right] \quad (3-19)$$

In terms of energy per mole, E , *instead* of energy per molecule, e , we have

$$f(E, T) = 2\pi \left(\frac{1}{\pi R T} \right)^{3/2} E^{1/2} \exp \left[\frac{-E}{R T} \right] \quad (3-20)$$

where E is in (cal/mol), R is in (cal/mol/K), and $f(E, T)$ is in mol/cal.

This function is plotted for two different temperatures in [Figure 3-4](#). The distribution function $f(E, T)$ is most easily interpreted by recognizing that $[f(E, T) dE]$ is the fraction of collision with energies between E and $E + dE$.

$$f(E, T) dE = 2\pi \left(\frac{1}{\pi k_B T} \right)^{3/2} E^{1/2} \exp \left[-\frac{E}{k_B T} \right] dE \quad (3-21)$$

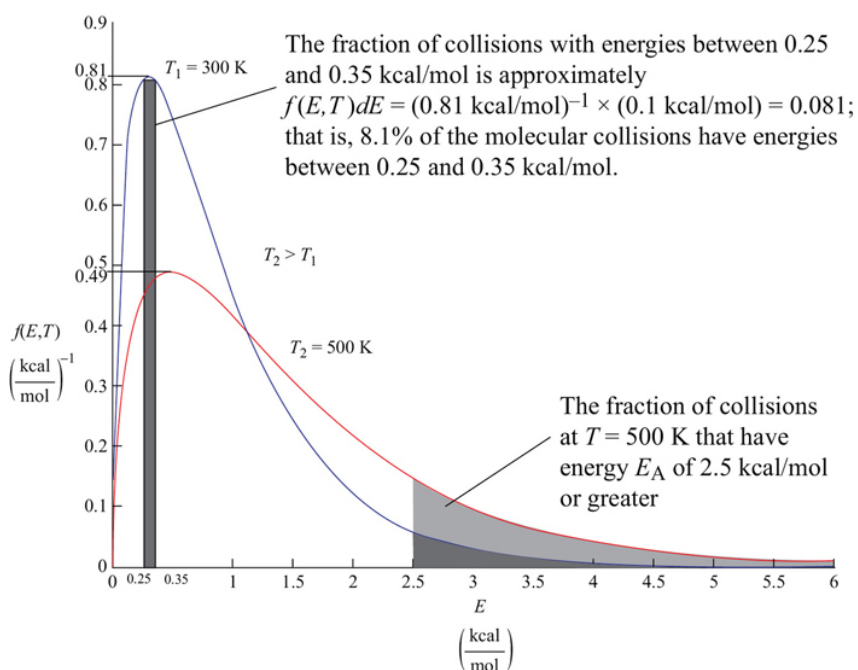


Figure 3-4 Energy distribution of reacting molecules.

For example, the fraction of collisions with energies between 0.25 and 0.35 kcal/mol would be

$$\left(\text{Fraction with energies between } (0.25 \text{ and } 0.35) \frac{\text{kcal}}{\text{mol}} \right) = \int_{0.25}^{0.35} f(E, T) dE$$

This fraction is shown by the shaded area in [Figure 3-4](#) and is approximated by the average value of $f(E, T)$ at $E = 0.3$ kcal/mol which is 0.81 mol/kcal.

$$f(E, T) dE = f\left(0.3, 300\text{K}\right) \Delta E = \frac{0.81 \text{ mol}}{\text{kcal}} \left(0.35 \frac{\text{kcal}}{\text{mol}} - 0.25 \frac{\text{kcal}}{\text{mol}}\right) = 0.081$$

Thus 8.1% of the molecular collisions have energies between 0.25 and 0.35 kcal/mol. Go to the [Chapter 3 Living Example Problem \(LEP\)](#) “*Variation of Energy Distribution with Temperature*” on the Web site and use Wolfram to see how the distribution changes as the temperature changes. Wolfram can be downloaded on your laptop for free (go to <http://www.wolfram.com/cdf-player/>).

We can also determine the fraction of collisions that have energies greater than a certain value, E_A

$$\left(\begin{array}{l} \text{Fraction of} \\ \text{Molecules} \quad E > E_A \\ \text{with} \end{array} \right) = F(E > E_A, T) = \int_{E_A}^{\infty} f(E, T) dE \quad (3-22)$$

This fraction is shown in [Figure 3-4](#) by the shaded area for $E_A = 2.5$ kcal/mole for $T = 300$ K (heavier shade) and for $T = 500$ K (lighter shade). One can easily see that for $T = 500$ K a greater fraction of the collisions that cross the barrier with $E_A = 2.5$ kcal/mol and react, which is consistent with our observation that the rates of reaction increase with increasing temperature.

For $E_A > 3RT$, we can obtain an analytical approximation for the fraction of molecules of collision with energies greater

than E_A by combining Equations (3-21) and (3-22) and integrating to get

$$\left(\begin{array}{c} \text{Fraction of collision} \\ \text{with energies greater} \\ \text{than } E_A \end{array} \right) = F(E > E_A, T) \cong \frac{2}{\sqrt{\pi}} \left(\frac{E_A}{RT} \right)^{1/2} \exp \left(-\frac{E_A}{RT} \right) \quad (3-23)$$

Figure 3-5 shows the fraction of collisions that have energies greater than E_A as a function of E_A for two different temperatures, 300 K and 600 K. One observes for an activation energy E_A of 20 kcal/mol and a temperature of 300 K the fraction of collisions with energies greater than 20 kcal/mol is 1.76×10^{-14} while at 600 K, the fraction increases to 2.39×10^{-7} , which is a 7 orders of magnitude difference.

In summary, to explain and give insight to the dependence of rate of reaction on concentration and temperature we introduced three concepts

**Co
nce
pt 1**

The rate increases with increasing reactant concentration,

**Co
nce
pt 2**

The rate is related to the potential energy barrier height and to the conversion of translational energy into potential energy, and

**Co
nce
pt 3**

The rate increases with the increasing fraction of collisions that have sufficient energy to cross over the barrier and form products.

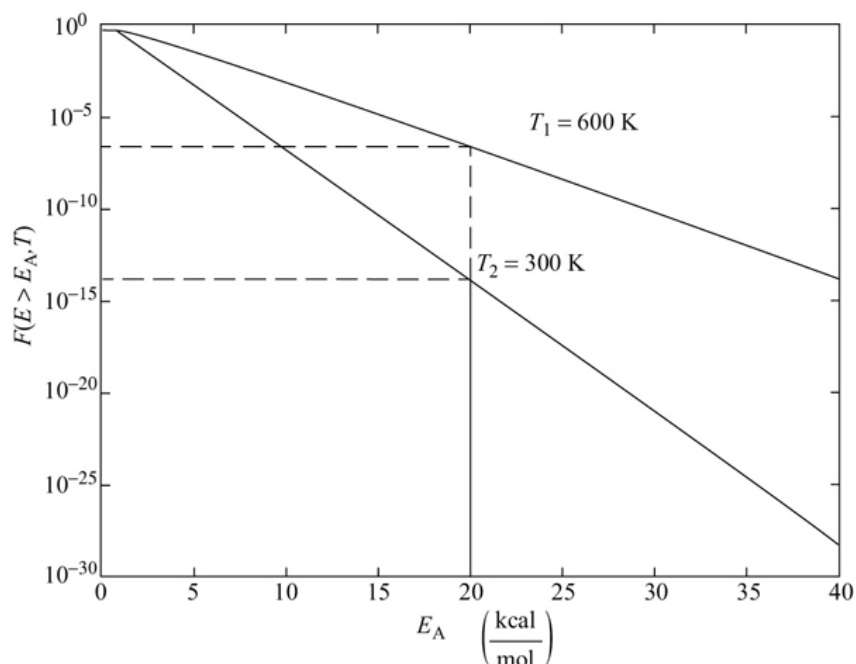


Figure 3-5 Fraction of collision with energies greater than E_A .

To carry this discussion to the next level is beyond the scope of this text as it involves averaging over a collection of pairs of molecules to find an average rate with which they pass over the transition state to become products.

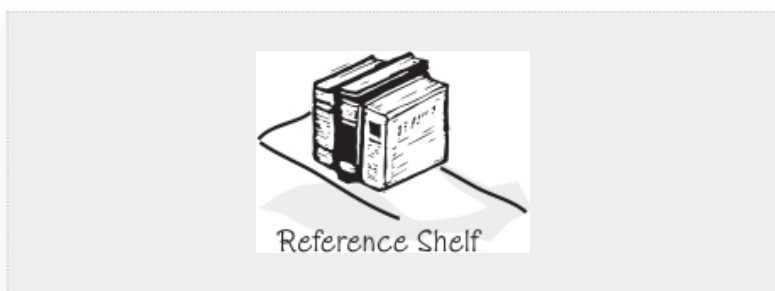
Recapping the last section, the energy of the individual molecules falls within a distribution of energies; that is, some molecules have more energy than others. One such distribution is the Boltzmann distribution, shown in [Figure 3-4](#), where $f(E, T)$ is the energy distribution function for the kinetic energies of the reacting molecules. It is interpreted most easily by recognizing the product $[f(E, T) dE]$ as the fraction of molecular collisions that have an energy between E and $(E + dE)$. For example, in [Figure 3-4](#), the fraction of collisions that have energies between 0.25 and 0.35 kcal/mol is 0.081, as shown by the shaded area on the left. The activation energy has been equated with a minimum energy that must be possessed by reacting molecules before the reaction will occur.

The fraction of the molecular collisions that have an energy E_A or greater is shown by the shaded areas at the right in [Figure 3-4](#). [Figure 3-5](#) shows the fraction of collisions with energies greater than E_A as a function of E_A at two different temperatures.[†]

3.3.3 The Arrhenius Plot

Postulation of the Arrhenius[‡] equation, Equation (3-18), remains the greatest single advancement in chemical kinetics, and retains its usefulness today, more than a century later. The activation energy, E , is determined experimentally by measuring the reaction rate at several different temperatures. After taking the natural logarithm of Equation (3-18), we obtain

$$\ln k_A = \ln A - \frac{E}{R} \left(\frac{1}{T} \right) \quad (3-24)$$



We see that the activation energy can be found from a plot of $\ln k_A$ as a function of $(1/T)$, which is called an *Arrhenius plot*. As can be seen in [Figure 3-6](#) the larger the activation energy, the larger the slope and the more temperature-sensitive the reaction. That is, for large E , an increase in just a few degrees in temperature can greatly increase k and thus increase the rate of reaction. The units of k_A will depend on the reaction order, and the fact that k in [Figure 3-6](#) has units of s^{-1} indicates the reaction here is first order.

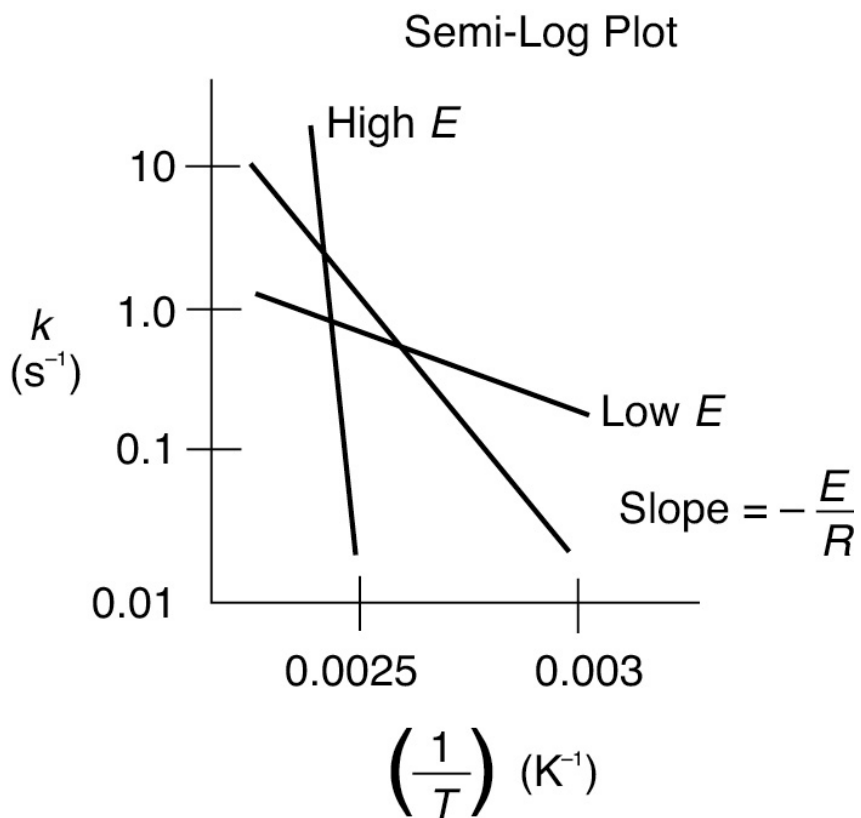


Figure 3-6 Calculation of the activation energy from an Arrhenius plot.

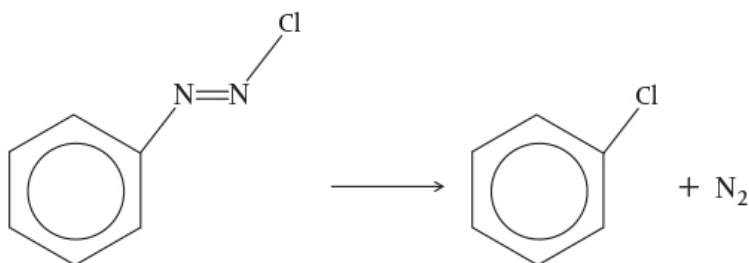
Calculation of the activation energy

[†] University of Colorado LearnChemE three videos: One on reaction coordinates (<https://www.youtube.com/watch?v=Yh9XdLJcTi4>) and Mr. Anderson's activation video (<https://www.youtube.com/watch?v=YacsIU97OFc>).

[‡] Arrhenius bio: <http://www.umich.edu/~elements/6e/03chap/summary-bioarr.html>.

Example 3-1 Determination of the Activation Energy

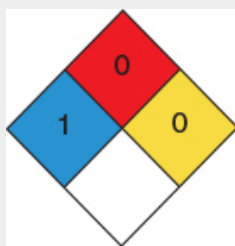
Calculate the activation energy for the decomposition of benzene diazonium chloride to give chlorobenzene and nitrogen



using the information in [Table E3-1.1](#) for this first-order reaction.

TABLE E3-1.1 DATA

$k \text{ (s}^{-1}\text{)}$	0.00043	0.00103	0.00180	0.00355	0.00717
$T \text{ (K)}$	313.0	319.0	323.0	328.0	333.0



Benzene Diazonium Chloride

Solution

We start by recalling Equation (3-24)

$$\ln k_A = \ln A - \frac{E}{R} \left(\frac{1}{T} \right) \quad (3-24)$$



We can use the data in [Table E3-1.1](#) to determine the activation energy, E , and frequency factor, A , in two different ways. One way is to make a semi-log plot of k versus $(1/T)$ and determine E from the slope $(-E/R)$ of an Arrhenius plot. Another way is to use Excel or Polymath to regress the data. The data in [Table E3-1.1](#) was entered in Excel and is shown in [Figure E3-1.1](#), which was then used to obtain [Figure E3-1.2](#).

	A	B	C
1	$k \text{ (s}^{-1}\text{)}$	$\ln(k)$	$1/T \text{ (K}^{-1}\text{)}$
2	0.00043	-7.75	0.00320
3	0.00103	-6.88	0.00314
4	0.00180	-6.32	0.00310
5	0.00355	-5.64	0.00305
6	0.00717	-4.94	0.00300

Figure E3-1.1 Excel spreadsheet.

Step-by-step tutorials on how to construct spreadsheets in Polymath and in Excel are on the Web site at

<http://umich.edu/~elements/6e/software/polymath-tutorial-linearpolyregression.html> and
http://umich.edu/~elements/6e/live/chapter03/Excel_tutorial.pdf.

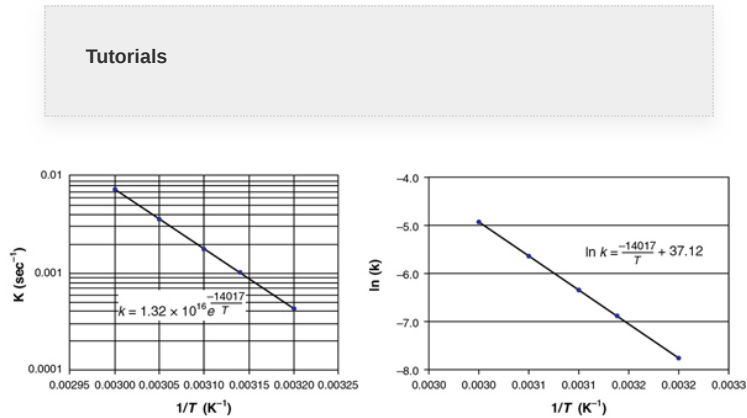


Figure E3-1.2 (a) Excel semi-log plot; (b) Excel normal plot after taking $\ln(k)$.

(<http://www.umich.edu/~elements/6e/software/polymath-tutorial-linearpolyregression.html>)

$$k = k_1 \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right]$$

The equation for the best fit of the data

$$\ln k = \frac{-14017}{T} + 37.12 \quad (\text{E3-1.1})$$

is also shown in Figure E3-1.2(b). From the slope of the line given in Figure E3-1.2(b) and Equation (3-20), we obtain

$$-\frac{E}{R} = -14017K$$

$$E = (14017K)R = (14017K) \left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right)$$

$$E = 116.5 \frac{\text{kJ}}{\text{mol}}$$

From Figure E3-1.2(b) and Equation (E3-1.1), we see

$$\ln A = 37.12$$

Taking the antilog, we find the frequency factor to be

$$A = 1.32 \times 10^{16} \text{ s}^{-1}$$

$$k = 1.32 \times 10^{16} \exp \left[-\frac{14017 \text{ K}}{T} \right] \text{ s}^{-1} \quad (\text{E3-1.2})$$

Analysis: The activation energy, E , and frequency factor, A , can be calculated if we know the specific reaction rate, k , at two temperatures, T_1 and T_2 . We can either use the Arrhenius equation (3-18) twice, once at T_1 and once at T_2 , to solve two equations for the two unknowns, A and E , **or** we can take the slope of a plot of $(\ln k)$ as a function of $(1/T)$; the slope will be equal to $(-E/R)$.

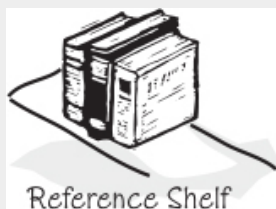
There is a rule of thumb that states that the rate of reaction doubles for every 10°C increase in temperature. However, this rule is true only for specific combinations of activation energies and temperatures. For example, if the activation energy is 53.6 kJ/mol , the rate will double only if the temperature is raised from 300 to 310 K . If the activation energy is 147 kJ/mol , the rule will be valid only if the temperature is raised from 500 to 510 K (see Problem P3-10_B for the derivation of this relationship).

The rate does not always double for a temperature increase of 10°C.



The larger the activation energy, the more temperature-sensitive is the rate of reaction. While there are no typical values of the frequency factor and activation energy for a first-order gas-phase reaction, if one were forced to make a guess, values of A and E might be 10^{13} s^{-1} and 100 kJ/mol. However, for families of reactions (e.g., halogenation), a number of correlations can be used to estimate the activation energy. One such correlation is the *Polanyi-Semenov equation*, which relates activation energy to the heat of reaction (see *Collision Theory in Professional Reference Shelf R3.1*

[<http://www.umich.edu/~elements/6e/03chap/prof-collision.html#VI>]). Another correlation relates the activation energy to differences in bond strengths between products and reactants.³ While the activation energy cannot be currently predicted *a priori*, significant research efforts are under way to calculate activation energies from first principles.⁴



One final comment on the Arrhenius equation, Equation (3-18). It can be put in a most useful form by finding the specific reaction rate at a temperature T_0 ; that is,

$$k(T_0) = Ae^{-E/RT_0}$$

and at a temperature T

$$k(T) = Ae^{-E/RT}$$

and taking the ratio to obtain

$$k(T) = k(T_0) e^{\frac{E}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)} \quad (3-25)$$

A most useful form of $k(T)$

This equation says that if we know the specific reaction rate $k(T_0)$ at a temperature, T_0 , and we know the activation energy, E , we can find the specific reaction rate $k(T)$ at any other temperature, T , for that reaction.

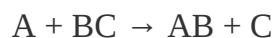
³ M. Boudart, *Kinetics of Chemical Processes*, Upper Saddle River, NJ: Prentice Hall, p. 168. J. W. Moore and R. G. Pearson, *Kinetics and Mechanisms*, 3rd ed. New York: Wiley, p. 199. S. W. Benson, *Thermochemical Kinetics*, 2nd ed. New York: Wiley.

⁴ R. Masel, *Chemical Kinetics and Catalysis*, New York: Wiley, 2001, p. 594.

3.4 MOLECULAR SIMULATIONS

3.4.1 Historical Perspective

For the last 10 years or so, molecular simulations have been used more and more to help understand chemical reactions along with their pathways and mechanisms. Consequently, to introduce you to this area, we will use MATLAB to simulate a simple reaction and view a couple of molecular simulation trajectories. Some of the earliest simulations were carried out by Professor Martin Karplus more than 50 years ago and are described in his groundbreaking journal article *J. Chem. Phys.*, 43, 3259 (1965) for the reaction



The forces and potential energies he used to describe the interaction as the two molecules approach each other are described in the Professional Reference Shelf R3.3 Molecular Dynamics (PRS R3.3)

(<http://www.umich.edu/~elements/6e/03chap/prof-moldyn.html>).

In Karplus's procedure, the trajectories and molecular collisions of species A and BC are calculated and analyzed to determine whether or not they have sufficient translational, vibrational, and kinetic energy, along with molecular orientation to either react or not react. A nonreactive trajectory and a reactive trajectory are shown in [Figures 3-7\(a\) and 3-7\(b\)](#), respectively. One notes the vibrations of the AB and BC molecules from the plot of R_{AB} and R_{BC} with time. In the Monte Carlo simulation, the randomly chosen input parameters are (1) the initial distance between A and BC, (2) the orientation of BC relative to A, and (3) the angular momentum of BC. Next, the reaction trajectories are calculated to learn whether the trajectory is reactive or nonreactive and the result is recorded. This process is repeated a number of times for different random input parameters and the number of reactive and nonreactive trajectories for these input parameters are again counted and recorded. The statistics of the number of reactive versus number of nonreactive trajectories are then used to develop a probability of reaction. The specific reaction-rate constant and the activation energy are determined from the probability of reaction (cf. PRS R3.3).

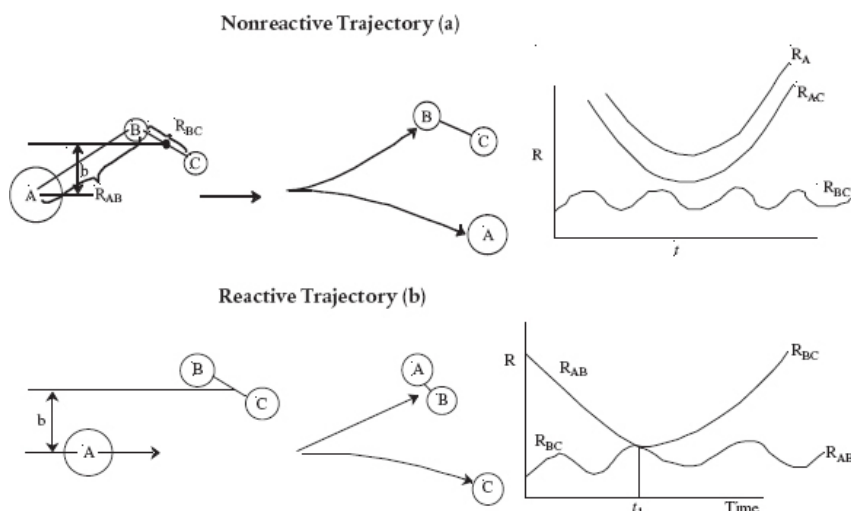
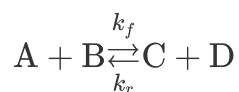


Figure 3-7 Molecular Trajectories (a) Nonreactive (b) Reactive.

Professor Karplus received the 2013 Nobel Prize for his pioneering work in molecular simulations.

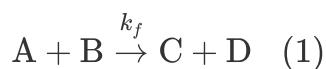
3.4.2 Stochastic Modeling of Reactions[†]

However, rather than tracking singular trajectories as Karplus did, we consider an ensemble of molecules and the collisions between both reactants and products and use stochastic modeling to determine the concentration trajectories of the reacting molecules. To illustrate the stochastic modeling of chemical reactions, we will use the reversible reaction

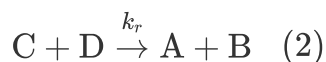


which we will write as separate reactions

Reaction (1)



Reaction (2)



that are assumed to be elementary and have deterministic rate laws given by $-r_A = k_f C_A C_B$ and $-r_C = k_r C_C C_D$.

To model these reactions stochastically, we define the probability that the “reaction i ” will occur per unit time, that is, r_i . This probability is related to the number of ways the reaction can occur per unit time, which is analogous to the deterministic rate law. The *probability function* of Reaction (1) occurring per unit time, r_f , is

$$r_f = k_f x_A x_B \quad (3-26)$$

and the *probability function* of Reaction (2) occurring per unit time is

$$r_r = k_r x_C x_D \quad (3-27)$$

where the terms x_i are the number of molecules of species i . Here r_f and r_r are the *probability functions* of the forward and the reverse reactions occurring per unit time and the rate constants k_f and k_r are probabilities that the collisions between molecules A and B give rise to Reaction (1) or between molecules C and D giving rise to Reaction (2) respectively.

The rate constants k_f and k_r have units of $\left[\frac{1}{(\text{no. of molecules})^2 \text{s}} \right]$.

The total reaction probability function, r_t , is

$$r_t = r_f + r_r. \quad (3-28)$$

[†] An overview of stochastic modeling can be found in a PowerPoint presentation on the Web site (<http://www.doc.ic.ac.uk/~jb/conferences/pasta2006/slides/stochastic-simulation-introduction.pdf>).

In carrying out the stochastic simulations, we randomly choose which reaction, that is, either (1) or (2), will occur in time step

t_i based on the reactive probabilities of each of the two reactions. The probability of Reaction (1) occurring is related to the ratio

$$f_1 = \frac{r_f}{r_f + r_r} = \frac{k_f x_A x_B}{k_f x_A x_B + k_r x_C x_D} \quad (3-29)$$

and the probability of Reaction (2) occurring is related to the ratio

$$f_2 = \frac{r_r}{r_f + r_r} = \frac{k_r x_C x_D}{k_f x_A x_B + k_r x_C x_D} \quad (3-30)$$

Next, we generate a random number, p_1 , in the interval (0, 1). If the random number p_1 is less than f_1 , that is, ($0 \leq p_1 \leq f_1$) then Reaction (1) occurs and the number of A and B molecules decrease by one each and the number of C and D molecules increase by one each and these numbers are then recorded at time t_i . If p_1 was not in that interval ($0 \leq p_1 < f_1$), then Reaction (2) occurs and the number of A and B molecules each increase by one and the number of C and D molecules each decrease by one. Consequently, the probability values of f_1 and f_2 will change for the next time step and for the next random number generation. Let's consider the first six-time steps in which the probability results show that Reaction (1) takes place in the first three-time steps, while Reaction (2) occurs in the fourth- and fifth-time steps, and then Reaction (1) occurs again in the sixth-time step. The number of C or D molecules after the first six steps are $1 \rightarrow 2 \rightarrow 3 \rightarrow 2 \rightarrow 1 \rightarrow 2$ as shown in Figure 3-8 (a) as a function of the step numbers, that is, i .

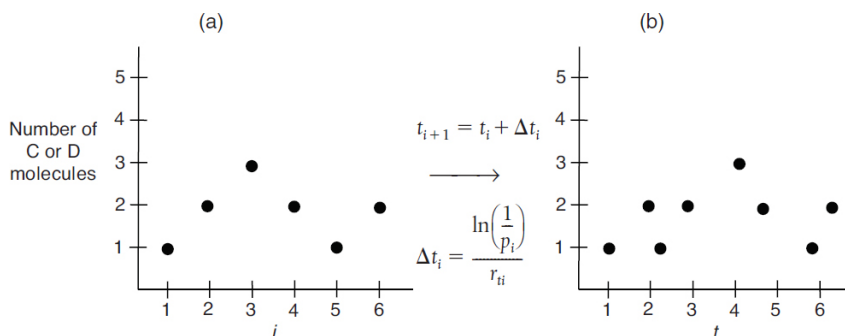


Figure 3-8 (a) Number of molecules as a function of a simulation run number i . (b) Number of molecules as a function of time, where r_{ti} is the total rate at time t_i .

We now will convert the step number to a time t . The time between a molecular collision of A and B is also random. To determine this time, we use the random number generated for simulation run number i , p_i ($0 < p_i < 1$). The corresponding time increment is

$$\Delta t_i = \frac{\ln\left(\frac{1}{p_i}\right)}{r_{ti}} \quad (3-31)$$

Where Equation (3-28) is evaluated at step i , Δt_i has the units of seconds. We update the time t by the equation

$$t_{i+1} = t_i + \Delta t_i \quad (3-32)$$

Figure 3-8(b) shows the number of C or D molecules as a function of time after the Figure 3-8(a) axis is converted to time using Equations (3-31) and (3-32).

If we continued the time steps in this fashion, the *overall* number of C and D molecules would continue to increase in a stochastic manner as shown in Figure 3-9(b). Analogously, the number of A and B molecules would continue to decrease, also shown in this figure.

Set input parameters

kf	<input type="text" value="1"/>
kb	<input type="text" value="1"/>
A	<input type="text" value="40"/>
B	<input type="text" value="40"/>
C	<input type="text" value="0"/>
D	<input type="text" value="0"/>

Figure 3-9(a) Graphical user interface in LEP.

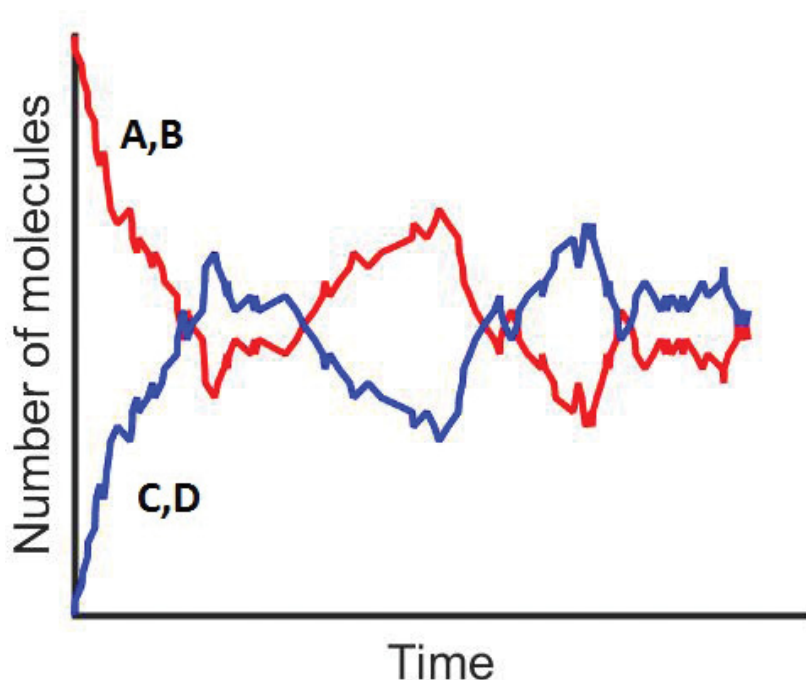


Figure 3-9(b) Molecular trajectories.

Stochastic modeling allows us to see on a molecular level how the reaction progresses. The *takeaway* lesson is that while the deterministic model shows the smooth reaction path of species C and D being formed, on the molecular scale we see C and D being formed, then reacting back to A and B and then being formed again.

Figure 3-9(b) shows how the number of molecules of species A and C fluctuate as the reaction progresses.

Now carry out the simulation by going to the Web, load the [Chapter 3 LEP](#) on molecular simulations and use the Graphical User Interface shown in [Figure 3-9\(a\)](#). Vary the number of molecules initially along with rate constants k_f and k_r (cf. LEP P3-1A (b)) and observe the trajectories similar to the one shown in [Figure 3-9\(b\)](#). A tutorial on how to run the simulation is given on the Web site along with the simulation of a series reaction ($A + B \rightleftharpoons C + D \rightleftharpoons E + F$).

3.5 PRESENT STATUS OF OUR APPROACH TO REACTOR SIZING AND DESIGN

In Chapter 2, we combined the different reactor mole balances with the definition of conversion to arrive at the design equation for each of four types of reactors, as shown in Table 3-2. Next we showed that if the rate of disappearance is known as a function of the conversion X

$$-r_A = g(X)$$



then it is possible to size CSTRs, PFRs, and PBRs operated at the same conditions under which $-r_A = g(X)$ was obtained.

In general, information in the form $-r_A = g(X)$ is not available. However, we have seen in Section 3.2 that the rate of disappearance of A, $-r_A$, is normally expressed in terms of the concentration of the reacting species. This functionality

$$-r_A = [k_A(T)] [\text{fn}(C_A, C_B, \dots)] \quad (3-2)$$

TABLE 3-2 DESIGN EQUATIONS

		Differential Form	Algebraic Form	Integral Form
Batch	Design equation	$N_{A0} \frac{dX}{dt} = -r_A V \quad (2-6)$		
	Stoichiometry	$t = N_{A0} \int_0^X \frac{dX}{-r_A V} \quad (2-9)$		
	Rate law			

ch

Basic Principles

$$V = \frac{F_{A0}X}{-r_A} \quad (2-13)$$

Fluidized Bed Reactor

$$W = \frac{F_{A0}X}{-r'_A}$$

Tutorial Problems

$$F_{A0} \frac{dX}{dV} = -r_A \quad (2-15)$$

$$V = F_{A0} \int_0^X \frac{dX}{-r_A} \quad (2-16)$$

R
)

$$F_{A0} \frac{dX}{dW} = -r'_A \quad (2-17)$$

$$W = F_{A0} \int_0^X \frac{dX}{-r'_A} \quad (2-18)$$

P
a
c
k
e
d
b
e
d
(
P
B
R
)

The design equations

is called a *rate law*. In Chapter 4, we show how the concentration of the reacting species may be written in terms of the conversion X

$$C_j = h_j(X) \quad (3-26)$$

$$\begin{array}{c} -r_A = f(C_j) \text{ and then we can design isothermal reactors} \\ + \\ C_j = h_j(X) \\ \downarrow \\ -r_A = g(X) \end{array}$$

With these additional relationships, one observes that if the rate law is given and the concentrations can be expressed as a function of conversion, *then in fact we have $-r_A$ as a function of X and this is all that is needed to evaluate the isothermal*

design equations. One can use either the numerical techniques described in Chapter 2 or, as we shall see in Chapter 5, a table of integrals, and/or software programs (e.g., Polymath).

3.6 AND NOW... A WORD FROM OUR SPONSOR—SAFETY 3 (AWFOS—S3 THE GHS DIAMOND)

The National Fire Protection Association (NFPA) diamond discussed in AWFOS—S2 is most commonly used in the United States, but is rarely used in Europe and other countries where the Globally Harmonized System (GHS) diamond is more common. While it is not legally required to use the GHS or the NFPA labeling systems, it is required that chemical containers do have some form of hazard identification on them that comply with the HazCom 2012 standards developed by the Occupation Safety and Health Administration (OSHA) (<https://www.osha.gov/law-regs.html>). Because countries in Europe and other countries use the GHS labeling system, this AWFOS—S outlines the GHS system that makes the import and export of chemicals easier and safer. The GHS system uses three categories of hazards rather than four like NFPA uses. The three different categories are flammables, health hazards, and environmental hazards and uses nine different pictograms, as shown in Figure 3-10. These pictograms are placed on containers to identify the hazard of the chemical being stored in the container. The Web site *Process Safety Across the Chemical Engineering Curriculum* (<http://umich.edu/~safeche/nfpa.html>) gives an excellent discussion along with many examples for each of the nine diamonds. We should note however that there are variations of the pictograms and the rules of when to use what variation of the labels can be found on pages 38–42 of the PDF document found on the Web site <https://www.osha.gov/dsg/hazcom/ghsguideoct05.pdf>.

GHS Pictograms and Hazards










 <p>Health Hazard</p> <ul style="list-style-type: none"> ◆ Carcinogen ◆ Mutagenicity ◆ Respiratory Sensitizer ◆ Reproductive Toxicity ◆ Target Organ Toxicity ◆ Aspiration Toxicity 	 <p>Flame</p> <ul style="list-style-type: none"> ◆ Flammables ◆ Pyrophorics ◆ Self-Heating ◆ Emits Flammable Gas ◆ Self-Reactives ◆ Organic Peroxides ◆ Desensitized Explosives 	 <p>Exclamation Mark</p> <ul style="list-style-type: none"> ◆ Irritant (skin and eye) ◆ Skin Sensitizer ◆ Acute Toxicity (harmful) ◆ Narcotic Effects ◆ Respiratory Tract Irritant ◆ Hazardous to Ozone Layer (nonmandatory)
 <p>Gas Cylinder</p> <ul style="list-style-type: none"> ◆ Gases Under Pressure 	 <p>Corrosion</p> <ul style="list-style-type: none"> ◆ Skin Corrosion/Burns ◆ Eye Damage ◆ Corrosive to Metals 	 <p>Explosive Bomb</p> <ul style="list-style-type: none"> ◆ Explosives ◆ Self-Reactives ◆ Organic Peroxides
 <p>Flame Over Circle</p> <ul style="list-style-type: none"> ◆ Oxidizing Gases, Liquids, and Solids 	 <p>Skull and Crossbones</p> <ul style="list-style-type: none"> ◆ Acute Toxicity (fatal or toxic) 	 <p>Environment (nonmandatory)</p> <ul style="list-style-type: none"> ◆ Aquatic Toxicity

Figure 3-10 Pictograms from the GHS Labeling.[†]

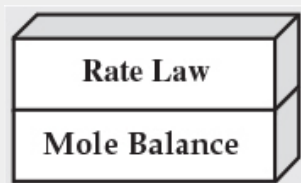
[†]Courtesy of American Chemical Society Eighth Edition of *Safety in Academic Chemistry Laboratories: Best Practices for First- and Second-Year University Students*, ACS, 1155 Sixteenth Street NW, Washington, DC 20036.

Many companies in the United States are changing from the NFPA labeling system to the GHS system (Figure 3-11).



Figure 3-11 The GHS in action. (Photo by fotosommer, Panther Media GmbH/Alamy Stock Photo) (<https://www.bradyid.com/applications/ghs-labeling-requirements>)[†]

Closure. Having completed this chapter, you should be able to write the rate law in terms of concentration and the Arrhenius temperature dependence. We have now completed the first two basic building blocks in our algorithm to study isothermal chemical reactions and reactors.



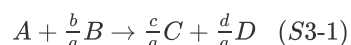
In Chapter 4, we focus on the third building block, **stoichiometry**, as we use the stoichiometric table to write the concentrations in terms of conversion to finally arrive at a relationship between the rate of reaction and conversion.

The CRE Algorithm

- Mole Balance, Ch 1
- Rate Law, Ch 3
- Stoichiometry, Ch 4
- Combine, Ch 5
- Evaluate, Ch 5
- Energy Balance, Ch 11

SUMMARY

1. Relative rates of reaction for the generic reaction:

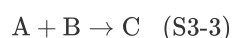


The relative rates of reaction can be written either as

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d} \quad \text{or} \quad \frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d} \quad (S3-2)$$

[†]Courtesy of American Chemical Society Eighth Edition of *Safety in Academic Chemistry Laboratories: Best Practices for First- and Second-Year University Students*, ACS, 1155 Sixteenth Street NW, Washington, DC 20036.

2. Reaction order is determined from experimental observation:



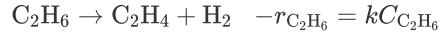
$$-r_A = kC_A^\alpha C_B^\beta$$

The reaction in Equation (S3-3) is α order with respect to species A and β order with respect to species B, whereas the overall order, n , is $(\alpha + \beta)$. If $\alpha = 1$ and $\beta = 2$, we would say that the reaction is first order with respect to A, second order with respect to B, and overall third order. We say a reaction follows an elementary rate law if the reaction orders agree with the stoichiometric coefficients for the reaction as written.

Examples of reactions that follow an elementary rate law:

Irreversible reactions

First order

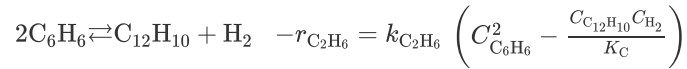


Second order



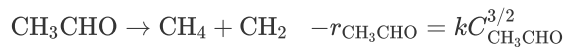
Reversible reactions

Second order

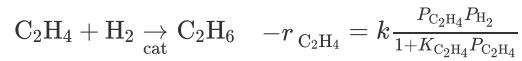


Examples of reactions that follow nonelementary rate laws:

Homogeneous



Heterogeneous reactions



3. The temperature dependence of a specific reaction rate is given by the *Arrhenius equation*

$$k = Ae^{-E/RT} \quad (\text{S3-4})$$

where A is the frequency factor and E the activation energy.

If we know the specific reaction rate, k , at a temperature, T_0 , and the activation energy, we can find k at any temperature, T

$$k(T) = k(T_0) \exp \left[\frac{E}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right] \quad (\text{S3-5})$$

Co The rate increases with increasing reactant concentrations,
nc
ept
1

Co The rate is related to the potential barrier height and to the
nc conversion of translational energy into potential energy, and
ept
2

Co The rate increases as the fraction of collisions that have

nc sufficient energy to cross over the barrier and form products
 ept increases.
 3

Similarly from Appendix C, Equation (C-9), if we know the partial pressure equilibrium constant K_P at a temperature, T_1 , and the heat of reaction, we can find the equilibrium constant at any other temperature

$$K_P(T) = K_P(T_1) \exp \left[\frac{\Delta H_{\text{Rx}}^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (\text{C-9})$$

CRE WEB SITE MATERIALS

(<http://www.umich.edu/~elements/6e/04chap/obj.html#/>)

Useful Links

Living
Example
Problems

Extra Help

Additional
Materials

Professional
Reference
Shelf

YouTube
Videos

Evaluation

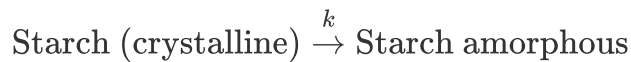
Self Tests

i>Clicker
Questions

Web Module

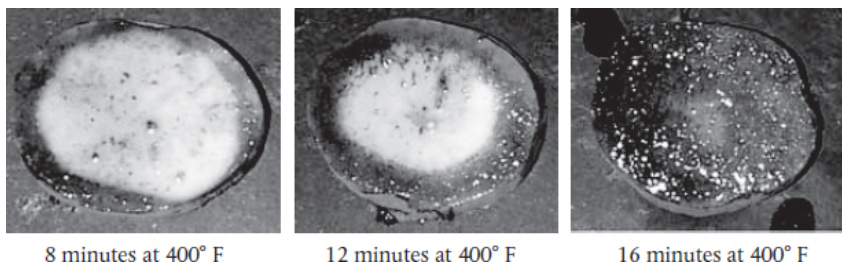
A. Chemical reaction engineering is applied to cooking a potato

(http://www.umich.edu/~elements/6e/web_mod/potato/index.htm)



with

$$k = Ae^{-E/RT}$$



• Professional Reference Shelf

(<http://umich.edu/~elements/6e/03chap/prof.html>)

R3.1 Collision Theory

(<http://umich.edu/~elements/6e/03chap/prof-collision.html>)

In this section, the fundamentals of collision theory are applied to the reaction

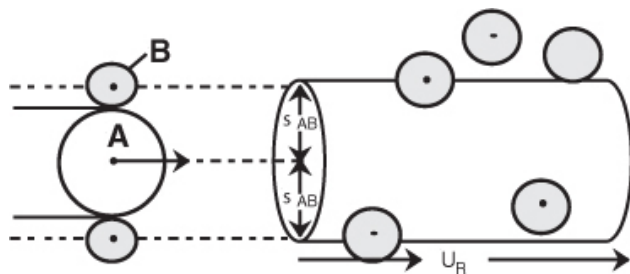
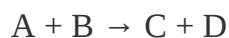


Figure R3.1 Schematic of collision cross section.

to arrive at the following rate law

$$-r_A = \pi \sigma_{AB}^2 \left(\frac{8\pi k_B T}{\mu \pi} \right)^{1/2} N_{Av} e^{-E_A/RT} C_A C_B = A e^{-E_A/RT} C_A C_B$$

The activation energy, E_A , can be estimated from the Polanyi equation

$$E_A = E_A^0 + \gamma_P \Delta H_{Rx}$$

R3.2 Transition-State Theory

(<http://umich.edu/~elements/6e/03chap/prof-transition.html>)

In this section, the rate law and rate-law parameters are derived for the reaction



using transition-state theory. Figure R3.2 shows the energy of the molecules along the reaction coordinate, which measures the progress of the reaction.

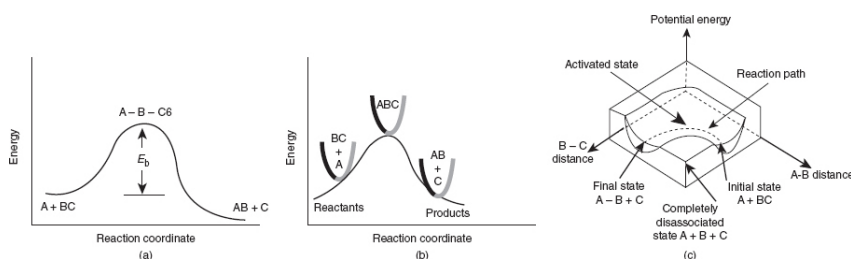


Figure R3.2 Reaction coordinate for (a) S_N2 reaction, and (b) generalized reaction. (c) 3-D energy surface for generalized reaction.

R3.3 Molecular Dynamics Simulations

(<http://umich.edu/~elements/6e/03chap/prof-moldyn.html>)

The reaction trajectories are calculated to determine the reaction cross section of the reacting molecules. These trajectories, which are identified as either (1) nonreactive or (2) reactive, are shown in Figure 3-7. The reaction probability is found by counting up the number of reactive trajectories after Karplus.[†] Professor Karplus received the 2013 Nobel Prize for his work on Molecular Dynamic Simulations.

QUESTIONS, SIMULATIONS, AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$A = \bullet \quad B = \blacksquare \quad C = \blacklozenge \quad D = \blacklozenge\blacklozenge$$




Questions

Q3-1_A QBR (*Question Before Reading*). How do you think the rate of reaction, $-r_A$, will depend on species concentrations and on temperature?

Q3-2_A i>clicker. Go to the Web site (http://www.umich.edu/~elements/6e/03chap/iclicker_ch3_q1.html) and view at least five i>clicker questions. Choose one that could be used as is, or a variation thereof, to be included on the next exam. You also could consider the opposite case: explain why the question should *not* be on the next exam. For either case, explain your reasoning.

[†] M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.*, 43 (9), 3259 (1965).

Q3-3_C (a) List the important concepts that you learned from this chapter. What concepts are you not clear about?

1. Explain the strategy to evaluate reactor design equations and how this chapter expands on **Chapter 2**.
2. The rate law for the reaction $(2A + B \rightarrow C)$ is $-r_A = k_A C_A^2 C_B$ with $k_A = 25 (\text{dm}^3/\text{mol})^2/\text{s}$. What are k_B and k_C ?
3. Listen to the audios  on the CRE Web site. Select a topic and explain it.
4. Which example on the CRE Web site's *Summary Notes* for Chapters 1 through 3 was most helpful?

Q3-4_A How would you rate the level importance of the GHS diamonds from 1 to 9 (9 being highest). For example,

is having the *gas cylinder* label more important than *exclamation mark*, if so, why? What are the GHS symbols for ethylene oxide?

Q3-5_A Go to the LearnChemE screencast link for Chapter 3 (<http://www.umich.edu/~elements/6e/03chap/learn-cheme-videos.html>).

1. View one of the screencast 5- to 6-minute video tutorials and list two of the most important points.
2. In Professor Andersen's video, what are the reaction orders wrt A and to B?

Q3-6_A AWFOS–S3 Could you, if possible, fit the various nine GHS diamonds into the four NFPA diamonds?

Q3-7_B It was a dark late August night with a full moon. Nevertheless, not fearing for my own safety as to what might be lurking, I took my voice recorder outside where I followed the sound to a nearby bush and made the following recording (<http://www.umich.edu/~elements/6e/03chap/summary-selftest1.html>).

1. What was the temperature to which I was exposed to? *Hint*: Problem P3-7_A may be of help or see *Big Bang Theory* episode for Sheldon Cooper's cricket analysis (https://www.youtube.com/watch?v=prafMmD_mx8).
2. The following government Web site (<https://www.loc.gov/rr/scitech/mysteries/cricket.html>) alludes to a correlation of chips and temperature. Can you derive that correlation using the Arrhenius Equation?

Computer Simulations and Experiments

P3-1_B (a) **LEP: Variation of Energy Distribution with Temperature.**

Wolfram and Python

1. Vary temperature, T , and activation energy, E , to learn their effects on energy distribution curve. Specifically, vary the parameters between their maximum and minimum values (i.e., high T , low E ; low T , low E ; high T , high E ; etc.) and write a few sentences describing what you find.

2. What should be the minimum temperature so that at least 50% molecules have energy greater than the activation energy you have chosen (e.g., 6 kcal/mol)?
3. After reviewing *Generating Ideas and Solutions* on the Web site ([http://www.umich.edu/~elements/6e/toc/SCPS,3rdEdBook\(Ch07\).pdf](http://www.umich.edu/~elements/6e/toc/SCPS,3rdEdBook(Ch07).pdf)). Choose one of the brainstorming techniques (e.g., lateral thinking) to suggest two questions that should be included in this problem.

(b) MATLAB Chemical Kinetics Simulations. Go to the Chapter 3 LEPs and choose *LEP-Mol-Sim.Zip* and carry out the following parameter variations. Before you run the simulation the first time, you will probably want to go through the tutorial.

1. For $k_f = k_r = 1.0$ Run the simulation when the number of A and B are
 1. A = 20 B = 20 C = D = 0
 2. A = 200 B = 200 C = D = 0
 3. A = 2,000 B = 2,000 C = D = 0
 4. A = 200 B = 2,000 C = D = 0

Is there any effect of the experiments (a)–(d) on the equilibrium concentration? What about the time taken to attain equilibrium? What conclusions do you draw from your experiments?

2. For 100 A molecules and 100 B molecules, vary the specific reaction–rate constants k_f and k_r and describe the differences in trajectories you observe.
3. What happens when you set either k_f or k_r to zero?
4. Why are there fluctuations in the concentration trajectories? Why are they not smooth? What causes the size of the fluctuations to increase or decrease?
5. What do you observe when you increase the initial number of molecules? Can you explain your observations?
6. Do the reactions stop once equilibrium is reached?
7. Write a conclusion on what you found in experiments (i)–(vi).

Problems

P3-2_B Exploring the Example Problems.

1. **Example 3-1. Activation Energy.** In the Excel spreadsheet, replace the value of k at 312.5 K with $k = 0.0009^{-1}\text{s}$ and determine the new values of E and k .
2. **Example 3-1.** Make a plot of k versus T and $\ln k$ versus $(1/T)$ for $E = 240$ kJ/mol and for $E = 60$ kJ/mol. (1) Write a couple of sentences describing what you find. (2) Next, write a paragraph describing the activation energy and how it affects chemical reaction rates, and what its origins are.

3. **Collision Theory**—*Professional Reference Shelf*. Make an outline of the steps that were used to derive

$$-r_A = Ae^{-E/RT} C_A C_B$$

P3-3_B OEQ (Old Exam Question). Molecular collision energies—refer to Figure 3-4 and to the Wolfram and Python LEP 3-1. cdf *Variation of Energy Distribution with Temperature*.

1. What fraction of molecular collisions have energies less than or equal to 2.5 kcal at 300 K? At 500 K?
2. What fraction of molecular collisions have energies between 3 and 4 kcal/mol at $T = 300$ K? At $T = 500$ K?
3. What fraction of molecular collisions have energies greater than the activation energy $E_A = 25$ kcal at $T = 300$ K? At $T = 500$ K?

P3-4_B

1. Use Figure 3-1(b) to sketch the trajectory over the saddle point when the BC and AB molecules vibrate with the minimum separation distance being 0.20 Angstroms and the maximum separation being 0.4 Angstroms.
2. At point Y, $R_{AB} = 2.8$ Angstroms, sketch the potential energy as a function of the distance R_{BC} noting the minimum at valley floor.
3. At Point X, $R_{BC} = 2.8$ Angstroms, sketch the potential energy as a function of R_{AB} noting the minimum on the valley floor.

P3-5_B Use Equation (3-20) to make a plot of $f(E, T)$ as a function of E for $T = 300, 500, 800,$ and 1200 K.

1. What is the fraction of molecules that have sufficient energy to pass over a energy barrier of 25 kcal at 300, 500, 800, and 1200 K?
2. For a temperature of 300 K, what is the ratio of the fraction of energies between 15 and 25 kcal to that for the same energy range (15–25 kcal) at 1200 K?
3. Make a plot of $F(E > E_A, T)$ as a function of (E_A/RT) for $(E_A/RT) > 3$. What is the fraction of collisions that have energies greater than 25 kcal/mole at 700 K?
4. What fraction of molecules have energies greater than 15 kcal/mol at 500 K?
5. Construct a plot of $F(E > E_A, T)$ versus T for $E_A = 3, 10, 25,$ and 40 kcal/mole. Describe what you find. *Hint:* Recall the range of validity for T in Equation (3-23).

P3-6_A OEQ (Old Exam Question). The following figures show the energy distribution function at 300 K for the

reaction $A + B \rightarrow C$.

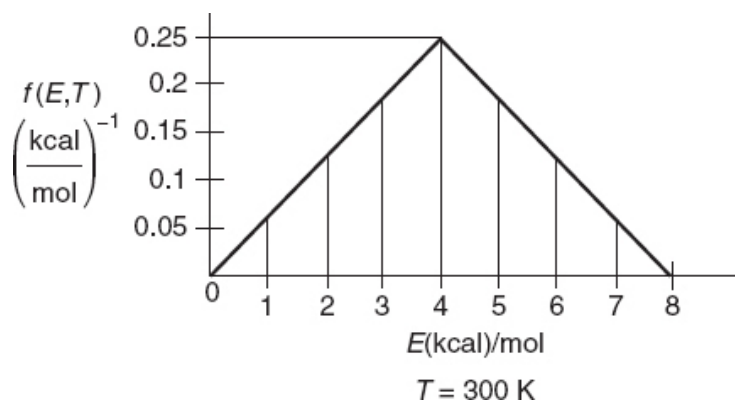


Figure P3-6(a)

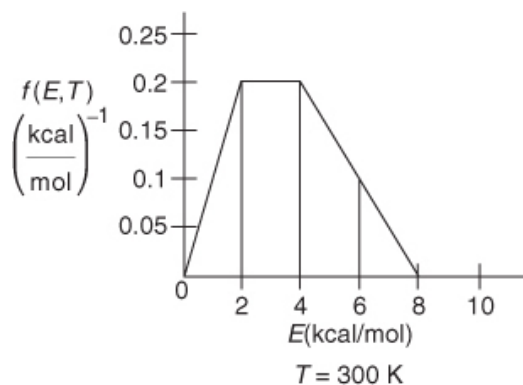


Figure P3-6(b)

For each figure, determine the following:

1. What fraction of the collisions have energies between 3 and 5 kcal/mol?
2. What fraction of collisions have energies greater than 5 kcal/mol? (**Ans:** Figure P3-6 (b) fraction = 0.28)
3. What is the fraction with energies greater than 0 kcal/mol?
4. What is the fraction with energies 8 kcal/mol or greater?
5. If the activation energy for Figure P3-6(b) is 8 kcal/mol, what fraction of molecules have an energy greater than E_A ?
6. Guess what (sketch) the shape of the curve $f(E, T)$ versus E shown in Figure P3-6(b) would look like if the temperature were increased to 400 K. (Remember: $\int_0^\infty f(E, T) dE = 1$.)

P3-7_A The frequency of fireflies flashing and the frequency of crickets chirping as a function of temperature follow.
Source: Keith J. Laidler, "Unconventional

applications of the Arrhenius law.” *J. Chem. Educ.*, 5, 343 (1972). Copyright (c) 1972, American Chemical Society. Reprinted by permission.



For fireflies:				For crickets:			
$T (^{\circ}\text{C})$	21.0	25.00	30.0	$T (^{\circ}\text{C})$	14.2	20.3	27.0
Flashes/min	9.0	12.16	16.2	Chirps/min	80	126	200

The running speed of ants and the flight speed of honeybees as a function of temperature are given below. Source: B. Heinrich, *The Hot-Blooded Insects*, Cambridge, MA: Harvard University Press, 1993.

For ants:					For honeybees:				
$T (^{\circ}\text{C})$	10	20	30	38	$T (^{\circ}\text{C})$	25	30	35	40
V (cm/s)	0.5	2	3.4	6.5	V (cm/s)	0.7	1.8	3	?

1. What do the firefly and cricket have in common? What are their differences?
2. What is the velocity of the honeybee at 40°C ? At -5°C ?
3. Nicolas wants to know if the bees, ants, crickets, and fireflies have anything in common. If so, what is it? You may also do a pair-wise comparison.
4. Would more data help clarify the relationships among frequency, speed, and temperature? If so, in what temperature should the data be obtained?

Pick an insect, and explain how you would carry out the experiment to obtain more data. For an alternative to this problem, see CDP3-A_B.

5. Data on the tenebrionid beetle whose body mass is 3.3 g show that it can push a 35-g ball of dung at 6.5 cm/s at 27°C, 13 cm/s at 37°C, and 18 cm/s at 40°C.

1. How fast can it push dung at 41.5° C? Source: B. Heinrich. *The Hot-Blooded Insects*, Cambridge, MA: Harvard University Press, 1993. (**Ans:** 19.2 cm/s at 41.5°C)



2. Use <http://www.umich.edu/~scps/html/probsolv/strategy/cteq.htm> to write three critical thinking questions and three creative questions.

P3-8_B OEQ (Old Exam Question). Troubleshooting.

Corrosion of high-nickel stainless steel plates was found to occur in a distillation column used at DuPont to separate HCN and water. Sulfuric acid is always added at the top of the column to prevent polymerization of HCN. Water collects at the bottom of the column and HCN collects at the top. The amount of corrosion on each tray is shown in Figure P3-8_B as a function of plate location in the column.

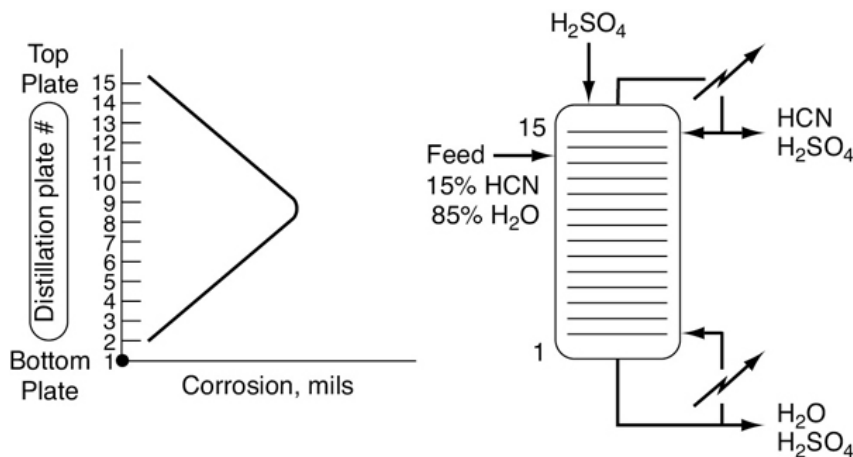


Figure P3-8_B Corrosion in a distillation column.



The bottommost temperature of the column is approximately 125°C and the topmost is 100°C. The corrosion rate is a function of temperature and the concentration of an HCN–H₂SO₄ complex.

1. Suggest an explanation for the observed corrosion-plate profile in the column. What effect would the column operating conditions have on the corrosion-plate profile?
2. Identify the components of the GHS diagram that you could apply to this problem.

P3-9_B Inspector Sgt. Ambercromby of Scotland Yard. It is believed, although never proven, that Bonnie murdered her first husband, Lefty, by poisoning the tepid brandy they drank together on their first anniversary. Lefty was unaware she had coated her glass with an antidote before she filled both glasses with the poisoned brandy. Bonnie married her second husband, Clyde, and some years later when she had tired of him, she called him one day to tell him of her new promotion at work and to suggest that they celebrate with a glass of brandy that evening. She had the fatal end in mind for Clyde. However, Clyde

suggested that instead of brandy, they celebrate with ice-cold Russian vodka and down it Cossack style, in one gulp. She agreed and decided to follow her previously successful plan and to put the poison in the vodka and the antidote in her glass. The next day, both were found dead. Sgt. Ambercromby arrives

#Seriously? What are the first three questions he asks? What are two possible explanations? Based on what you learned from this chapter, what do you feel Sgt. Ambercromby suggested as the most logical explanation?



Who done it?

Source: Professor Flavio Marin Flores, ITESM, Monterrey, Mexico. *Hint:* View the YouTube video (www.youtube.com) made by the chemical reaction engineering students at the University of Alabama, titled *The Black Widow*. You can access it from the CRE Web site (www.umich.edu/~elements/6e) using the YouTube Videos link under *By Concepts* on the CRE home page.

P3-10_B Activation Energy

1. The rule of thumb that the rate of reaction doubles for a 10°C increase in temperature occurs only at a specific temperature for a given activation energy. Develop a relationship between the temperature and activation energy for which the rule of thumb holds. Neglect any variations in concentrations. For $E_A = 50 \text{ kcal/mol}$, over what temperature range ($T_2 = T_1 + 10^\circ\text{C}$) is this rule of thumb valid?



- Write a paragraph explaining activation energy, E , and how it affects the chemical reaction rate. Refer to [Section 3.3](#) and especially the *Professional Reference Shelf Sections R3.1, R3.2, and R3.3* if necessary.

P3-11C The initial reaction rate for the elementary reaction



was measured as a function of temperature when the concentration of A was 2 M and that of B was 1.5 M.

$-r_A(\text{mol/dm}^3 \cdot \text{s}):$	0.002	0.046	0.72	8.33
---	-------	-------	------	------

$T(\text{K}):$	300	320	340	360
----------------	-----	-----	-----	-----

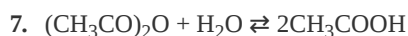
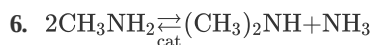
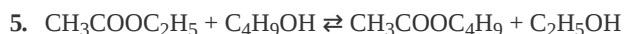
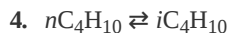
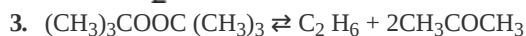
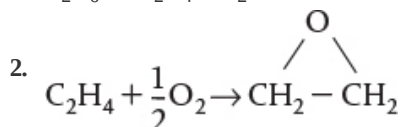
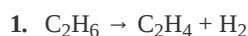
- What is the activation energy?
- What is the frequency factor?
- What is the rate constant as a function of temperature using Equation (S3-5) and $T_0 = 27^\circ\text{C}$ as the base case?

P3-12B Determine the rate law for the reaction described in each of the cases below involving species A, B, and C. The rate laws should be elementary as written for reactions that are either of the form $A \rightarrow B$ or $A + B \rightarrow C$.

- The units of the specific reaction rate are $k = \left[\frac{\text{dm}^3}{\text{mol} \cdot \text{h}} \right]$: Rate Law

- The units of the specific reaction rate are $k = \left[\frac{\text{mol}}{\text{kg-cat} \cdot \text{h} (\text{atm})^2} \right]$: Rate Law _____
- The units of the specific reaction rate are $k = \left[\frac{1}{\text{h}} \right]$: Rate Law _____
- The units of a nonelementary reaction rate are $k = \left[\frac{\text{mol}}{\text{dm}^3 \cdot \text{h}} \right]$: Rate Law _____

P3-13_A (a) Write the rate law for the following reactions assuming each reaction follows an elementary rate law. Give the units of k_A for each, keeping in mind some are homogeneous and some reactants are heterogeneous.



P3-14_A

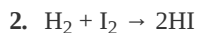
1. **OEQ** (Old Exam Questions). Write the rate law for the reaction



if the reaction

- is second order in B and overall third order, $-r_A = \underline{\hspace{2cm}}$
- is zero order in A and first order in B, $-r_A = \underline{\hspace{2cm}}$
- is zero order in both A and B, $-r_A = \underline{\hspace{2cm}}$
- is first order in A and overall zero order, $-r_A = \underline{\hspace{2cm}}$

2. Find and write the rate laws for the following reactions:



Hint: See Chapter 9 Learning Resources: A. Hydrogen Bromide.

P3-15_B The rate laws for each of the reactions listed below were obtained at low temperatures. The reactions are highly exothermic and therefore reversible at high

temperatures. Suggest a rate law for each of the reactions [(a), (b), and (c)] at high temperatures, which may or may not be elementary.

1. The reaction



is irreversible at low temperatures and the rate law is

$$-r_A = kC_A$$

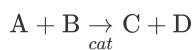
2. The reaction



is irreversible at low temperatures and the rate law is

$$-r_A = kC_A^{1/2} C_B$$

3. The gas–solid catalyzed reaction



is irreversible at low temperatures and the rate law is

$$-r_A = \frac{kP_A P_B}{1 + K_A P_A + K_B P_B}$$

In each case, make sure that the rate laws at high temperatures are thermodynamically consistent at equilibrium (cf. Appendix C).

P3-16_B Solar Chemical Energy Storage. The major ways to utilize, capture, or store the sun's energy are solar thermal (see Problem P8-16_B), solar voltaic, biomass conversion, solar water splitting (Problem P10-13_B), and solar chemical. *Solar chemical* refers to processes that harness and store solar energy by adsorbing light in a reversible chemical reaction; see http://en.wikipedia.org/wiki/Solar_chemical. For example, the photodimerization of anthracene absorbs and stores solar energy that can be released when the reverse reaction takes place.

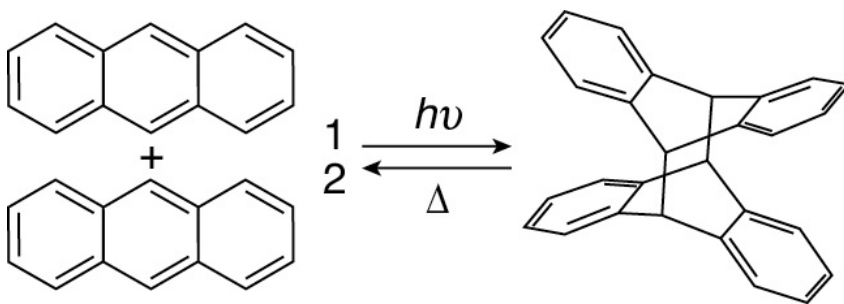


Figure P3-16.1 Anthracene dimerization.

Another reaction of interest is the Norbornadiene–Quadricyclane (NQ) couple, where solar energy is adsorbed and stored in one direction and released in the other.

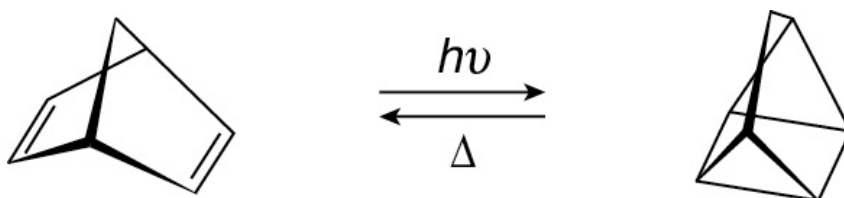


Figure P3-16.2 The Norbornadiene–Quadricyclane (NQ) couple is of potential interest for sunlight energy storage.

1. Suggest a rate law for the reversible photodimerization of anthracene.
2. Suggest a rate law for the reversible storage of energy by the NQ couple.

SUPPLEMENTARY READING

1. Two references relating to the discussion of activation energy have already been cited in this chapter. Activation energy is usually discussed in terms of either collision theory or transition-state theory. A concise and readable account of these two theories may or may not be found in

THORNTON W. BURGESS, *The Adventures of Reddy Fox*.

New York: Dover Publications, Inc., 1913.

K. J. LAIDLER, *Chemical Kinetics*. New York: Harper & Row, 1987, Chap. 3.

R. MASEL, *Chemical Kinetics and Catalysis*. New York: Wiley, 2001, p. 594.

2. Prof. Dr. Sven Köttlov of Jofostan University has pointed out that in addition to the books listed above, the rate laws and activation energies can be found in NBS circulars, such as those shown below [Table 3-1](#) on pages 81–82. Also check chemistry literature, for example, *Journal of Physical Chemistry*. For more on molecular modeling, see <http://cache.org/teaching-resources-center/molecular-modeling>.

4. Stoichiometry

If you are thinking about someone while reading this book, you are most definitely in love.

—Tim Newberger Undergraduate ChE Student
W2013

Overview. In Chapter 2, we carried out the sizing and sequencing of flow reactors given the reaction rate, $-r_A$, as a function of conversion X . To find $-r_A = f(X)$ is a two-step process. In Chapter 3, we described (Step 1) how the rate of reaction, $-r_A$, is related to concentration and temperature, that is, $-r_A = [k_A(T)\text{fn}(C_A, C_B \dots)]$. In this chapter, we show how concentration can be related to conversion (Step 2), $C_i = g(X)$, and once we do that, we will have $-r_A = f(X)$ and can design a multitude of reaction systems. We will use stoichiometric tables, along with the definitions of concentration, to find the concentration as a function of conversion.

Batch	Flow
$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V}$	$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v}$
\downarrow	$\swarrow \searrow$
$V = V_0$	Liquid, $v = v_0$ Gas, $v = v_0(1 + \epsilon X) \frac{P_0}{P} \frac{T}{T_0}$
$C_A = C_{A0}(1-X)$	\downarrow
	$C_A = C_{A0}(1-X)$ $C_A = C_{A0} \frac{(1-X)}{(1 + \epsilon X)} \frac{P}{P_0} \frac{T_0}{T}$

- For batch systems the reactor is most always rigid, so $V = V_0$, and one then uses the stoichiometric table to express concentration as a function of conversion: $C_A = N_A/V_0 = C_{A0}(1-X)$.
- For liquid-phase flow systems, the volumetric flow rate is considered to be constant, $v = v_0$, and $C_A = (F_{A0}/v_0)(1-X) = C_{A0}(1-X)$.
- For gas-phase flow systems, the process becomes more complicated, as the volumetric flow rate for gases can vary with conversion, temperature, and pressure, and we need to develop the relationship relating v and X , that is, $v = v_0(1 + \epsilon X)(P_0/P)(T/T_0)$ and thus

$$C_A = \frac{C_{A0}(1-X)}{(1 + \epsilon X)} \frac{P}{P_0} \frac{T_0}{T} = C_{A0} \frac{(1-X)}{(1 + \epsilon X)} \frac{T_0}{T}$$

- For most gas–solid catalyst reactions, the rate laws are typically written in terms of partial pressures, which can also be written in terms of conversion.

$$P_A = C_A RT = P_{A0} \frac{(1-X)}{(1+\varepsilon X)} \frac{P}{P_0} = P_{A0} \frac{(1-X)}{(1+\varepsilon X)} p$$

After completing this chapter, you will be able to write the rate of reaction as a function of conversion and calculate the equilibrium conversion for both batch and flow reactors.

Now that we have shown how the rate law can be expressed as a function of concentrations, we need only express concentration as a function of conversion and sequence in order to carry out calculations similar to those presented in [Chapter 2](#) to size reactors. If the rate law depends on more than one species, we must relate the concentrations of the different species to each other. This relationship is most easily established with the aid of a stoichiometric table. This table presents the stoichiometric relationships between reacting molecules for single reactions. That is, it tells us how many molecules of one species will be formed during a chemical reaction when a given number of molecules of another species disappears. These relationships will be developed for the general reaction

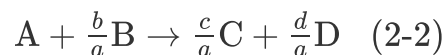


Recall that we have already used stoichiometry to relate the *relative rates of reaction* for Equation (2-1):

$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d} \quad (3-1)$$

This stoichiometric relationship relating reaction rates will be used in [Chapters 6 and 8](#).

In formulating our stoichiometric table, we shall take **species A as our basis of calculation** (i.e., the limiting reactant) and then divide through by the stoichiometric coefficient of A



in order to put everything on a basis of “*per mole of A.*”

Next, we develop the stoichiometric relationships for reacting species that give the change in the number of moles of each species (i.e., A, B, C, and D).

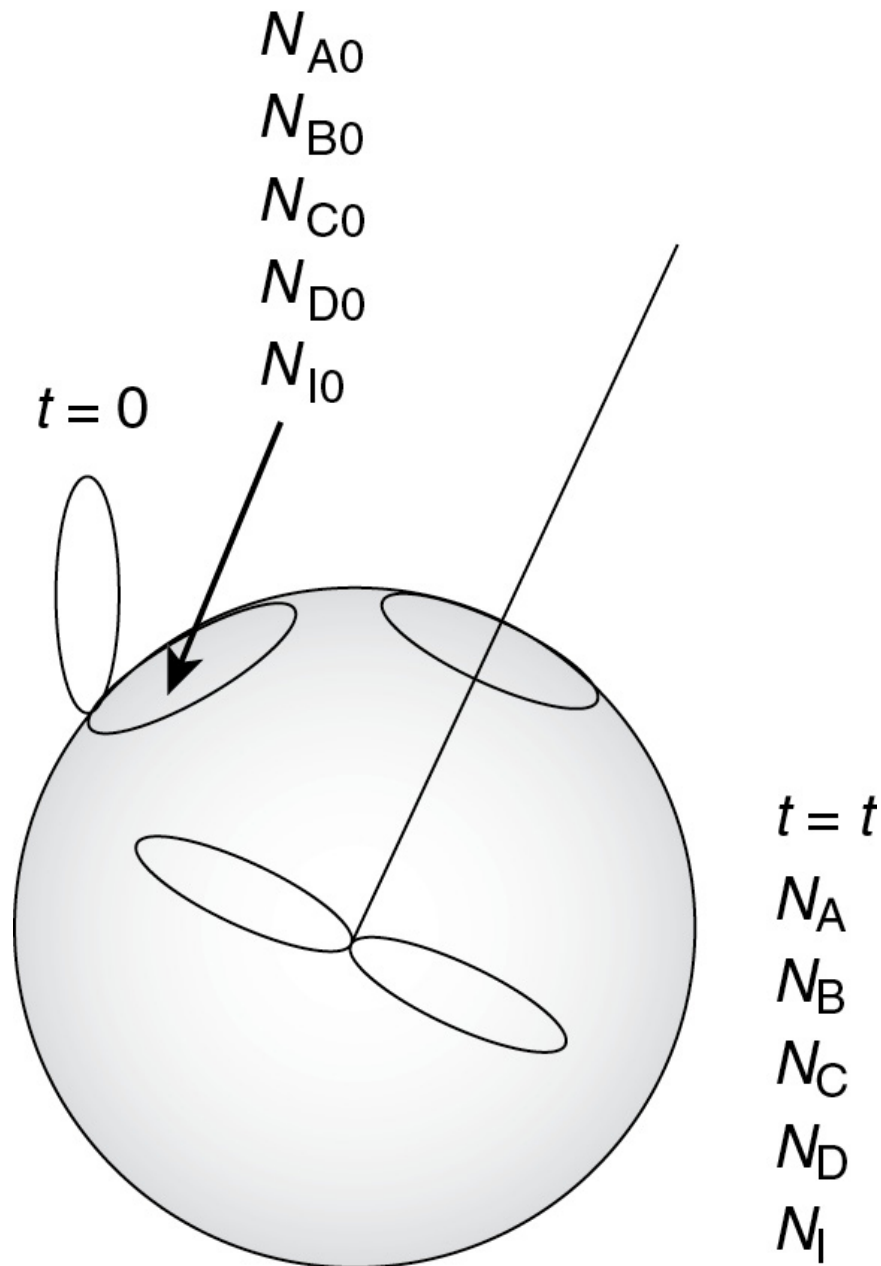


Figure 4-1 Batch reactor. (Schematic with special permission by Renwahr.)

(<http://encyclopedia.che.engin.umich.edu/Pages/Reactors/Batch/Batch.html>)

4.1 BATCH REACTORS (BRS)

Batch reactors (BRs) are primarily used for the production of specialty chemicals and to obtain reaction rate data in order to determine reaction-rate laws and rate-law parameters such as k , the specific reaction rate.

Figure 4-1 shows a starving artist’s rendition of a batch system in which we will carry out the reaction given by Equation (2-2). At time $t = 0$, we will open the reactor and place a number of moles of species A, B, C, and D, and inerts I (N_{A0} , N_{B0} , N_{C0} , N_{D0} , and N_{I0} , respectively) into the reactor and then of course close the port hole.

Species A is our basis of calculation, and N_{A0} is the number of moles of A initially present in the reactor. After a time t , $N_{A0}X$ moles of A are consumed in the system as a result of the chemical reaction, leaving $(N_{A0} - N_{A0}X)$ moles of A in the system. That is, the number of moles of A remaining in the reactor after a conversion X has been achieved is

$$N_A = N_{A0} - N_{A0}X = N_{A0}(1 - X)$$

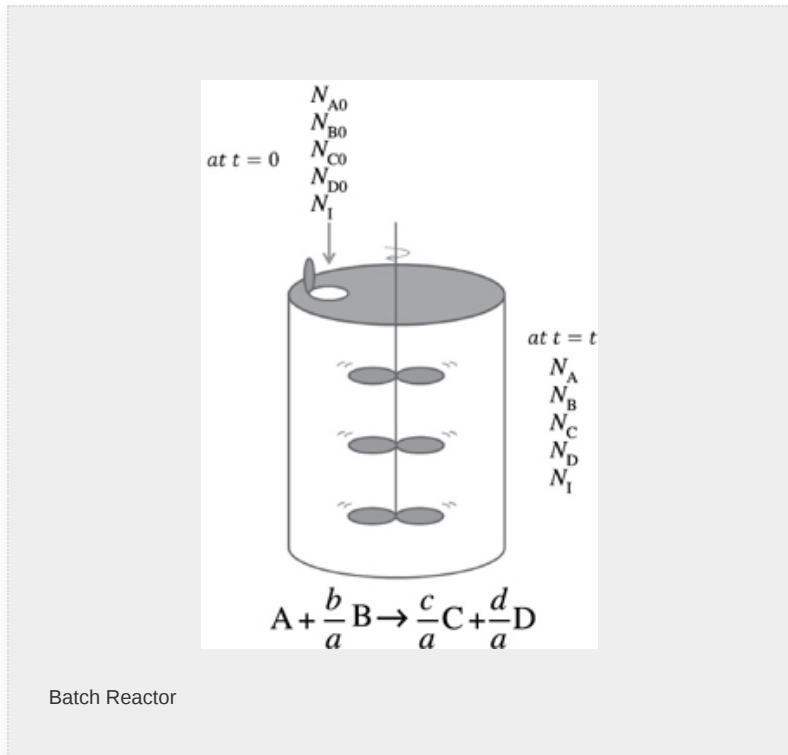
We now will use conversion in a similar fashion to express the number of moles of B, C, and D in terms of conversion.

To determine the number of moles of each species remaining after $N_{A0}X$ moles of A have reacted, we form the stoichiometric table (Table 4-1). This stoichiometric table presents the following information:

TABLE 4-1 STOICHIOMETRIC TABLE FOR A BATCH SYSTEM

<i>Species</i> <i>Initially (mol)</i> <i>Change (mol)</i> <i>Remaining (mol)</i>			
A	N_A	$-(N_{A0}X)$	$N_A = N_A N_{A0} - N_{A0}X$

	N_0		
B	N_B	$-\frac{b}{a}(N_{A0}X)$	$N_B = N_{B0} - \frac{b}{a}N_{A0}X$
	0		
C	N_C	$\frac{c}{a}(N_{A0}X)$	$N_C = N_{C0} + \frac{c}{a}N_{A0}X$
	0		
D	N_D	$\frac{d}{a}(N_{A0}X)$	$N_D = N_{D0} + \frac{d}{a}N_{A0}X$
	0		
I (inerts)	N_{I0}	$-$	$N_I = N_{I0}$
Totals	N_T		$N_T = N_{T0} + \underbrace{\left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)}_{\delta} N_{A0}X$
	0		



Column 1: the species in the reaction

Column 2: the number of moles of each species initially present

Column 3: the change in the number of moles brought about by reaction

Column 4: the number of moles remaining in the system at time t

Components of the stoichiometric table

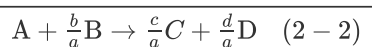
To calculate the number of moles of species B remaining at time t , we recall that at time t the number of moles of A that have reacted is $N_{A0}X$. For every mole of A that reacts, b/a moles of B must react; therefore, the total number of moles of B that have reacted is

$$\begin{aligned}\text{Moles B reacted} &= \frac{\text{Moles B reacted}}{\text{Moles A reacted}} \cdot \text{Moles A reacted} \\ &= \frac{b}{a}(N_{A0}X)\end{aligned}$$

Because B is disappearing from the system, the sign of the “change” is negative. N_{B0} is the number of moles of B initially in the system. Therefore, the number of moles of B remaining in the system, N_B , at a time t , is the number of moles of B initially minus the moles of B that have reacted and is given in the last column of Table 4-1 as

$$N_B = N_{B0} - \frac{b}{a}N_{A0}X$$

The complete stoichiometric table delineated in Table 4-1 is for all species in the general reaction



Let’s take a look at the totals in the last column of Table 4-1. The stoichiometric coefficients in parentheses

$(d/a + c/a - b/a - 1)$ represent the change in the total number of moles per mole of A reacted. Because this term occurs so often in our calculations, it is given the symbol δ :

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \quad (4-1)$$

The parameter δ

Definition of δ

$$\delta = \frac{\text{Change in the total number of moles}}{\text{Moles of A reacted}}$$

The total number of moles can now be calculated from the equation

$$N_T = N_{T0} + \delta(N_{A0}X)$$

We recall from Chapters 1 and 3 that the kinetic rate law (e.g., $-r_A = kC_A^2$) is a function solely of the intensive properties of the reacting system (e.g., temperature, pressure, concentration, and catalysts, if any). The reaction rate, $-r_A$, usually depends on the concentration of the reacting species raised to some power. Consequently, to determine the reaction rate as a function of conversion, X , we need to know the concentrations of the reacting species as a function of conversion, X . Let's do it!

We want $C_j = h_j(X)$

4.1.1 Batch Concentrations for the Generic Reaction, Equation (2-2)

The concentration of A is the number of moles of A per unit volume

$$C_A = \frac{N_A}{V}$$

Batch concentration

After writing similar equations for B, C, and D, we use the *stoichiometric table* to express the concentration of each component in terms of the conversion X :

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V} \quad (4-2)$$

$$C_B = \frac{N_B}{V} = \frac{N_{B0} - (b/a)N_{A0}X}{V} \quad (4-3)$$

$$C_C = \frac{N_C}{V} = \frac{N_{C0} + (c/a)N_{A0}X}{V} \quad (4-4)$$

$$C_D = \frac{N_D}{V} = \frac{N_{D0} + (d/a)N_{A0}X}{V} \quad (4-5)$$

Because almost all batch reactors are solid vessels, the reactor volume is constant, so we can take $V = V_0$, then

$$C_A = \frac{N_A}{V_0} = \frac{N_{A0}(1-X)}{V_0}$$

$$C_A = C_{A0}(1-X) \quad (4-6)$$

Constant Volume, $V = V_0$

We will soon see that Equation (4-6) for constant-volume batch reactors also applies to continuous-flow *liquid-phase* systems.

We further simplify these equations by defining the parameter Θ_i , which allows us to factor out N_{A0} in each of the expressions for concentration

$$\Theta_i = \frac{N_{i0}}{N_{A0}} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}},$$

$$\Theta_i = \frac{\text{Moles of species "i" initially}}{\text{Moles of species A initially}}$$

$$C_B = \frac{N_{A0}[N_{B0}/N_{A0} - (b/a)X]}{V_0} = \frac{N_{A0}[\Theta_B - (b/a)X]}{V_0}$$

$$C_B = C_{A0} \left(\Theta_B - \frac{b}{a}X \right) \quad (4-7)$$

$$\text{with } \Theta_B = \frac{N_{B0}}{N_{A0}}$$

Feed

Equalmolar:

$$\Theta_B = 1$$

Stoichiometric:

$$\Theta_B = \frac{b}{a}$$

for an equalmolar feed $\Theta_B = 1$ and for a stoichiometric feed $\Theta_B = b/a$.

Continuing for species C and D

$$C_C = \frac{N_{A0}[\Theta_C + (c/a)X]}{V_0}$$

$$C_C = C_{A0}\left(\Theta_C + \frac{c}{a}X\right) \quad (4-8)$$

$$\text{with } \Theta_C = \frac{N_{C0}}{N_{A0}}$$

Concentration for constant-volume batch reactors **and** for liquid-phase continuous-flow reactors

$$C_D = \frac{N_{A0}[\Theta_D + (d/a)X]}{V_0}$$

$$C_D = C_{A0}\left(\Theta_D + \frac{d}{a}X\right) \quad (4-9)$$

$$\text{with } \Theta_D = \frac{N_{D0}}{N_{A0}}$$

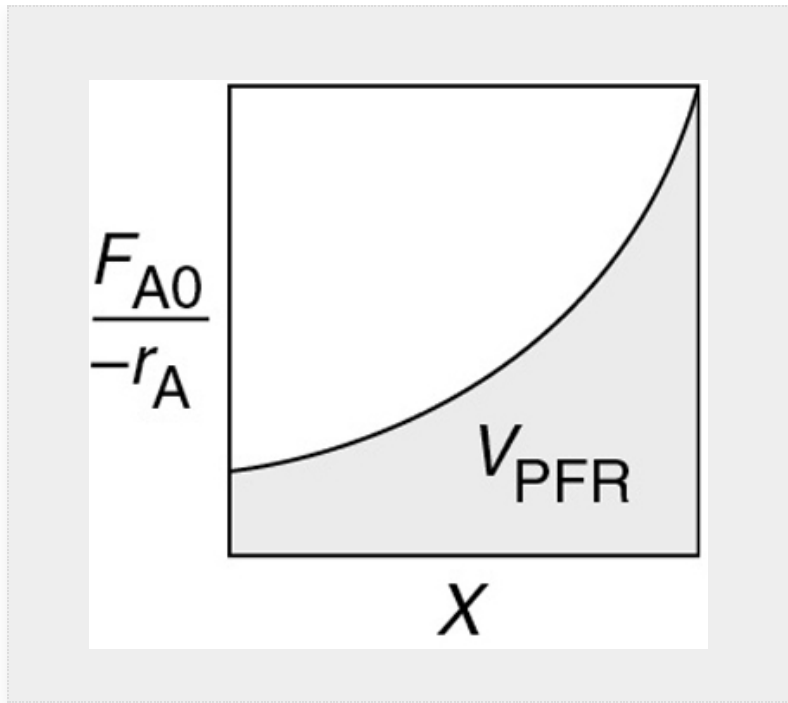
For constant-volume batch reactors, for example, steel containers $V = V_0$, we now have concentration as a function of conversion. If we know the rate law, we can now obtain $-r_A = f(X)$ to couple with the differential mole balance in terms of conversion in order to solve for the reaction time, t , to achieve a specified conversion, X .

For liquid-phase reactions taking place in solution, the solvent usually dominates the situation. For example, most liquid-phase organic reactions do not change density during the course of the reaction and represent still another case for which the constant-volume simplifications apply. As a result, changes in the density of the solute **do not** affect the overall density of the solution significantly and therefore it is essentially a constant-volume reaction process, $V = V_0$ and $v = v_0$. Consequently, Equations (4-6)–(4-9) can be used for liquid-phase reactions as well as constant-volume ($V = V_0$) gas-phase reactions. An important exception to this general rule exists for some polymerization processes.

For liquids $V = V_0$ and $v = v_0$

To summarize for constant-volume batch systems *and* for liquid-phase reactions, we can use a rate law for Reaction (2-2) such as $-r_A = k_A C_A C_B$ to obtain $= f(X)$; that is,

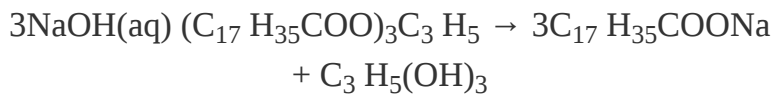
$$-r_A = k C_A C_B = k C_{A0}^2 (1 - X) \left(\Theta_B - \frac{b}{a} X \right) = f(X)$$



Substituting for the given parameters k , C_{A0} , and Θ_B , we can now use the techniques in [Chapter 2](#) to size the CSTRs and PFRs for liquid-phase reactions.

Example 4–1 Expressing $C_j = h_j(X)$ for a Liquid-Phase Batch Reaction

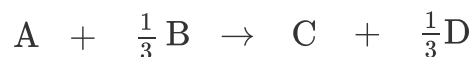
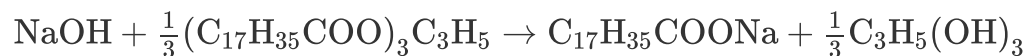
Soap is necessary to clean such things as dirty softball and soccer players' uniforms, dirty hands, and foul mouths. Soap consists of the sodium and potassium salts of various fatty acids, such as oleic, stearic, palmitic, lauric, and myristic acids. The saponification reaction for the formation of soap from aqueous caustic soda and glyceryl stearate is



Letting X represent the conversion of sodium hydroxide (the moles of sodium hydroxide reacted per mole of sodium hydroxide initially present), set up a stoichiometric table expressing the concentration of each species in terms of its initial concentration and the conversion, X .

Solution

Because we have taken sodium hydroxide as our basis of calculation, we divide through by the stoichiometric coefficient of sodium hydroxide to put the reaction expression in the form



Choosing a basis of calculation

We may next perform the calculations shown in Table E4-1.1. Because this reaction is a liquid-phase reaction, the density ρ is considered to be constant; therefore, $V = V_0$

$$C_A = \frac{N_A}{V} = \frac{N_A}{V_0} = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X)$$

$$\Theta_B = \frac{C_{B0}}{C_{A0}} \quad \Theta_C = \frac{C_{C0}}{C_{A0}} \quad \Theta_D = \frac{C_{D0}}{C_{A0}}$$

TABLE E4-1.1 STOICHIOMETRIC TABLE FOR LIQUID-PHASE SOAP REACTION

Species	Symbol	Initially	Change	Remaining	Concentration
NaOH	A	N_{A0}	$-N_{A0}X$	$N_{A0}(1-X)$	$C_{A0}(1-X)$
$(C_{17}H_{35}COO)_3C_3H_5$	B	N_B	$-\frac{1}{3}N_{A0}X$	$N_{A0}\left(\Theta_B - \frac{X}{3}\right)$	$C_{A0}\left(\Theta_B - \frac{X}{3}\right)$
$C_{17}H_{35}COONa$	C	N_C	$N_{A0}X$	$N_{A0}(\Theta_C + X)$	$C_{A0}(\Theta_C + X)$
$C_3H_5(OH)_3$	D	N_{D0}	$-\frac{1}{3}N_{A0}X$	$N_{A0}\left(\Theta_D + \frac{X}{3}\right)$	$C_{A0}\left(\Theta_D + \frac{X}{3}\right)$
Water (inert)	I	N_{I0}	—	N_{I0}	C_{I0}

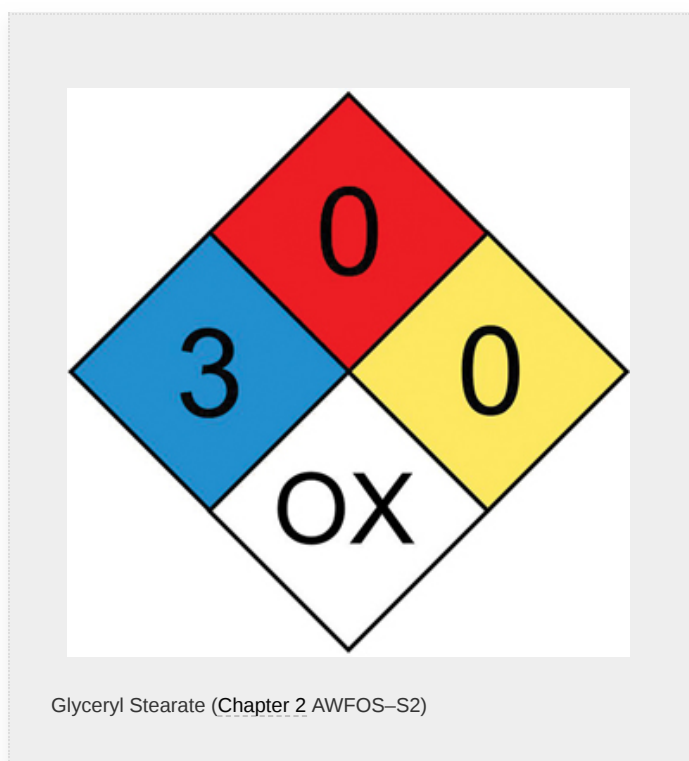
Totals	N_T	0	$N_T = N_{T0}$
	0		

Stoichiometric table (batch)

Analysis: The purpose of this example was to show how the generic reaction in Table 4-1 is applied to a real reaction and how to develop the corresponding stoichiometric table.

Example 4–2 What Is the Limiting Reactant?

Having set up the stoichiometric table in [Example 4-1](#), one can now readily use it to calculate the concentrations at a given conversion. If the initial mixture consists of sodium hydroxide at a concentration of 10 mol/dm^3 (i.e., 10 mol/L or 10 kmol/m^3) and glyceryl stearate at a concentration of 2 mol/dm^3 , what are the concentrations of glycerol stearate, B, and of glycerine, D, when the conversion of sodium hydroxide is **(a)** 20% and **(b)** 90%?



Solution

Only the reactants NaOH and $(\text{C}_{17} \text{H}_{35}\text{COO})_3\text{C}_3 \text{H}_5$ are initially present; therefore, $\Theta_C = \Theta_D = 0$.

1. For 20% conversion of NaOH

$$C_D = C_{A0} \left(\frac{X}{3} \right) = (10) \left(\frac{0.2}{3} \right) = 0.67 \text{ mol/L} = 0.67 \text{ mol/dm}^3$$

$$C_B = C_{A0} \left(\Theta_B - \frac{X}{3} \right) = 10 \left(\frac{2}{10} - \frac{0.2}{3} \right) = 10(0.133) = 1.33 \text{ mol/dm}^3$$

2. For 90% conversion of NaOH

$$C_D = C_{A0} \left(\frac{X}{3} \right) = 10 \left(\frac{0.9}{3} \right) = 3 \text{ mol/dm}^3$$

Let us find C_B

$$C_B = 10 \left(\frac{2}{10} - \frac{0.9}{3} \right) = 10(0.2 - 0.3) = -1 \text{ mol/dm}^3$$

Oops!! Negative concentration—impossible! What went wrong?

Analysis: We purposely chose the wrong basis of calculation to make the point that we **must** choose the limiting reactant as our basis of calculation!! Ninety-percent conversion of NaOH is not possible because glyceryl stearate is the limiting reactant and is used up before 90% of the NaOH can be reacted. Glyceryl stearate should have been our basis of calculation and therefore we should not have divided the reaction as written by the stoichiometric coefficient of 3. It's always important to make sure you learn something from a mistake, such as choosing the wrong basis of calculation. There is no such thing as **failure, unless one fails to learn** from it.

The basis of calculation **must** be the limiting reactant.

#LifeLesson!

4.2 FLOW SYSTEMS

The form of the stoichiometric table for a continuous-flow system (see [Figure 4-2](#)) is virtually identical to that for a batch system ([Table 4-1](#)), except that we replace N_{j0} by F_{j0} and N_j by

F_j (Table 4-2). Again taking A as the basis, we divide Equation (2-1) through by the stoichiometric coefficient of A to obtain

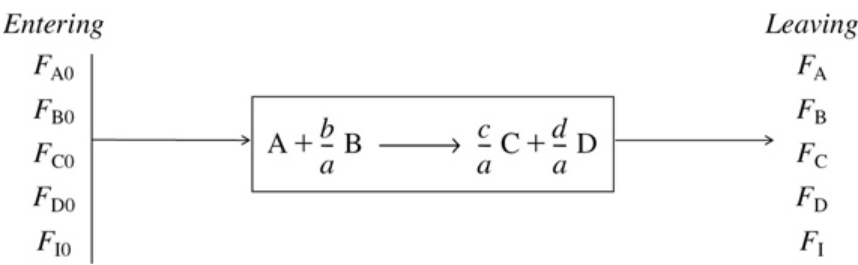
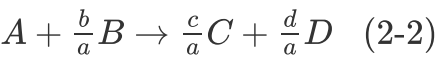


Figure 4-2 Flow reactor.

TABLE 4-2 STOICHIOMETRIC TABLE FOR A FLOW SYSTEM

Species	Feed Rate to Reactor (mol/time)	Change within Reactor (mol/time)	Effluent Rate from Reactor (mol/time)
A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1 - X)$
B	$F_{B0} = \Theta_B F_{A0}$	$-\frac{b}{a}F_{A0}X$	$F_B = F_{A0}\left(\Theta_B - \frac{b}{a}X\right)$
C	$F_{C0} = \Theta_C F_{A0}$	$\frac{c}{a}F_{A0}X$	$F_C = F_{A0}\left(\Theta_C + \frac{c}{a}X\right)$
D	$F_{D0} = \Theta_D F_{A0}$	$\frac{d}{a}F_{A0}X$	$F_D = F_{A0}\left(\Theta_D + \frac{d}{a}X\right)$
I	F_{I0}	—	$F_I = F_{A0}\Theta_I$

$$\Theta_I F_{A0}$$

Tot
als

$$F_{T0}$$

$$F_T = F_{T0} + \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right) F_{A0} X$$

$$F_T = F_{T0} + \delta F_{A0} X$$

Stoichiometric table for a flow system

where

$$\Theta_B = \frac{F_{B0}}{F_{A0}} = \frac{C_{B0} v_0}{C_{A0} v_0} = \frac{C_{B0}}{C_{A0}} = \frac{y_{B0}}{y_{A0}}$$

and Θ_C , Θ_D , and Θ_I are defined similarly

and, as before,

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \quad (4-1)$$

4.2.1 Equations for Concentrations in Flow Systems

For a flow system, the concentration C_A at a given point can be determined from the molar flow rate F_A and the volumetric flow rate v at that point:

$$C_A = \frac{F_A}{v} = \frac{\text{moles/time}}{\text{liters/time}} = \frac{\text{moles}}{\text{liter}} \quad (4-10)$$

Definition of concentration for a flow system

Units of v are typically given in terms of liters per second, cubic decimeters per second, or cubic feet per minute. We now can write the concentrations of A, B, C, and D for the general reaction given by Equation (2-2) in terms of their respective entering molar flow rates (F_{A0} , F_{B0} , F_{C0} , F_{D0}), the conversion, X , and the volumetric flow rate, v .

$$\begin{aligned} C_A &= \frac{F_A}{v} = \frac{F_{A0}}{v}(1 - X) & C_B &= \frac{F_B}{v} = \frac{F_{B0} - (b/a)F_{A0}X}{v} \\ C_C &= \frac{F_C}{v} = \frac{F_{C0} + (c/a)F_{A0}X}{v} & C_D &= \frac{F_D}{v} = \frac{F_{D0} - (d/a)F_{A0}X}{v} \end{aligned} \quad (4-11)$$

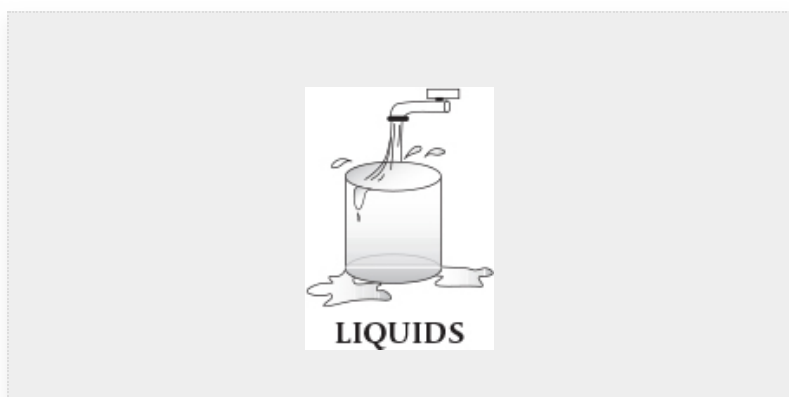
We now focus on determining the volumetric flow rate, v .

4.2.2 Liquid-Phase Concentrations

For liquids, the fluid volume change with reaction is negligible when no phase changes are taking place. Consequently, we can take

$$v = v_0$$

Then



$$C_A = \frac{F_{A0}}{v_0}(1 - X) = C_{A0}(1 - X) \quad (4-12)$$

$$C_B = C_{A0}\left(\Theta_B - \frac{b}{a}X\right), \quad (4-13)$$

For liquids

$$C_A = C_{A0}(1 - X)$$

$$C_B = C_{A0} \left(\Theta_B - \frac{b}{a} X \right)$$

Therefore, for a given rate law we have $-r_A = g(X)$

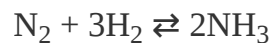
and so forth, for C_C and C_D .

Consequently, using any one of the rate laws in [Chapter 3](#), we can now find $-r_A = f(X)$ for liquid-phase reactions. **However**, for gas-phase reactions the volumetric flow rate most often changes during the course of the reaction because of a change in the total number of moles or a change in temperature or pressure. Hence, one cannot always use Equation (4-13) to express concentration as a function of conversion for gas-phase reactions. No worries. In the next section we will sort this out.

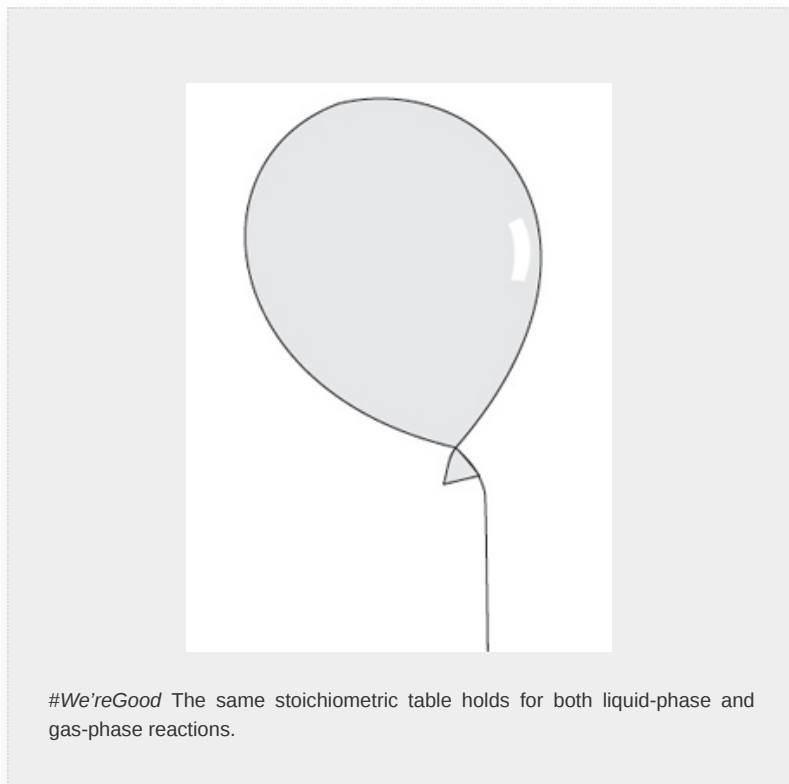
4.2.3 Gas-Phase Concentrations

In our previous discussions, we considered primarily systems in which the reaction volume or volumetric flow rate did not vary as the reaction progressed. Most batch and liquid-phase and some gas-phase systems fall into this category. There are other systems, though, in which either V or v **does** vary, and these will now be considered.

A situation where one encounters a varying flow rate occurs quite frequently in gas-phase reactions that do not have an equal number of product and reactant moles. For example, in the synthesis of ammonia



4 mol of reactants gives 2 mol of product. In flow systems where this type of reaction occurs, the molar flow rate will be changing as the reaction progresses. Because equal numbers of moles occupy equal volumes in the gas phase at the same temperature and pressure, the volumetric flow rate will also change.



In the stoichiometric tables presented on the preceding pages, it was not necessary to make assumptions concerning a volume change in the first four columns of the table (i.e., the species, initial number of moles or molar feed rate, change within the reactor, and the remaining number of moles or the molar effluent rate). All of these columns of the stoichiometric table are independent of the volume or density, and they are *identical* for constant-volume (constant-density) and varying-volume (varying-density) situations. Only when concentration is expressed as a function of conversion does variable density enter the picture.

Flow Reactors with Variable Volumetric Flow Rate. To derive the concentrations of each species in terms of conversion for a gas-phase flow system, we shall start by using the relationships for the total concentration. The total concentration, C_T , at any point in the reactor is the total molar flow rate, F_T , divided by the volumetric flow rate, v (cf. Equation (4-10)). In the gas phase, the total concentration is also found from the gas law, $C_T = P/ZRT$. Equating these two relationships gives

$$C_T = \frac{F_T}{v} = \frac{P}{ZRT} \quad (4-14)$$

At the entrance to the reactor

$$C_{T0} = \frac{F_{T0}}{v_0} = \frac{P_0}{Z_0RT_0} \quad (4-15)$$

Taking the ratio of Equation (4-14) to Equation (4-15) and assuming negligible changes in the compressibility factor occur, that is, $Z \cong Z_0$, during the course of the reaction, we have upon rearrangement

$$v = v_0 \left(\frac{F_T}{F_{T0}} \right) \frac{P_0}{P} \left(\frac{T}{T_0} \right) \quad (4-16)$$

Gas-phase reactions

We can now express the concentration of species j for a flow system in terms of its flow rate, F_j , the temperature, T , and total pressure, P .

$$C_j = \frac{F_j}{v} = \frac{F_j}{v_0 \left(\frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{T}{T_0} \right)} = \left(\frac{F_{T0}}{v_0} \right) \left(\frac{F_j}{F_T} \right) \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$$

$$C_j = C_{T0} = \left(\frac{F_j}{F_T} \right) \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right) \quad (4-17)$$

Use this **gas-phase** concentration equation for membrane reactors (Chapter 6) and for multiple reactions (Chapter 8).

The total molar flow rate is just the sum of the molar flow rates of each of the species in the system and is

$$F_T = F_A + F_B + F_C + F_D + F_I + \dots = \sum_{j=1}^n F_j \quad (4-18)$$

We can also write Equation (4-17) in terms of the mole fraction of species j , y_j , and the pressure ratio, p , with respect to the initial or entering conditions, that is, sub “0”

$$y_i = \frac{F_j}{F_T}$$

$$p = \frac{P}{P_0}$$

$$C_j = C_{T0} y_j p \frac{T_0}{T} \quad (4-19)$$

Gas phase



The molar flow rates, F_j , are found by solving the mole balance equations. The concentration given by Equation (4-17) will be used for measures other than conversion when we discuss membrane reactors (Chapter 6) and multiple gas-phase reactions (Chapter 8).

Now, let's express the concentration in terms of conversion for gas flow systems. From Table 4-2, the total molar flow rate can be written in terms of conversion and is

$$F_T = F_{T0} + F_{A0} \delta X$$

We divide this equation through by F_{T0}

$$\frac{F_T}{F_{T0}} = 1 + \frac{F_{A0}}{F_{T0}} \delta X = 1 + \overbrace{y_{A0} \delta}^{\varepsilon} X$$

Then

$$\frac{F_T}{F_{T0}} = 1 + \varepsilon X \quad (4-20)$$

where y_{A0} is the mole fraction of A at the inlet (i.e., (F_{A0}/F_{T0})), and where δ is given by Equation (4-1) and ε is given by

$$\varepsilon = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right) \frac{F_{A0}}{F_{T0}} = y_{A0} \delta$$

$$\boxed{\varepsilon = y_{A0} \delta} \quad (4-21)$$

Relationship between δ and ε

Equation (4-21) holds for both batch and flow systems. To interpret ε , let's rearrange Equation (4-20) at complete conversion (i.e., $X = 1$ and $F_T = F_{Tp}$)

$$\varepsilon = \frac{F_{Tp} - F_{T0}}{F_{T0}}$$

$$\boxed{\varepsilon = \frac{\text{Change in total number of moles for complete conversion}}{\text{Total moles fed}}} \quad (4-22)$$

Interpretation of ϵ

Substituting for (F_T/F_{T0}) in Equation (4-16) for the volumetric flow rate, v , we have

$$v = v_0 (1 + \epsilon X) \frac{P_0}{P} \left(\frac{T}{T_0} \right) \quad (4-23)$$

Gas-phase volumetric flow rate

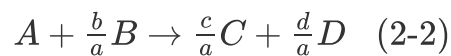
The concentration of species j in a flow system is

$$C_j = \frac{F_j}{v} \quad (4-24)$$

The molar flow rate of species j is

$$F_j = F_{j0} + v_j (F_{A0}X) = F_{A0}(\Theta_j + v_jX)$$

where v_j is the stoichiometric coefficient for species j , which is negative for reactants and positive for products. For example, for the reaction



$$v_A = -1, v_B = -b/a, v_C = c/a, v_D = d/a, \text{ and } \Theta_j = F_{j0}/F_{A0}.$$

Substituting for the gas volumetric flow rate, v , using Equation (4-23) and for F_j , we have

$$C_j = \frac{F_{A0}(\Theta_j + v_jX)}{v_0 \left((1 + \epsilon X) \frac{P_0}{P} \frac{T}{T_0} \right)}$$

Rearranging

$$C_j = \frac{C_{A0}(\Theta_j + v_j X)}{1 + \varepsilon X} \left(\frac{P}{P_0} \right) \frac{T_0}{T} \quad (4-25)$$

Gas-phase concentration as a function of conversion

Recall that $y_{A0} = F_{A0}/F_{T0}$, $C_{A0} = y_{A0}C_{T0}$, and ε is given by Equation (4-21) (i.e., $\varepsilon = y_{A0}\delta$).

The stoichiometric table for the gas-phase reaction (2-2) is given in Table 4-3.

TABLE 4-3 CONCENTRATIONS IN A VARIABLE-VOLUME GAS FLOW SYSTEM

$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v} = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} \left(\frac{T_0}{T} \right) \frac{P}{P_0} = C_{A0} \left(\frac{1-X}{1+\varepsilon X} \right) \frac{T_0}{T} \left(\frac{P}{P_0} \right)$			
$C_B = \frac{F_B}{v} = \frac{F_{A0}[\Theta_B - (b/a)X]}{v} = \frac{F_{A0}[\Theta_B - (b/a)X]}{v_0(1+\varepsilon X)} \left(\frac{T_0}{T} \right) \frac{P}{P_0} = C_{A0} \left(\frac{\Theta_B - (b/a)X}{1+\varepsilon X} \right) \frac{T_0}{T} \left(\frac{P}{P_0} \right)$			
$C_C = \frac{F_C}{v} = \frac{F_{A0}[\Theta_C + (c/a)X]}{v} = \frac{F_{A0}[\Theta_C + (c/a)X]}{v_0(1+\varepsilon X)} \left(\frac{T_0}{T} \right) \frac{P}{P_0} = C_{A0} \left(\frac{\Theta_C + (c/a)X}{1+\varepsilon X} \right) \frac{T_0}{T} \left(\frac{P}{P_0} \right)$			
$C_D = \frac{F_D}{v} = \frac{F_{A0}[\Theta_D + (d/a)X]}{v} = \frac{F_{A0}[\Theta_D + (d/a)X]}{v_0(1+\varepsilon X)} \left(\frac{T_0}{T} \right) \frac{P}{P_0} = C_{A0} \left(\frac{\Theta_D + (d/a)X}{1+\varepsilon X} \right) \frac{T_0}{T} \left(\frac{P}{P_0} \right)$			
$C_I = \frac{F_I}{v} = \frac{F_{A0}\Theta_I}{v} = \frac{F_{A0}\Theta_I}{v_0(1+\varepsilon X)} \left(\frac{T_0}{T} \right) \frac{P}{P_0} = \frac{C_{A0}\Theta_I}{1+\varepsilon X} \frac{T_0}{T} \left(\frac{P}{P_0} \right)$			

At last!

We now have

$$C_j = h_j(X)$$

and

$$-r_A = g(X)$$

for variable-volume **gas-phase** reactions.

One of the major objectives of this chapter is to learn how to express any given rate law $-r_A$ as a function of conversion. The schematic diagram in [Figure 4-3](#) helps to summarize our discussion on this point. The concentration of the reactant species B in the generic reaction is expressed as a function of conversion in both flow and batch systems for various conditions of temperature, pressure, and volume.

At last, by coupling [Table 4-3](#) with the rate law for single gas-phase reactions, we obtain what we needed and used in [Chapter 2](#) to size and sequence flow reactors, that is,

$$-r_A = f(X)$$

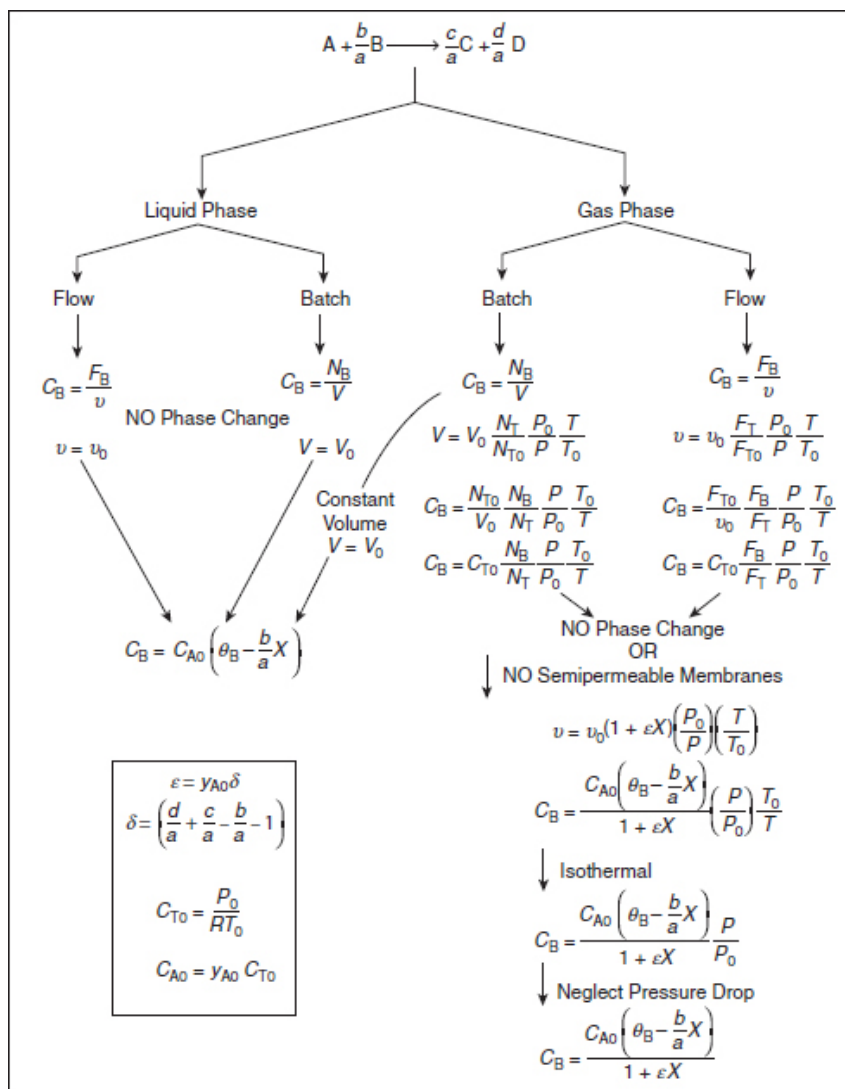
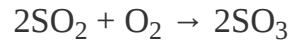


Figure 4-3 Expressing concentration as a function of conversion.

Example 4–3 Determining $C_j = h_j(X)$ for a Gas-Phase Reaction

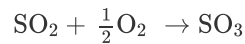
A mixture of 28% SO_2 and 72% air is charged to a flow reactor in which is oxidized.



1. First, set up a stoichiometric table using only the symbols (i.e., Θ_i, F_i).
2. Next, prepare a second table evaluating the species concentrations as a function of conversion for the case when the total pressure is 1485 kPa (14.7 atm) and the temperature is constant at 227°C.
3. Evaluate the parameters and make a plot of each of the concentrations SO_2 , SO_3 , N_2 as a function of conversion.

Solution

1. **Stoichiometric table.** Taking SO_2 as the basis of calculation, we divide the reaction through by the stoichiometric coefficient of our chosen basis of calculation



The stoichiometric table is given in Table E4-3.1.

TABLE E4-3.1 STOICHIOMETRIC TABLE FOR
 $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3$

Species				
Symbol	Initially	Change	Remaining	
S	A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1 - X)$
O ₂	B	F_{B0}	$-\frac{F_{A0}X}{2}$	$F_B = F_{A0}\left(\Theta_B - \frac{1}{2}X\right)$
		=		
		$\Theta_B F_{A0}$		
S	C	0	$+F_{A0}X$	$F_C = F_{A0}X$
O ₃				
N ₂	I	$F_{I0} =$	$—$	$F_I = F_{I0} = \Theta_I F_{A0}$
		$\Theta_I F_A$		

<u>0</u>		
To	F_{T0}	$F_T = F_{T0} - \frac{F_{A0}X}{2}$
tal		
s		

2. Expressing the concentration as a function of conversion.

From the definition of conversion, we substitute not only for the molar flow rate of SO_2 (A) in terms of conversion but also for the volumetric flow rate as a function of conversion

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v}$$

Recalling Equation (4-23), we have

$$v = v_0 (1 + \varepsilon X) \frac{P_0}{P} \left(\frac{T}{T_0} \right) \quad (4-23)$$

Neglecting pressure drop in the reaction, $P = P_0$, yields

$$v = v_0 (1 + \varepsilon X) \frac{T}{T_0}$$

Neglecting pressure drop, $P = P_0$, that is, $p = \frac{P}{P_0} \approx 1$

If the reaction is also carried out isothermally, $T = T_0$, we obtain

$$v = v_0(1 + \varepsilon X)$$

$$C_A = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} = C_{A0} \left(\frac{1-X}{1+\varepsilon X} \right) \quad (\text{E4-3.1})$$

Isothermal operation, $T = T_0$

Similarly for B also with $T = T_0$ and $P = P_0$ (i.e., $p = 1$)

$$C_B = C_{A0} \frac{\left(\Theta_B - \frac{b}{a} X \right)}{1 + \varepsilon X} p \frac{T_0}{T} = \frac{C_{A0} \left(\Theta_B - \frac{1}{2} X \right)}{1 + \varepsilon X} \quad (\text{E4-3.2})$$

3. Parameter evaluation and plots of concentrations as a function of conversion.

The inlet concentration of A is equal to the inlet mole fraction of A multiplied by the total inlet molar concentration. The total concentration can be calculated from an equation of state such as the ideal gas law. Recall that $y_{A0} = 0.28$, $T_0 = 500$ K, and $P_0 = 1485$ kPa.

$$C_{A0} = y_{A0} C_{T0} = y_{A0} \left(\frac{P_0}{RT_0} \right)$$

$$= 0.28 \left[\frac{1485 \text{ kPa}}{8.314 \text{ kPa} \cdot \text{dm}^3 / (\text{mol} \cdot \text{K}) \times 500 \text{ K}} \right]$$

$$= 0.1 \text{ mol/dm}^3 \quad \underline{\text{Answer}}$$

The total concentration at constant temperature and pressure is

$$C_T = \frac{F_T}{v} = \frac{F_{T0} + \overbrace{y_{A0} \delta X}^{\epsilon} F_{T0}}{v_0(1 + \epsilon X)} = \frac{F_{T0}(1 + \cancel{\epsilon X})}{v_0(1 + \cancel{\epsilon X})} = \frac{F_{T0}}{v_0} = C_{T0} \quad (\text{E4-3.3})$$

$$C_{T0} = \frac{P_0}{RT_0} = \frac{1485 \text{ kPa}}{[8.314 \text{ kPa} \cdot \text{dm}^3 / (\text{mol} \cdot \text{K})] (500 \text{ K})} = 0.357 \frac{\text{mol}}{\text{dm}^3} \quad (\text{E4-3.4})$$

We now evaluate ϵ .

$$\epsilon = y_{A0} \delta = (0.28) \left(1 - 1 - \frac{1}{2} \right) = -0.14 \quad (\text{E4-3.5})$$

Initially, 72% of the total number of moles is air containing 21% O₂ and 79% N₂, along with 28% SO₂.

$$F_{A0} = (0.28) (F_{T0})$$

$$F_{B0} = (0.72) (0.21) (F_{T0})$$

$$\Theta_B = \frac{F_{B0}}{F_{A0}} = \frac{(0.72)(0.21)}{0.28} = 0.54 \quad \underline{\text{Answer}}$$

$$\Theta_I = \frac{F_{I0}}{F_{A0}} = \frac{(0.72)(0.79)}{0.28}$$

Substituting for C_{A0} and ϵ in the species concentrations:

$$\text{SO}_2: \quad C_A = C_{A0} \left(\frac{1-X}{1+\epsilon X} \right) = 0.1 \left(\frac{1-X}{1-0.14X} \right) \text{ mol/dm}^3 \quad (\text{E4-3.6})$$

$$\text{O}_2: \quad C_B = C_{A0} \left(\frac{\Theta_B - \frac{1}{2}X}{1+\epsilon X} \right) = \frac{0.1(0.54-0.5X)}{1-0.14X} \text{ mol/dm}^3 \quad (\text{E4-3.7})$$

$$\text{SO}_3: \quad C_c = \left(\frac{C_{A0}X}{1+\epsilon X} \right) = \frac{0.1X}{1-0.14X} \text{ mol/dm}^3 \quad (\text{E4-3.8})$$

$$\text{N}_2: \quad C_1 = \frac{C_{A0}\Theta_1}{1+\epsilon X} = \frac{(0.1)(2.03)}{1-0.14X} \text{ mol/dm}^3 \quad (\text{E4-3.9})$$

The concentrations of different species at various conversions are calculated in [Table E4-3.2](#) and plotted in [Figure E4-3.1](#). **Note** that the concentration of is changing even though it is an inert species in this reaction!! #Seriously?

TABLE E4-3.2 CONCENTRATION AS A FUNCTION OF CONVERSION

$C_i \text{ (mol/dm}^3\text{)}$						
<i>Species</i> $X = 0.0X = 0.25X = 0.5X = 0.75X = 1.0$						
SO ₂	$C_A =$	0.100	0.078	0.054	0.028	0.000
O ₂	$C_B =$	0.054	0.043	0.031	0.018	0.005
SO ₃	$C_C =$	0.000	0.026	0.054	0.084	0.116
N ₂	$C_I =$	<u>0.203</u>	<u>0.210</u>	<u>0.218</u>	<u>0.227</u>	<u>0.236</u>
Total	$C_T =$	0.357	0.357	0.357	0.357	0.357

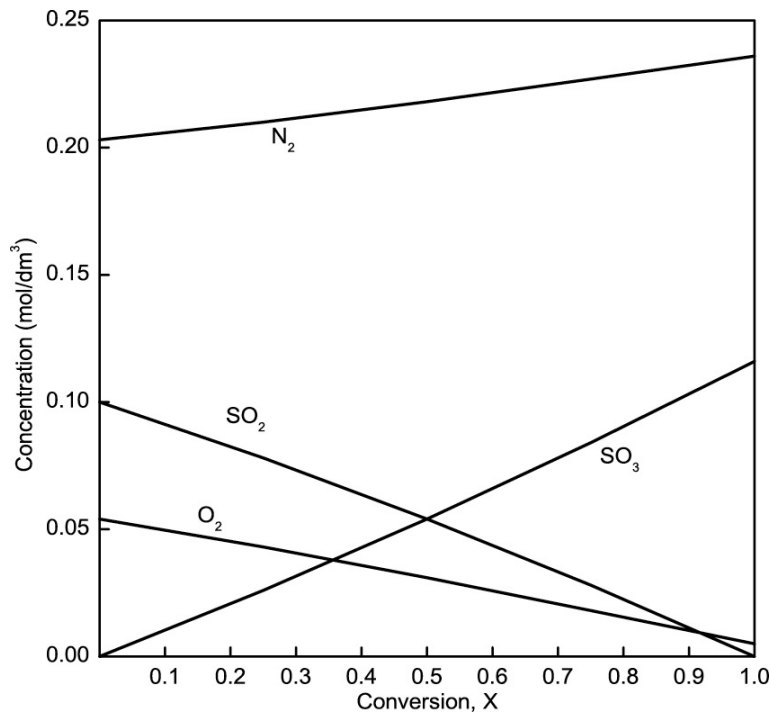


Figure E4-3.1 Concentration as a function of conversion.

Note: Because the volumetric flow rate varies with conversion, $u = u_0(1 - 0.14X)$, the concentration of inerts (N_2) is *not* constant.

Now we could use techniques presented in [Chapter 2](#) to size reactors.

We are now in a position to express $-r_A$ as a function of X and use the techniques in [Chapter 2](#) to size and sequence reactors. *However*, we will use a better method to solve CRE problems, namely a Table of Integrals ([Appendix A](#)) or the Polymath, MATLAB, Wolfram, or Python software, discussed in the next chapter.

Analysis: In this example, we first formed a stoichiometric table in terms of molar flow rates. We

then showed how to express the concentrations of each species in a gas-phase reaction in which there is a change in the total number of moles. Next, we plotted each species concentration as a function of conversion and noted that the concentration of the inert, N_2 , was not constant but increased with increasing conversion because of the decrease in the total molar flow rate, F_T , with conversion.

As previously mentioned many, if not most, rate laws for catalyst reactions are given in terms of partial pressures. Luckily, partial pressures are easily related to conversion with the aid of the ideal gas law and Equation (4-17).

$$P_i = C_i RT = C_{T0} \frac{F_i}{F_T} \overbrace{\left(\frac{P}{P_0} \right)}^p \frac{T_0}{T} RT = \overbrace{C_{T0} RT_0}^{P_{T0}} \overbrace{\frac{F_i}{F_T}}^{y_i} p$$

The following equation is used when the mole balance is written in terms of molar flow rates:

$$P_i = P_{T0} \left(\frac{F_i}{F_T} \right) p \quad (4-26)$$

However, when the mole balance is written in terms of conversion, we use Equation (4-25):

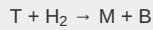
$$\begin{aligned} P_i &= C_i RT = C_{A0} \frac{(\Theta_i + v_i X)}{(1 + \varepsilon X)} \frac{P}{P_0} \frac{T_0}{T} RT \\ &= \overbrace{C_{A0} RT_0}^{P_{A0}} \frac{(\Theta_i + v_i X)}{(1 + \varepsilon X)} p \end{aligned}$$

$$P_i = P_{A0} \frac{(\Theta_i + v_i X)}{1 + \varepsilon X} p \quad (4-27)$$

For example, the rate law for the hydrodemethylation of toluene (T) to form methane (M) and benzene (B) given by

Equation (10-80) on page 483 can now be written in terms of conversion.

$$-r'_T = \frac{kP_{A0}^2(1-X)(\Theta_{H_2}-X)}{1+K_BP_{A0}X+K_BP_{A0}(1-X)}(p)^2$$



If you haven't decided which computer to buy or borrow, or don't have your integral tables, I suppose you could resort to the graphical techniques in Chapter 2 and use a Levenspiel plot, $F_{A0}/-r'_A$ versus X , to achieve a specified conversion of toluene. *However*, that may put you at a severe disadvantage as other chemical reaction engineers will be using software packages (e.g., Poly-math) to solve chemical reaction engineering problems.

**Example 4–4 Expressing the Rate Law for SO₂
Oxidation in Terms of Partial Pressures and
Conversions**

The SO₂ oxidation discussed in [Example 4-3](#) is to be carried out over a solid platinum catalyst. As with almost all gas–solid catalytic reactions, the catalytic rate law is expressed in terms of partial pressures instead of concentrations. The rate law for this SO₂ oxidation was found experimentally to be¹

$$-r'_{\text{SO}_2} = \frac{k \left[P_{\text{SO}_2} \sqrt{P_{\text{O}_2} - \frac{P_{\text{SO}_3}}{K_P}} \right]}{\left(1 + \sqrt{P_{\text{O}_2} K_{\text{O}_2} + P_{\text{SO}_3} K_{\text{SO}_3}} \right)^2}, \text{ mol SO}_2 \text{ oxidized / (h) / (g-cat)} \quad (\text{E4-4.1})$$

¹ O. A. Uychara and K. M. Watson, *Ind. Engrg. Chem*, 35, 541.

where P_i (kPa, bar, or atm) is the partial pressure of species i .

The reaction is to be carried out isothermally at 400°C. At this temperature, the rate constant k per gram of catalyst (g-cat), the adsorption constants for O₂ (K_{O_2}) and SO₂ (K_{SO_2}), and the pressure equilibrium constant, K_P , were experimentally found to be

$$k = 9.7 \text{ mol SO}_2 / \text{atm}^{3/2} / \text{h/g-cat}$$

$$K_{\text{O}_2} = 38.5 \text{ atm}^{-1}, K_{\text{SO}_3} = 42.5 \text{ atm}^{-1}, \text{ and } K_P = 930 \text{ atm}^{-1/2}$$

The total pressure and the feed composition (e.g., 28% SO₂) are the same as in [Example 4-3](#). Consequently, the entering partial pressure of SO₂ is 4.1 atm. There is virtually no pressure drop in this reactor.

1. Write the rate law as a function of conversion evaluating all other parameters.

2. Prepare a Levenspiel plot by sketching the reciprocal rate $[1/(-r_A)]$ as a function of X up to the equilibrium conversion X_e , and note where the rate goes to zero and $[1/(-r_A)]$ goes to infinity.

Solution

Part (a)

No Pressure Drop and Isothermal Operation

For SO_2

First we need to recall the relationship between partial pressure and concentration, followed by the relationship between concentration and conversion. Because we know how to express concentration as a function of conversion, we therefore know how to express partial pressure as a function of conversion.

$$P_{\text{SO}_2} = C_{\text{SO}_2} RT = \frac{F_{\text{SO}_2}}{v} RT = \frac{F_{\text{SO}_2,0}(1-X)RT}{v_0(1+\epsilon X) \frac{T}{T_0} \frac{P_0}{P}} = \frac{F_{\text{SO}_2,0}}{v_0} \frac{RT_0(1-X) \frac{P}{P_0}}{1+\epsilon X}$$

$$P_{\text{SO}_2} = \frac{P_{\text{SO}_2,0}(1-X) \frac{P}{P_0}}{(1+\epsilon X)} = \frac{P_{\text{SO}_2,0}(1-X)P}{(1+\epsilon X)} \quad (\text{E4-4.2})$$

$$P_i = P_{A0} \frac{(\Theta_i + v_i X)}{(1+\epsilon X)} \frac{P}{P_0} = P_{A0} \frac{(\Theta_i + v_i X)}{(1+\epsilon X)} p$$

For no pressure drop $P = P_0$, that is, $p = 1$

$$P_{\text{SO}_2} = \frac{P_{\text{SO}_2,0}(1-X)}{(1+\epsilon X)}$$

$$P_{\text{SO}_2,0} = y_{\text{SO}_2,0} P_0 = 4.1 \text{ atm} \quad (\text{E4-4.3})$$

For SO_3

$$P_{\text{SO}_3} = C_{\text{SO}_3} RT = \frac{C_{\text{SO}_2,0} RT_0 X}{(1+\varepsilon X)} = \frac{P_{\text{SO}_2,0} X}{1+\varepsilon X} \quad (\text{E4-4.4})$$

For O₂

$$P_{\text{O}_2} = C_{\text{O}_2} RT = C_{\text{SO}_2,0} \frac{(\Theta_B - \frac{1}{2}X) RT_0}{1+\varepsilon X} = P_{\text{SO}_2,0} \frac{(\Theta_B - \frac{1}{2}X)}{1+\varepsilon X} \quad (\text{E4-4.5})$$

From Example 4-3

$$\Theta_B = 0.54$$

Factoring out $\frac{1}{2}$ in Equation (E4-4.5) gives

$$P_{\text{O}_2} = P_{\text{SO}_2,0} = \frac{(\Theta_B - \frac{1}{2}X)}{(1+\varepsilon X)} = \frac{P_{\text{SO}_2,0}(1.08-X)}{2(1+\varepsilon X)} \quad (\text{E4-4.6})$$

From Equation (E4-3.5)

$$\varepsilon = -0.14 \quad (\text{E4-3.5})$$

Substitute for the partial pressure in the rate-law equation (E4-4.1)

$$-r'_{\text{SO}_2} = k \left[\frac{P_{\text{SO}_2,0}^{3/2} \left(\frac{1-X}{1-0.14X} \right) \sqrt{\frac{(1.08-X)}{2(1-0.14X)}} - \frac{P_{\text{SO}_2,0} X}{(1-0.14X)} \left(\frac{1}{930 \text{ atm}^{-1/2}} \right)}{\left(1 + \sqrt{\frac{38.5 P_{\text{SO}_2,0} (1.08-X)}{2(1-0.14X)}} + \frac{42.5 P_{\text{SO}_2,0} X}{(1-0.14X)} \right)^2} \right] \quad (\text{E4-4.7})$$

with $k = 9.7 \text{ mol SO}_2/\text{atm}^{3/2}/\text{h/g-cat}$ $P_{\text{SO}_2,0} = 4.1 \text{ atm}$,
 $P_{\text{SO}_2,0}^{3/2} = 8.3 \text{ atm}^{3/2}$

$$-r'_{\text{SO}_2} = 9.7 \frac{\text{mol}}{\text{hg-cat atm}^{3/2}} \left[\frac{\frac{8.3 \text{ atm}^{3/2} (1-X)}{(1-0.14X)} \sqrt{\frac{1.08-X}{2(1-0.14X)}} - \frac{0.0044 \text{ atm}^{3/2} X}{(1-0.14X)}}{\left(1 + \sqrt{\frac{79(1.08-X)}{(1-0.14X)}} + \frac{174X}{1-0.14X} \right)^2} \right] \quad (\text{E4-4.8})$$

$$-r'_A = f(x)$$

Part (b)

We can now use Equation (E4-4.8) to plot the reciprocal rate as a function of X as shown in Figure E4-4.1 to design a packed-bed catalytic reactor. We note at the equilibrium conversion, X_e , the reciprocal rate goes to infinity. We could now use a Levenspiel plot to find the catalyst weight W in a packed-bed reactor (PBR) to achieve a specified conversion.

$$F_{A0} \frac{dX}{dW} = -r_A' \quad (2-17)$$

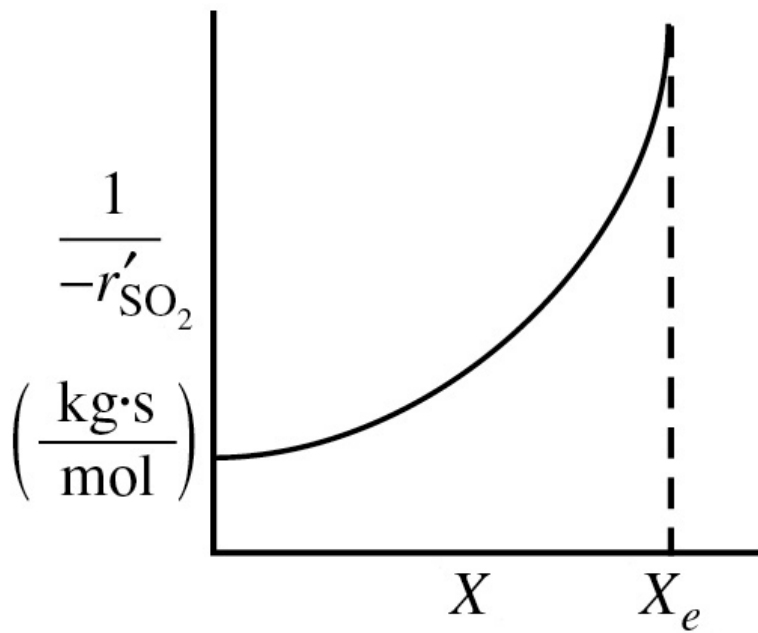


Figure E4-4.1 Reciprocal rate of SO₂ oxidation as a function of conversion.

Levenspiel plots are useful for conceptually visualizing the differences in reactor sizes and the sequencing of reactors. However, we will see in Chapter 5 that using numerical software packages are *so much better* ways to solve for the catalysis weight, W , than using Levenspiel plots. For example, we would couple Equation (E4-4.8) with Equation (2-17) and use an ordinary differential equation (ODE) solver, such as

Polymath or MATLAB, to find the conversion X as a function of catalyst weight W . So, be sure to buy, rent, or borrow a laptop computer before attempting to solve the problems in Chapter 5 and beyond.

Analysis: In most heterogeneous catalytic reactions, rate laws are expressed in terms of partial pressures instead of concentration. However, we see that through the use of the ideal gas law we could *easily* express the partial pressure as a function of concentration then use the stoichiometric table and conversion in order to express the rate law as a function of conversion. In addition, for most all heterogeneous reactions you will usually find a term like $(1 + K_A P_A + K_B P_B + \dots)$ in the denominator of the rate law, as will be explained in Chapter 10.

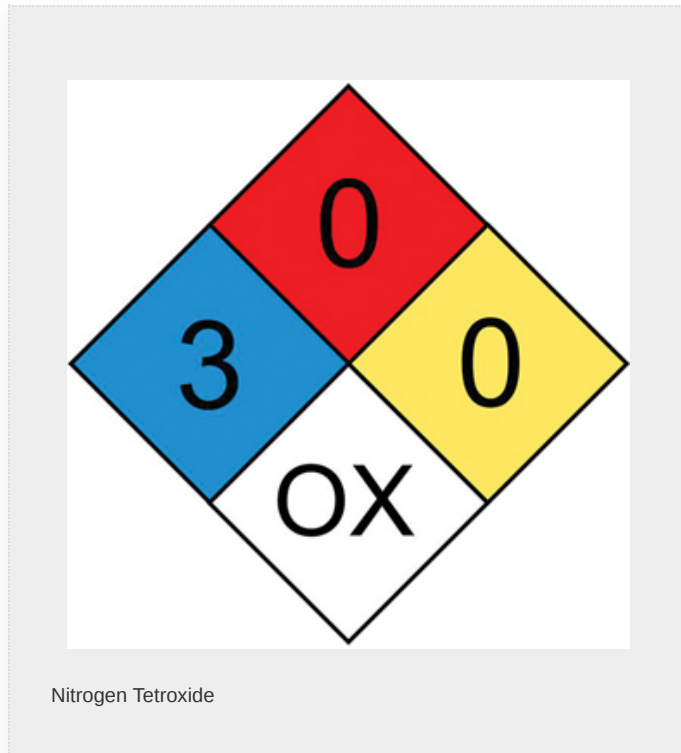
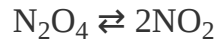
4.3 REVERSIBLE REACTIONS AND EQUILIBRIUM CONVERSION

Thus far in this chapter, we have focused mostly on irreversible reactions. The procedure one uses for the isothermal reactor design of reversible reactions is virtually the same as that for irreversible reactions, with one notable exception: the maximum conversion that can be achieved at the reaction temperature is the equilibrium conversion, X_e . In the following example, it will be shown how our algorithm for reactor design is easily extended to reversible reactions.

Need to first calculate X_e

Example 4–5 Calculating the Equilibrium Conversion

The reversible gas-phase decomposition of nitrogen tetroxide, N_2O_4 , to nitrogen dioxide, NO_2 ,



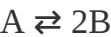
is to be carried out at constant temperature. The feed consists of pure N_2O_4 at 340 K and 202.6 kPa (2 atm). The concentration equilibrium constant, K_C , at 340 K is $0.1 \text{ mol} / \text{dm}^3$ and the rate constant $k_{\text{N}_2\text{O}_4}$ and the rate constant is 0.5 min^{-1} .

1. Set up a stoichiometric table and then calculate the equilibrium conversion of N_2O_4 in a constant-volume batch reactor.
2. Set up a stoichiometric table and then calculate the equilibrium conversion of N_2O_4 in a flow reactor.
3. Assuming the reaction is elementary, express the rate of reaction solely as a function of conversion for a flow system

and for a batch system.

- 4. Determine the CSTR volume necessary to achieve 80% of the equilibrium conversion.

Solution



At equilibrium, the concentrations of the reacting species are related by the relationship dictated by thermodynamics (cf. see Equation (3-10) and Appendix C).

$$K_C = \frac{C_{\text{Be}}^2}{C_{\text{Ae}}} \quad (\text{E4-5.1})$$

- 1. Batch system—constant volume, $V = V_0$.

TABLE E4-5.1 STOICHIOMETRIC TABLE FOR BATCH REACTOR

Species Symbol Initially Change Remaining				
N ₂ O ₄	A	N _{A0}	− N _{A0} X	N _A = N _{A0} (1 − X)
NO ₂	B	0	+2N _{A0} X	N _B = 2N _{A0} X
		N _{T0} = N _{A0}	N _T = N _{T0} + N _{A0} X	

Living Example Problem

For batch systems $C_i = N_i/V$

$$C_A = \frac{N_A}{V} = \frac{N_A}{V_0} = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X) \quad (\text{E4-5.2})$$

$$C_B = \frac{N_B}{V} = \frac{N_B}{V_0} = \frac{2N_{A0}X}{V_0} = 2C_{A0}X \quad (\text{E4-5.3})$$

$$C_{A0} = \frac{y_{A0}P_0}{RT_0} = \frac{(1)(2 \text{ atm})}{(0.082 \text{ atm}\cdot\text{dm}^3/\text{mol}\cdot\text{K})(340 \text{ K})}$$

$$= 0.07174 \text{ mol/dm}^3 \quad \text{Answer}$$

At equilibrium in a batch reactor, $X = X_{\text{eb}}$, we substitute Equations (E4-5.2) and (E4-5.3) into Equation (E4-5.1)

$$K_c = \frac{C_{\text{Be}}^2}{C_{\text{Ae}}} = \frac{4C_{A0}^2 X_{\text{eb}}^2}{C_{A0}(1-X_{\text{eb}})} = \frac{4C_{A0} X_{\text{eb}}^2}{1-X_{\text{eb}}}$$

(math-math-math-math) to get

$$X_{\text{eb}} = \sqrt{\frac{K_c(1-X)}{4C_{A0}}} \quad (\text{E4-5.4})$$

We will use the software package Polymath to solve for the equilibrium conversion and let X_{eb} represent the equilibrium conversion in a constant-volume batch reactor. Equation (E4-5.4) written in Polymath format becomes

$$f(X_{\text{eb}}) = X_{\text{eb}} - [K_c * (1 - X_{\text{eb}})/(4*C_{A0})]^{0.5}$$

The Polymath program and solution are given in Table E4-5.2. When looking at Equation (E4-5.4), you probably asked yourself, “Why not use the quadratic formula to solve for the equilibrium conversion in both batch and flow systems?” That is from Equation (E4-5.4) we would have

$$\text{Batch: } X_{\text{eb}} = \frac{1}{8} \left[\left(-1 + \sqrt{1 + 16C_{A0}/K_c} \right) / (C_{A0}/K_c) \right]$$

and from Equation (E4-5.8) we would have

$$\text{Flow: } X_{\text{ef}} = \left[\frac{(\varepsilon - 1) + \sqrt{(\varepsilon + 1)^2 + 4(\varepsilon + 4C_{A0}/K_c)}}{2(\varepsilon + 4C_{A0}/K_c)} \right]$$

There is a Polymath tutorial in the Summary Notes for Chapter 1 on the CRE Web site.

The answer is that future problems will be nonlinear and require Polymath solutions; therefore, this simple exercise increases the reader's ease in using Polymath.

TABLE E4-5.2 POLYMATH PROGRAM AND SOLUTION FOR BOTH BATCH AND FLOW SYSTEMS

Nonlinear equations

- 1 $f(X_{ef}) = X_{ef} - (K_c(1 - X_{ef}) / (1 + \epsilon X_{ef})) / (4 C_{Ao})^{0.5} = 0$
- 2 $f(X_{eb}) = X_{eb} - (K_c(1 - X_{eb}) / (4 C_{Ao}))^{0.5} = 0$

Explicit equations

- 1 $C_{Ao} = 0.07174$
- 2 $\epsilon = 1.0$
- 3 $K_c = 0.1$

Calculated values of NLE variables

	Variable	Value	f(x)	Initial Guess
1	Xeb	0.4412597	7.266E-09	0.4
2	Xef	0.5083548	2.622E-10	0.5

	Variable	Value
1	Cao	0.07174
2	epsilon	1.
3	Kc	0.1

Polymath Tutorial Chapter 1



As seen in Table E4-5.2, the equilibrium conversion in a constant-volume batch reactor (X_{eb}) is

$$X_{eb} = 0.44$$

Note: A tutorial on Polymath can be found in the summary notes for Chapter 1 and on the CRE Web site (www.umich.edu/~elements/6e/tutorials/Polymath_LEP_tutorial.pdf).

2. **Flow system.** The stoichiometric table is the same as that for a batch system except that the number of moles of each species, N_i , is replaced by the molar flow rate of that species, F_i . For constant temperature and pressure, the volumetric flow rate $v = v_0(1 + \epsilon X)$, is and the resulting concentrations of species A and B are

TABLE E4-5.3 STOICHIOMETRIC TABLE FOR
CONTINUOUS-FLOW REACTOR

Species Symbol Entering Change Leaving				
N ₂ O ₂	A	F _{A0}	– F _{A0} X	F _A = F _{A0} (1– X)
NO ₂	B	0	+2F _{A0} X	F _B = 2F _{A0} X
		F _T = F _{A0}	F _T = F _{T0} + F _{A0} X	

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v} = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} = \frac{C_{A0}(1-X)}{1+\varepsilon X} \quad (\text{E4-5.5})$$

$$C_B = \frac{F_B}{v} = \frac{2F_{A0}X}{v_0(1+\varepsilon X)} = \frac{2C_{A0}X}{(1+\varepsilon X)} \quad (\text{E4-5.6})$$

At equilibrium, $X = X_{ef}$, we can substitute Equations (E4-5.5) and (E4-5.6) into Equation (E4-5.1) to obtain the expression

$$K_C = \frac{C_{Be}^2}{C_{Ae}} = \frac{[2C_{A0}X_{ef}/(1+\varepsilon X_{ef})]^2}{C_{A0}(1-X_{ef})/(1+\varepsilon X_{ef})}$$

Simplifying gives

$$K_C = \frac{4C_{A0}X_{ef}^2}{(1-X_{ef})(1+\varepsilon X_{ef})} \quad (\text{E4-5.7})$$

Rearranging to use Polymath yields

$$X_{ef} = \sqrt{\frac{K_C(1-X_{ef})(1+\varepsilon X_{ef})}{4C_{A0}}} \quad (\text{E4-5.8})$$

For a flow system with pure N₂O₄ feed, $\varepsilon = y_{A0} \delta = 1(2-1)=1$.

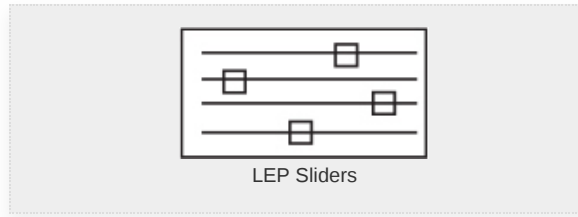
We shall let X_{ef} represent the equilibrium conversion in a flow system. Equation (E4-5.8) written in the Polymath format becomes

$$f(X_{ef}) = X_{ef} - [K_C * (1 - X_{ef}) * (1 + \varepsilon * X_{ef}) / 4 / C_{A0}]^{0.5}$$

This solution is also shown in Table E4-5.3 $X_{ef} = 0.51$

Note that the equilibrium conversion in a flow reactor (i.e., $X_{ef} = 0.51$), with no pressure drop, is greater than the equilibrium conversion in a constant-volume batch reactor ($X_{eb} = 0.44$). Recalling Le Châtelier's principle, can you suggest an explanation for this difference in X_e ? This example is

continued in Problem P4-1_A (a). Be sure to use Wolfram and/or Python in the Living Example Problems (LEPs) to see how the ratio (X_{eb}/X_{ef}) varies with ε and C_{T0} .



3. **Rate laws.** Assuming that the reaction follows an elementary rate law, then

$$-r_A = k_A \left[C_A - \frac{C_B^2}{K_C} \right] \quad (\text{E4-5.9})$$

1. *For a constant volume ($V = V_0$) batch system*

Here, $C_A = N_A/V_0$ and $C_B = N_B/V_0$. Substituting Equations (E4-5.2) and (E4-5.3) into the rate law, we obtain the rate of disappearance of A as a function of conversion

$$-r_A = k_A \left[C_A - \frac{C_B^2}{K_C} \right] = k_A \left[C_{A0} (1 - X) - \frac{4C_{A0}^2 X^2}{K_C} \right] \quad (\text{E4-5.10})$$

$$-r_A = f(X) \text{ for a batch reactor with } V = V_0$$

2. *For a flow system*

Here, $C_A = F_A/v$ and $C_B = F_B/v$ with $v = v_0 (1 + \varepsilon X)$. Consequently, we can substitute Equations (E4-5.5) and (E4-5.6) into Equation (E4-5.9) to obtain

$$-r_A = k_A \left[\frac{C_{A0}(1-X)}{1+\varepsilon X} - \frac{4C_{A0}^2 X^2}{K_C(1+\varepsilon X)^2} \right] \quad (\text{E4-5.11})$$

$$-r_A = f(X) \text{ for a flow reactor}$$

As expected, the dependence of reaction rate on conversion, that is, $-r_A = f(X)$, for a constant-volume batch system (i.e., Equation (E4-5.10)) is different

than that for a flow system (Equation (E4-5.11)) for gas-phase reactions.

If we substitute the values for C_{A0} , K_C , ε , and $k_A = 0.5 \text{ min}^{-1}$ in Equation (E4-5.11), we obtain $-r_A$ solely as a function of X for the flow system.

$$-r_A = \frac{0.5}{\text{min}} \left[0.072 \frac{\text{mol}(1-X)}{\text{dm}^3(1+X)} - \frac{4(0.075 \text{ mol/dm}^3)^2 X^2}{0.01 \text{ mol/dm}^3(1+X)^2} \right]$$

$$-r_A = 0.036 \left[\frac{(1-X)}{(1+X)} - \frac{2.88 X^2}{(1+X)^2} \right] \left(\frac{\text{mol}}{\text{dm}^3 \cdot \text{min}} \right) \quad (\text{E4-5.12})$$

We can now use Equation (E4-5.12) to prepare our Levenspiel plot to find either the CSTR or PFR volume.

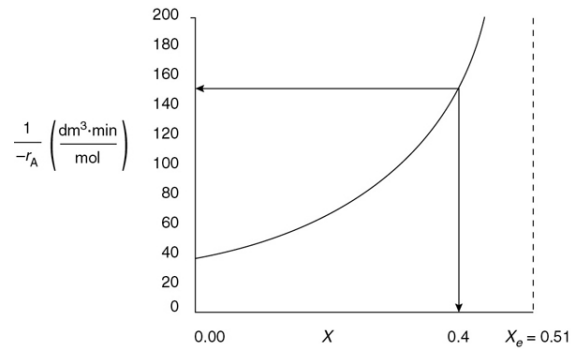


Figure E4-5.1 Levenspiel plot for a flow system.

$$X_e = 0.51$$

We see as we approach equilibrium, $X_e = 0.51$, $-r_A$ goes to zero and $(1/-r_A)$ goes to infinity.

4. **CSTR volume.** Just for fun (and this *really* is fun), let's fast forward and calculate the CSTR reactor volume necessary to achieve 80% of the equilibrium conversion of 51% (i.e., $X = 0.8X_e = (0.8)(0.51) = 0.4$) for a molar feed rate of A of 3 mol/min.

Plotting the reciprocal of Equation (E4-5.12) to obtain Levenspiel plot as we did in Chapter 2, it can be seen in Figure E4-5.1 when $X = 0.4$ then as

$$\left(\frac{1}{-r_A} \right)_{x=0.4} = 143 \frac{\text{dm}^3 \text{ min}}{\text{mol}}$$

then for $F_{A0} = 3 \text{ mol/min}$



Keeping an eye on things to come

$$\begin{aligned}
 V &= F_{A0} X \left(\frac{1}{-r_A} \right)_{X=0.4} \\
 &= \left(\frac{3 \text{ mol}}{\text{min}} \right) (0.4) (143) \frac{\text{dm}^3 \text{ min}}{\text{mol}} \\
 V &= 171 \text{ dm}^3
 \end{aligned}$$

A quicker way to find the CSTR volume, rather than drawing a Levenspiel plot, is to simply evaluate Equation (E4-5.12) at $X = 0.4$

$$-r_A = 0.036 \left[\frac{(1-0.4)}{(1+0.4)} - \frac{2.88(0.4)^2}{(1+(0.4))^2} \right] = 0.0070 \text{ mol/dm}^3/\text{min}$$

Using Equation (2-13), we can now find the reactor volume

$$\begin{aligned}
 V &= \frac{F_{A0} X}{-r_A|_X} = \frac{F_{A0}(0.4)}{-r_A|_{0.4}} = \frac{(3 \text{ mol/min})(0.4)}{0.0070 \frac{\text{mol}}{\text{dm}^3 \cdot \text{min}}} \\
 V &= 171 \text{ dm}^3 = 0.171 \text{ m}^3
 \end{aligned}$$

The CSTR volume required to achieve 40% conversion is 0.171 m^3 . See Problem P4-1A (b) to calculate the PFR volume.

Analysis: The purpose of this example was to calculate the equilibrium conversion first for a constant-volume *batch reactor* in part (a), and then for a constant pressure *flow reactor* in part (b). One notes that there is a change in the total number of moles in this reaction and, as a result, these two equilibrium conversions (batch and flow) are not the same!! We next showed in part (c) how to express $-r_A = f(X)$ for a reversible gas-phase reaction. Here we noted that the equations for the reaction-rate laws as a function of conversion, that is, $-r_A = f(X)$, are different for batch and flow reactors. Finally, in Part (d) having $-r_A = f(X)$, we specified a molar flow rate of A (i.e., 3.0 mol A/min) and calculated the CSTR volume necessary to achieve 40% conversion. We did this calculation to give insight to the types of analyses we, as chemical

reaction engineers, will carry out as we move into similar but more complex calculations in Chapters 5 and 6.

4.4 AND NOW... A WORD FROM OUR SPONSOR—SAFETY 4 (AWFOS–S4 THE SWISS CHEESE MODEL)

The Swiss Cheese Model shown in Figure 4-4 is another risk assessment tool, one that offers a deeper understanding into the layers of protection for chemical processes. This section (i.e., 4.4) is presented to give an overview of the model while the *Process Safety Across the Chemical Engineering Curriculum* Web site

(http://umich.edu/~safeche/swiss_cheese.html) gives more in-depth explanation. A layer of protection is either a preventative action put in place to reduce the chance that an incident will occur, or a mitigating action put in place to lessen the severity of an accident. These layers of protection can include using inherently safer designs, following proper lab procedures, wearing adequate personal protective equipment (PPE), and having an emergency response plan.

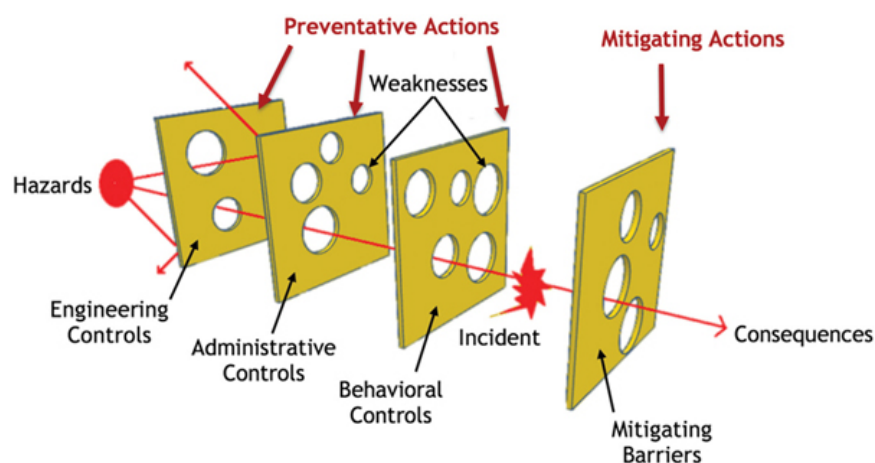


Figure 4-4 Swiss Cheese Model.

Even with the different levels or layers of protection, represented in Figure 4-4 as Swiss cheese slices, there is a possibility that a hazard will result in an incident. For an incident to occur, there must be vulnerability in each layer of protection, represented by holes in the slices of cheese. A hole is a weakness in that layer of protection (e.g., a backup cooling system, a faulty pressure relief valve). The size and number of holes in the cheese represent the relative lack of reliability of that layer. *This model illustrates the importance of having redundant and strong protective layers so that hazards do not pass through multiple protective actions undetected and unresolved.*

Understanding and implementing each protective level is important when running a chemical process. Table 4-4 shows and discusses each of the three control “cheese” slices (i.e., Engineering, Administrative, and Behavioral) while Table 4-5 shows and discusses the mitigating barriers.

TABLE 4-4 PREVENTATIVE ACTIONS

<i>Engineering ControlsAdministrative ControlsBehavioral Controls</i>		
<i>Engineering controls involve preventative actions that are designed into the system, for example, pressure</i>	<i>Administrative controls involve managerial actions taken to ensure everyone involved in the process possesses the same knowledge of the established safety procedures, for example, Management of Change (MoC) procedures: Before making a change to a process, employees are required to identify, review, and approve modifications to ensure changes are implemented safely.</i>	<i>Behavioral controls focus on actions that individuals can take to prevent an accident from occurring by using proper tools, and following lab procedures, MoC</i>

relief valves on heat exchangers.	and safety checklists as instructed.
--	--

TABLE 4-5 MITIGATING ACTIONS

<div>Mitigating Barriers</div> <p>These barriers focus on actions that lessen the severity or impact of an accident, for example, having an emergency response plan, wearing personal protective equipment (PPE), or the installation of a fire suppression system.</p>

Engineering Controls, Administrative Controls, and Behavioral Controls represent Preventative Actions designed to reduce the likelihood of an incident occurring, while Mitigating Barriers represent Mitigating Actions designed to lessen the impact or severity of an incident. It’s important to recognize that all of these layers of protection will have some weaknesses.

The main purpose of the Swiss Cheese Model is to visualize the vulnerability and how a hazard may be able to pass through the many different preventative actions in place.

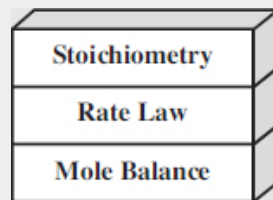
Further Reading on the Swiss Cheese Model:

Board, U.S. Chemical Safety and Hazard Investigation.
Fire at Praxair St. Louis: Dangers of Propylene
Cylinders. Washington DC, 2006.

D. Hatch, P. McCulloch, and I. Travers. “Visual
HAZOP,” *Chem. Eng.*, (917), 27–32 (2017,
November).

USCSB. “CSB Safety Video: Dangers of Propylene
Cylinders.” Online video clip. YouTube, 10 October
2007. Web. 8 May 2018.

Closure. Having completed this chapter, you should be able to write the rate law solely in terms of conversion and the reaction-rate parameters, (e.g., k , K_C) for both liquid-phase and gas-phase reactions. Once expressing $-r_A = f(X)$ is accomplished, you can proceed to use the techniques in **Chapter 2** to calculate reactor sizes and conversion for single CSTRs, PFRs, and PBRs, as well as those connected in series. However, in **Chapter 5** we will show you how to carry out these calculations *much more easily* by instead using a Table of Integrals or software such as Polymath, MATLAB, Python, or Wolfram without having to resort to Levenspiel plots. After studying this chapter, you should also be able to calculate the equilibrium conversion for both constant-volume batch reactors and for constant-pressure flow reactors. We have now completed the following building blocks of our CRE tower.



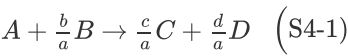
In **Chapter 5**, we will focus on the fourth and fifth blocks: Combine and Evaluate. In **Chapter 5**, we will focus on the **combine** and **evaluation** building blocks, which will then complete our algorithm for isothermal chemical reactor design.

The CRE Algorithm

- Mole Balance, [Chapter 1](#)
- Rate Law, [Chapter 3](#)
- Stoichiometry, [Chapter 4](#)
- Combine, [Chapter 5](#)
- Evaluate, [Chapter 5](#)
- Energy Balance, [Chapter 11](#)

SUMMARY

1. The *stoichiometric table* for the reaction given by Equation (S4-1) being carried out in a flow system is



2. In the case of ideal gases, Equation (S4-3) relates volumetric flow rate to conversion.

Batch reactor constant volume: V = V_0

V = V_0 \quad (S4-2)

Flow systems: Gas:

v = v_0 \left(\frac{P_0}{P} \right) (1 + \epsilon X) \frac{T}{T_0} \quad (S4-3)

Liquid: ()

v = v_0 \quad (S4- 4)

SpeciesEnteringChangeLeaving			
A	F_{A0}	-F_{A0}X	F_{A0}(1 - X)
B	F_{B0}	-\left(\frac{b}{a}\right) F_{A0}X	F_{A0}\left(\Theta_B - \frac{b}{a}X\right)
C	F_{C0}	\left(\frac{c}{a}\right) F_{A0}X	F_{A0}\left(\Theta_C + \frac{c}{a}X\right)
D	F_{D0}	\left(\frac{d}{a}\right) F_{A0}X	F_{A0}\left(\Theta_D + \frac{d}{a}X\right)
I	F_{I0}	---	F_{I0}

Totals	F_{T0}	$\delta F_{A0}X$	$F_T = F_{T0} + \delta F_{A0}X$
--------	----------	------------------	---------------------------------

Definitions of δ and ε : For the general reaction given by Equation (S4-1), we have

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \quad (\text{S4-5})$$

$$\delta = \frac{\text{Change in total number of moles}}{\text{mole of A reacted}}$$

and

$$\varepsilon = y_{A0}\delta \quad (\text{S4-6})$$

$$\varepsilon = \frac{\text{Change in total number of moles for complete conversion}}{\text{Total number of moles fed to the reactor}}$$

3. For incompressible liquids or for batch gas-phase reactions taking place in a constant volume, $V = V_0$, the concentrations of species A and C in the reaction given by Equation (S4-1) can be written as

$$C_A = \frac{F_A}{v} = \frac{F_{A0}}{v_0}(1 - X) = C_{A0}(1 - X) \quad (\text{S4-7})$$

$$C_c = C_{A0}(\Theta_c + \frac{c}{a}X) \quad (\text{S4-8})$$

Equations (S4-7) and (S4-8) also hold for gas-phase reactions carried out in constant-volume batch reactors.

4. For gas-phase reactions in continuous-flow reactors, we use the definition of concentration ($C_A = F_A/v$) along with the stoichiometric table and Equation (S4-3) to write the concentration of A and C in terms of conversion.

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v} = C_{A0} \left[\frac{1-X}{1+\varepsilon X} \right] P \left(\frac{T_0}{T} \right) \quad (\text{S4-9})$$

$$C_c = \frac{F_c}{v} = C_{A0} \left[\frac{\Theta_c + (c/a)X}{1+\varepsilon X} \right] P \left(\frac{T_0}{T} \right) \quad (\text{S4-10})$$

with $\Theta_c = \frac{F_{c0}}{F_{A0}} = \frac{C_{c0}}{C_{A0}} = \frac{y_{c0}}{y_{A0}}$ and $p = \frac{p}{p_0}$

5. In terms of gas-phase molar flow rates, the concentration of species i is

$$C_i = C_{T0} \frac{F_i}{F_T} \frac{P}{P_0} \frac{T_0}{T} \quad (\text{S4-11})$$

Equation (S4-11) must be used for membrane reactors (Chapter 6) and for multiple reactions (Chapter 8).

6. Many catalytic rate laws are given in terms of partial pressure, for example,

$$-r'_A = \frac{K_A P_A}{1 + K_A P_A} \quad (\text{S4-12})$$

The partial pressure is related to conversion through the stoichiometric table. For any species “i” in the reaction

$$P_i = P_{A0} \frac{(\Theta_i + v_i X)}{(1 + \epsilon X)} \quad (\text{S4-13})$$

For species A

$$P_A = P_{A0} \frac{(1-X)}{(1+\epsilon X)} p$$

Substituting in the rate law

$$-r'_A = \frac{K_A P_{A0} \frac{(1-X)}{(1+\epsilon X)} P}{1 + K_A P_{A0} \frac{(1-X)}{(1+\epsilon X)} P} = \frac{k P_{A0} (1-X) p}{(1+\epsilon X) + K_A P_{A0} (1-X) P} \quad (\text{S4-14})$$

CRE WEB SITE MATERIALS

(<http://www.umich.edu/~elements/6e/04chap/obj.html>)

Useful Links

Living
Example
Problems

Extra
Help

Additional
Materials

Professional
Reference
Shelf

Computer
Simulation
Problem
Statements

YouTube
Videos

Evaluation

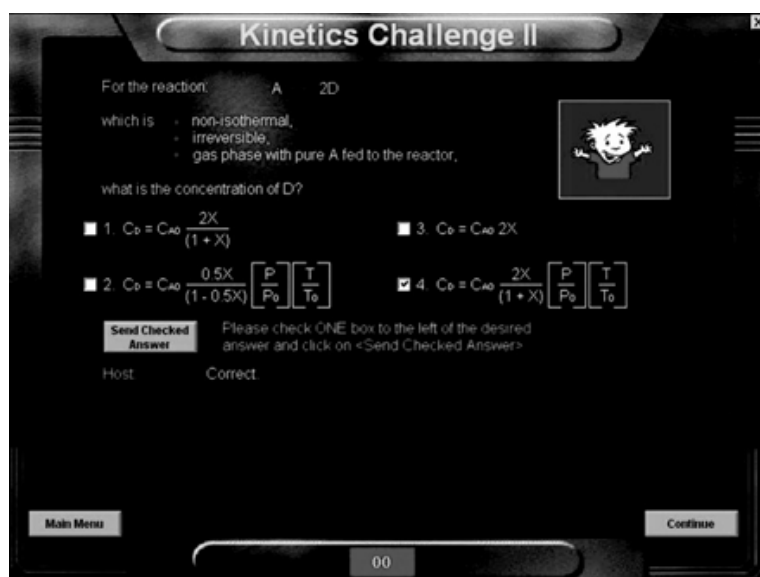
Self Tests

i>Clicker
Questions

Interactive Computer Games

(<http://umich.edu/~elements/6e/icm/index.html>) Quiz Show II Jeopardy (<http://umich.edu/~elements/6e/icm/kinchal2.html>). A

Jeopardy Game competition between AIChE student chapters is held at the annual AIChE meeting.



QUESTIONS AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$A = \bullet \quad B = \blacksquare \quad C = \blacklozenge \quad D = \blacklozenge\blacklozenge$$

QUESTIONS

Q4-1_A QBR (*Question Before Reading*). What are the differences in writing the concentrations as a function of conversion for gas-phase and liquid-phase reactions?

Q4-2_A i>clicker. Go to the Web site (http://www.umich.edu/~elements/6e/04chap/iclicker_ch4_q1.html) and view at least five i>clicker questions. Choose one that could be used as is, or a variation thereof, to be included on the next exam. You also could consider the opposite case, explaining why the

question should *not* be on the next exam. In either case, explain your reasoning.

Q4-3_A Example 4-1. Would the example be correct if water were considered an inert? Explain.

Q4-4_A Example 4-2. How would the answer change if the initial concentration of glyceryl stearate were 3 mol/dm³? Rework Example 4-2 correctly using the information given in the problem statement.

Q4-5_A Example 4-3. Under what conditions will the concentration of the inert nitrogen be constant? Plot Equation (E4-5.2) in terms of $(1/-r_A)$ as a function of X up to value of $X = 0.99$. What did you find?

Q4-6_A Can you name the English rock group that was famous worldwide in the 1970s and 1980s and whose lead singer was Freddie Mercury? The group had a resurgence in 2019 when Adam Lambert took over for Freddie, who had died in 1991. *Hint:* See Problem P5-22_A.

Q4-7_A What did you learn from the *Swiss Cheese Model* (e.g., make a list)?

Q4-8_A Go to the LearnChemE screencast link for Chapter 4 (<http://www.umich.edu/~elements/6e/04chap/learn-cheme-videos.html>).

1. View one or more of the screencast 5- to 6-minute videos and write a two-sentence evaluation.
2. What did the screencast do well and what could be improved?

Q4-9_A AWFOS–S4 Swiss Cheese Model.

1. What is the main purpose of implementing the Swiss Cheese Model in a workplace?
2. Categorize engineering controls, administrative controls, behavioral controls, and mitigating barriers as preventative actions or mitigating actions. List an example of each.

3. What happens when all of the weaknesses/vulnerabilities in the controls/barriers line up?
4. What was the *takeaway lesson* from this safety section?

COMPUTER SIMULATIONS AND EXPERIMENTS

P4-1_A (a) Example 4-4: SO₂ Oxidation

Wolfram and Python

1. Vary Θ_B and observe the change in reaction rate. Go to the extremes and explain what is causing the curve to change the way it does.
2. Vary the parameters and list the parameters that have the greatest and the least effect on the reaction rate.
3. Write a set of conclusions about the experiments you carried out by varying the sliders in parts (i) through (iii).

Polymath

4. Using the molar flow rate of SO₂ (A) of 3 mol/h and Figure E4-4.1, calculate the fluidized bed (i.e., CSTR catalyst weight) necessary for 40% conversion.
5. Next, consider the entering flow rate of SO₂ is 1000 mol/h. Plot $(F_{A0}/-r_A)$ as a function of X to determine the fluidized bed catalyst weight necessary to achieve 30% conversion, and 99% of the equilibrium conversion, that is, $X = 0.99 X_e$.

(b) Example 4-5: Equilibrium Conversion

1. Using Figure E4-5.1 and the methods in Chapter 2, estimate the PFR volume for 40% conversion for a molar flow rate of A of 5 dm³/min.
2. Using Figure E4-5.1 and the methods in Chapter 2, estimate the time to achieve 40% conversion in a batch reactor when the initial concentration is 0.05 mol/dm³.

Wolfram and Python

3. What values of K_C and C_{A0} cause X_{ef} to be the farthest away from X_{eb} ?
4. What values of K_C and C_{A0} will cause X_{eb} and X_{ef} to be the closest together?
5. Observe the plot of the ratio of $\left(\frac{X_{eb}}{X_{er}}\right)$ as a function of y_{A0} . Vary the values of K_C and C_{T0} . What conclusions can you draw?
6. Write a set of conclusions from your experiment (i) through (vi).

INTERACTIVE COMPUTER GAMES

P4-2_A Load the Interactive Computer Games (ICG) Kinetic

Challenge from the CRE Web site. Play the game and then record your performance number for the module

that indicates your mastering of the material. Your professor has the key to decode your performance number. ICG Kinetics Challenge Performance # _____.

A *Jeopardy Game* competition between AIChE student chapters is held at the annual AIChE meeting. You might find one of these questions asked.

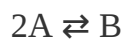
Kinetics Challenge II

Rate	Law	Stoich
------	-----	--------

100	100	100
200	200	200
300	300	300

PROBLEMS

P4-3_A The elementary reversible reaction



is carried out in a flow reactor where pure A is fed at a concentration of 4.0 mol/dm^3 . If the equilibrium conversion is found to be 60%,

1. What is the equilibrium constant, K_C if the reaction is a gas-phase reaction? (**Ans:** Gas: $K_C = 0.328 \text{ dm}^3/\text{mol}$)
2. What is the K_C if the reaction is a liquid-phase reaction? (**Ans:** Liquid: $K_C = 0.469 \text{ dm}^3/\text{mol}$)

- Write $=r_A$ solely as a function of conversion (i.e., evaluating all symbols) when the reaction is an elementary, reversible, gas-phase, isothermal reaction with no pressure drop with $k_A = 2 \text{ dm}^6/\text{mol}\cdot\text{s}$ and $K_C = 0.5$ all in proper units.
- Repeat (c) for a constant-volume batch reactor.

P4-4_B Stoichiometry. The elementary gas reaction

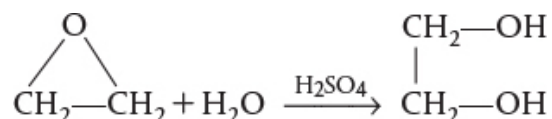


is carried out isothermally in a PFR with no pressure drop. The feed is equal molar in A and B, and the entering concentration of A is 0.1 mol/dm^3 . Set up a stoichiometric table and then determine the following.

- What is the entering concentration (mol/dm^3) of B?
- What are the concentrations of A and C (mol/dm^3) at 25% conversion of A?
- What is the concentration of B (mol/dm^3) at 25% conversion of A?
(Ans: $C_B = 0.1 \text{ mol/dm}^3$)
- What is the concentration of B (mol/dm^3) at 100% conversion of A?
- If at a particular conversion the rate of formation of C is 2 mol/min/dm^3 , what is the rate of formation of A at the same conversion?
- Write $=r_A$ solely as a function of conversion (i.e., evaluating all symbols) when the reaction is an elementary, irreversible, gas-phase, isothermal reaction with no pressure drop with an equal molar feed and with $C_{A0} = 2.0 \text{ mol/dm}^3$ at $k_A = 2 \text{ dm}^6/\text{mol}\cdot\text{s}$.
- What is the rate of reaction at $X = 0.5$?

P4-5_A Set up a stoichiometric table for each of the following reactions and express the concentration of each species in the reaction as a function of conversion, evaluating all constants (e.g., $=$, $=$). Next, assume the reaction follows an elementary rate law, and write the reaction rate solely as a function of conversion, that is, $-r_A = f(X)$.

- For the liquid-phase reaction



the entering concentrations of ethylene oxide and water, after mixing the inlet streams, are 16.13 and 55.5 mol/dm^3 , respectively. The specific reaction rate is $k = 0.1 \text{ dm}^3/\text{mol} \cdot \text{s}$ at 300 K with $E = 12500 \text{ cal/mol}$.

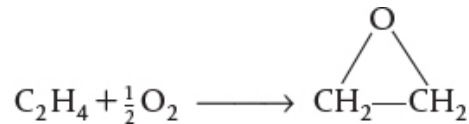
1. After finding $-r_A = f(X)$, calculate the CSTR space-time, τ , for 90% conversion at 300 K and also at 350 K .
2. If the volumetric flow rate is 200 liters per second, what are the corresponding reactor volumes? (**Ans:** At 300 K : $V = 439 \text{ dm}^3$ and at 350 K : $V = 22 \text{ dm}^3$)

2. For the isothermal gas-phase pyrolysis



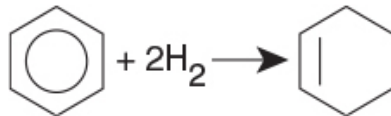
pure ethane enters a flow reactor at 6 atm and 1100 K , with $\Delta P = 0$. Set up a stoichiometric table and then write $-r_A = f(X)$. How would your equation for the concentration and reaction rate, that is, $-r_A = f(X)$, change if the reaction were to be carried out in a constant-volume batch reactor?

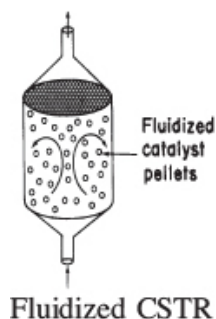
3. For the isothermal, isobaric, catalytic gas-phase oxidation



the feed enters a PBR at 6 atm and 260°C , and is a stoichiometric mixture of only oxygen and ethylene. Set up a stoichiometric table and then write $-r'_A$ as a function of partial pressures. Express the partial pressures and $-r'_A$ as a function of conversion for (1) a fluidized batch reactor and (2) a PBR. Finally, write $-r'_A$ solely as a function of the rate constant and conversion.

4. Set up a stoichiometric table for the isothermal, catalytic gas-phase reaction carried out in a fluidized CSTR.



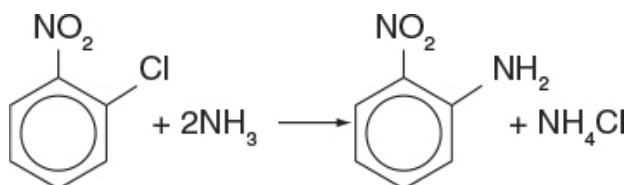


The feed is stoichiometric and enters at 6 atm and 170°C. What catalyst weight is required to reach 80% conversion in a fluidized CSTR at 170°C and at 270°C? The rate constant is defined with respect to benzene and $v_0 = 50 \text{ dm}^3/\text{min}$.

$$K_B = \frac{53 \text{ mol}}{\text{Kgcat} \cdot \text{min} \cdot \text{atm}^3} \text{ at } 300 \text{ K with } E = 80 \text{ kJ/mol}$$

First write the rate law in terms of partial pressures and then express the rate law as a function of conversion. Assume $\Delta P \approx 0$.

P4-6A *Orthonitroaniline* (an important intermediate in dyes—called *fast orange*) is formed from the reaction of *orthonitrochlorobenzene* (ONCB) and aqueous ammonia (see explosion in [Figure E13-2.1](#) in [Example 13-2](#)).



The liquid-phase reaction is first order in both ONCB and ammonia with $k = 0.0017 \text{ m}^3/\text{kmol} \cdot \text{min}$ at 188°C with $E = 11273 \text{ cal/mol}$. The initial entering concentrations of ONCB and ammonia are 1.8 and 6.6 kmol/m^3 , respectively (more on this reaction in [Chapter 13](#)).

1. Set up a stoichiometric table for this reaction for a flow system.
2. Write the rate law for the rate of disappearance of ONCB in terms of concentration.
3. Explain how parts (a) and (b) would be different for a batch system.

(d) Write $-r_A$ solely as a function of conversion.

$$-r_A = \underline{\hspace{2cm}}$$

5. What is the initial rate of reaction ($X = 0$)

at 188°C? $-r_A = \underline{\hspace{2cm}}$

at 25°C? $-r_A = \underline{\hspace{2cm}}$

at 288°C? $-r_A = \underline{\hspace{2cm}}$

6. What is the rate of reaction when $X = 0.90$

at 188°C? $-r_A = \underline{\hspace{2cm}}$

at 25°C? $-r_A = \underline{\hspace{2cm}}$

at 288°C? $-r_A = \underline{\hspace{2cm}}$

7. What would be the corresponding CSTR reactor volume at 25°C to achieve 90% conversion and at 288°C for a feed rate of $2 \text{ dm}^3/\text{min}$

at 25°C? $V = \underline{\hspace{2cm}}$

at 288°C? $V = \underline{\hspace{2cm}}$

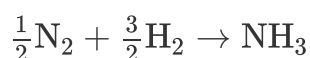
P4-7_B OEQ (Old Exam Question). Consider the following elementary gas-phase reversible reaction to be carried out isothermally with no pressure drop and for an equal molar feed of A and B with $C_{A0} = 2.0 \text{ mol/dm}^3$.



- What is the concentration of B initially? $C_{B0} = \underline{\hspace{2cm}}$ (mol/dm^3)
- What is the limiting reactant? $\underline{\hspace{2cm}}$
- What is the exit concentration of B when the conversion of A is 25%?
 $C_B = \underline{\hspace{2cm}}$ (mol/dm^3)

4. Write $-r_A$ solely as a function of conversion (i.e., evaluating all symbols) when the reaction is an elementary, reversible, gas-phase, isothermal reaction with no pressure drop with an equal molar feed and with $C_{A0} = 2.0 \text{ mol/dm}^3$, $k_A = 2 \text{ dm}^6/\text{mol}^2\cdot\text{s}$, and $K_C = 0.5$ all in proper units $-r_A = \underline{\hspace{2cm}}$.
5. What is the equilibrium conversion?
6. What is the rate when the conversion is
 1. 0%?
 2. 50%?
 3. $0.99 X_e$?

P4-8B OEQ (Old Exam Question). The gas-phase reaction

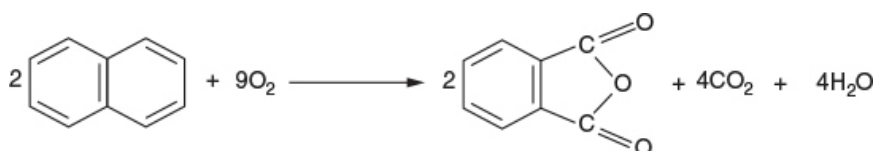


is to be carried out isothermally first in a flow reactor. The molar feed is 50% H_2 and 50% N_2 , at a pressure of 16.4 atm and at a temperature of 227°C .

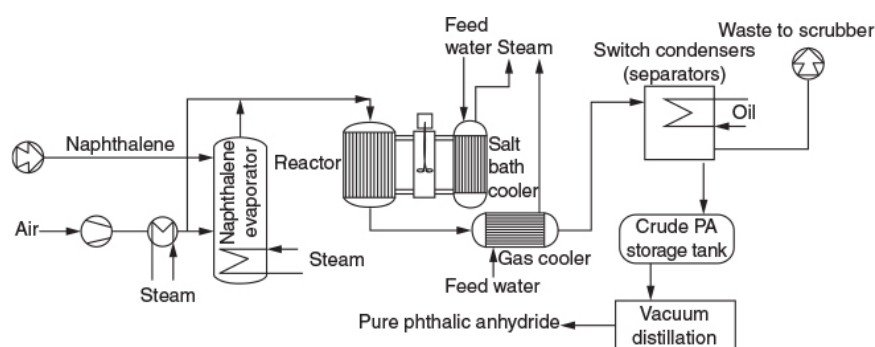
1. Construct a complete stoichiometric table.
2. Express the concentrations in mol/dm^3 of each for the reacting species as a function of conversion. Evaluate C_{A0} , δ , and ϵ , and then calculate the concentrations of ammonia and hydrogen when the conversion of H_2 is 60%. (**Ans:** $C_{\text{H}_2} = 0.1 \text{ mol/dm}^3$)
3. Suppose by chance the reaction is elementary with $k_{\text{N}_2} = 40 \text{ dm}^3/\text{mol}\cdot\text{s}$. Write the rate of reaction *solely* as a function of conversion for (1) a flow reactor and for (2) a constant-volume batch reactor.

P4-9B OEQ (Old Exam Question). There were 820 million pounds of phthalic anhydride produced in the United States in 1995. One of the end uses of phthalic anhydride is in the fiberglass of sailboat hulls. Phthalic anhydride can be produced by the partial oxidation of naphthalene in either a fixed or a fluidized catalytic bed. A flow sheet for the commercial process is shown below. Here, the reaction is carried out in fixed bed reactor with a vanadium pentoxide catalyst packed in 25 mm

diameter tubes. A production rate of 31,000 tons per year would require 15,000 tubes.



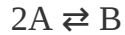
Assume the reaction is first order in oxygen and second order in naphthalene with $k_N = 0.01 \text{ dm}^6/\text{mol}^2/\text{s}$.



Adapted from Process Technology and Flowsheet Volume II. Reprints from Chemical Engineering, McGraw Hill Pub. Co., p. 111.

1. Set up a stoichiometric table for this reaction for an initial mixture of 3.5% naphthalene and 96.5% air (mol %), and use this table to develop the relations listed in parts (b) and (c). The initial/entering pressure and temperature are $P_0 = 10 \text{ atm}$ and $T_0 = 500 \text{ K}$.
2. Express the following solely as a function of the conversion of naphthalene, X for a constant-volume isothermal batch reactor $V = V_0$.
(1) The concentration of O_2 , C_{O_2} . (2) The total pressure P . (3) The rate of reaction, $-r_N$. (4) Then calculate the time to achieve 90% conversion.
3. Repeat (b) for an isothermal flow reactor to find C_{O_2} , volumetric flow rate and the reaction rate $-r_N$ as a function of conversion.
4. What CSTR and PFR volumes are necessary to achieve 98% conversion of naphthalene for an entering volumetric flow rate of $10 \text{ dm}^3/\text{s}$.
5. Write a few sentences about the above flow sheet to manufacture phthalic anhydride.

P4-10_B OEQ (Old Exam Question). The elementary reversible reaction



is carried out isothermally in a flow reactor with no pressure drop and where pure A is fed at a concentration of 4.0 mol/dm^3 . If the equilibrium conversion is found to be 60%

1. What is the equilibrium constant, K_C , if the reaction occurs in the gas phase?
2. What is the K_C if the reaction is a liquid-phase reaction?

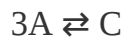
P4-11_B Consider the elementary gas-phase reversible reaction is carried out isothermally



Pure A enters at a temperature of 400 K and a pressure of 10 atm. At this temperature, $K_C = 0.25(\text{mol/dm}^3)^2$. Write the rate law and then calculate the equilibrium conversion for each of the following situations:

1. The gas-phase reaction is carried out in a constant-volume batch reactor.
2. The gas-phase reaction is carried out in a constant-pressure batch reactor.
3. Can you explain the reason why there would be a difference in the two values of the equilibrium conversion?

P4-12_B Repeat parts (a)–(c) of Problem **P4-11_B** for the reaction



Pure A enters at 400 K, 10 atm and the equilibrium constant is $K_C = 2.5 (\text{dm}^3/\text{mol})^2$.

4. Compare the equilibrium conversions in Problems P4-11_B and P4-12_B. Explain the trends, for example, is X_e for constant pressure always greater than X_e for constant volume? Explain the reasons for the similarities and differences in the equilibrium conversions in the two reactions.

P4-13_C OEQ (Old Exam Question). Consider a *cylindrical batch reactor* that has one end fitted with a

frictionless piston attached to a spring (Figure P4-13C). The reaction



with the rate law

$$-r_A = k_1 C_A^2 C_B$$

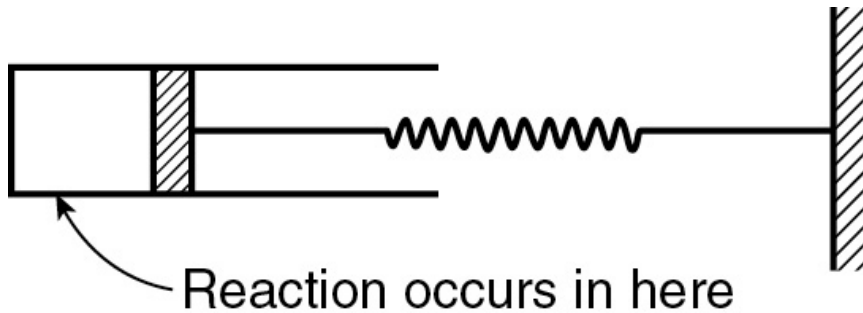


Figure P4-13C

is taking place in this type of reactor.

1. Write the rate law solely as a function of conversion, numerically evaluating all possible symbols. (Ans: $-r_A = 5.03 \times 10^{-9} [(1 - X)^3 / (1 + 3X)^{3/2}]$ lb mol/ft³·s.)
2. What is the conversion and rate of reaction when $V = 0.2$ ft³? (Ans: $X = 0.259$, $-r_A = 8.63 \times 10^{-10}$ lb mol/ft³·s.)

Additional information:

Equal moles of A and B are present at $t = 0$

Initial volume: 0.15 ft^3

Value of k_1 : $1.0 (\text{ft}^3/\text{lb mol})^2 \cdot \text{s}^{-1}$

The spring constant is such that the relationship between the volume of the reactor and pressure within the reactor is

$$V = (0.1)(P) \quad (V \text{ in } \text{ft}^3, P \text{ in atm})$$

Temperature of system (considered constant): 140°F

Gas constant: $0.73 \text{ ft}^3 \cdot \text{atm}/\text{lb mol} \cdot ^\circ\text{R}$

SUPPLEMENTARY READING

Further elaboration of the development of the general balance equation may be found on the CRE Web site

www.umich.edu/~elements/6e/index.html and also may or may not be found in

G. KEILLOR AND T. RUSSELL, *Dusty and Lefty: The Lives of the Cowboys* (Audio CD), St. Paul, MN: Highbridge Audio, 2006.

R. M. FELDER, R. W. ROUSSEAU, and L. G. Bullard, *Elementary Principles of Chemical Processes*, 4th ed. Global Edition, Singapore: John Wiley & Sons Singapore PTE Ltd., 2017, Chap. 4.

5. Isothermal Reactor Design: Conversion

Why, a four-year-old child could understand this.

Someone get me a four-year-old child.

—Groucho Marx

Overview. Chapters 1 and 2 discussed mole balances on reactors and the manipulation of these balances to predict batch reaction times and flow reactor sizes. Chapter 3 discussed reactions and reaction-rate laws, and Chapter 4 discussed reaction stoichiometry. In Chapters 5 and 6, we combine reactions and reactors as we bring all the material in the preceding four chapters together to arrive at a logical structure for the design of various types of reactors. By using this structure, one should be able to solve reactor engineering problems by reasoning, rather than by memorizing numerous equations together with the various restrictions and conditions under which each equation applies (e.g., whether or not there is a change in the total number of moles).



Tying everything together

In this chapter, we use the mole balances written in terms of conversion, shown in Chapter 2, Table S2-1, to study isothermal reactor designs. Conversion is the preferred parameter to measure progress for single reactions occurring in batch reactors (BRs), CSTRs, PFRs, and PBRs. Both batch reactor times and flow reactor volumes to achieve a given conversion will be calculated.

We have chosen four different reactions and four different reactors to illustrate the salient principles of isothermal reactor design using conversion as a variable, namely

- The use of a laboratory batch reactor to determine the specific reaction-rate constant, k , for the liquid-phase reaction to form ethylene glycol.
- The design of an industrial CSTR to produce ethylene glycol using k from the batch experiment.
- The design of a PFR for the gas-phase pyrolysis of ethane to form ethylene.
- The design of a packed-bed reactor with pressure drop to form ethylene oxide from the partial oxidation of ethylene.

When we put all these reactions and reactors together, we will see we have designed a chemical plant to produce 200 million pounds per year of ethylene glycol.

5.1 DESIGN STRUCTURE FOR ISOTHERMAL REACTORS

One of the primary goals of this chapter is to solve chemical reaction engineering (CRE) problems by using logic rather than memorizing which equation applies where. It is the author's experience that following this structure, shown in [Figure 5-1](#), will lead to a greater understanding of isothermal reactor design. We begin by applying our general mole balance equation (level ①) to a specific reactor to arrive at the design equation for that reactor (level ②). If the feed conditions are specified (e.g., N_{A0} or F_{A0}), all that is required to evaluate the design equation is the rate of reaction as a function of conversion at the same conditions as those at which the reactor is to be operated (e.g., temperature and pressure). When $-r_A = f(X)$ is known or given, one can go directly from level ③ to the last level, level ④, to determine either the batch time or reactor volume necessary to achieve the specified conversion.

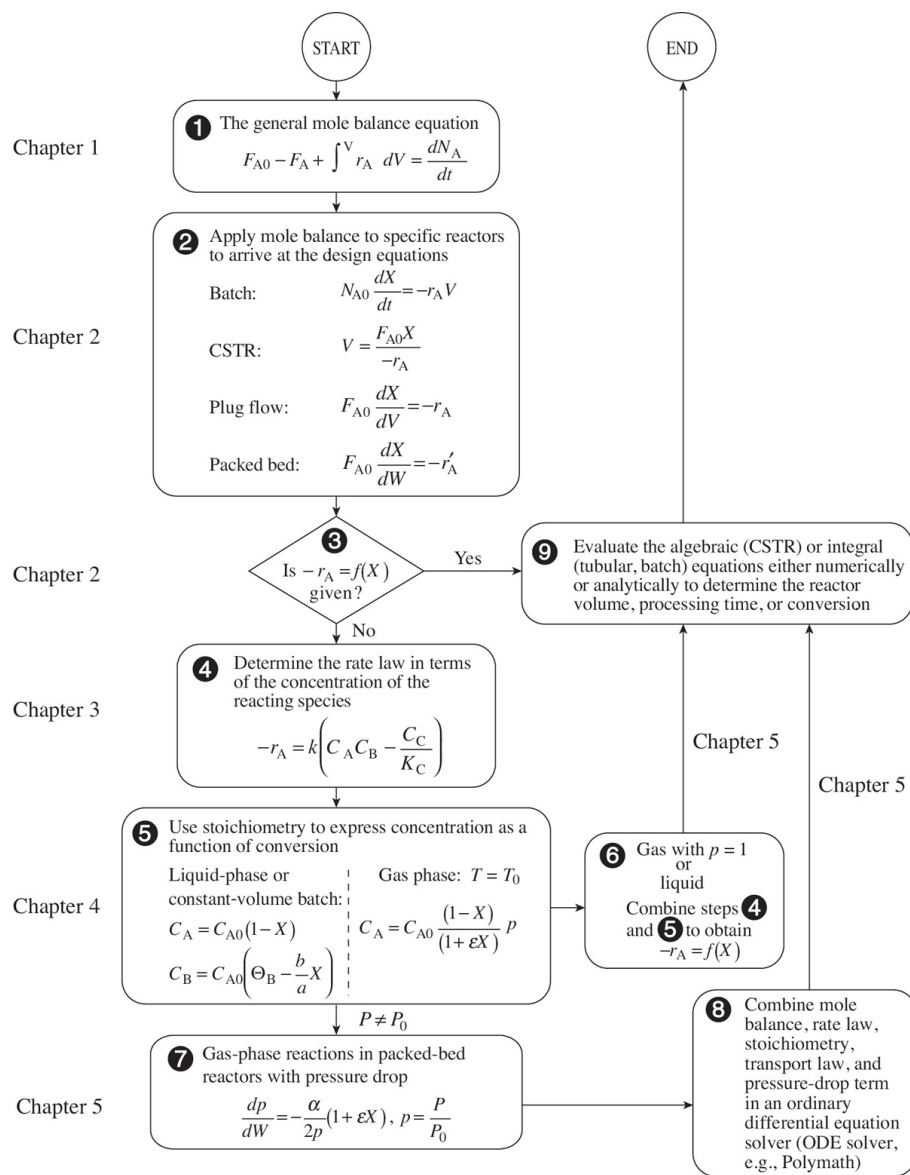


Figure 5-1 Isothermal-reaction design algorithm for conversion.

Logic versus memorization

Use the algorithm rather than memorizing equations.

When the rate of reaction is not given explicitly as a function of conversion, we must proceed to level **4**, where the rate law

must be determined by either finding it in books or journals or by determining it experimentally in the laboratory. Techniques for obtaining and analyzing rate data to determine the reaction order and rate constant are presented in Chapter 7. After the rate law has been established, one has only to use stoichiometry (level ⑤) together with the conditions of the system (e.g., constant volume, temperature) to express concentration as a function of conversion.

For liquid-phase reactions and for gas-phase reactions with no pressure drop ($P = P_0$), one can combine the information in levels ④ and ⑤ to express the rate of reaction as a function of conversion and arrive at level ⑥. It is now possible to determine either the time or reactor volume necessary to achieve the desired conversion by substituting the relationship linking conversion and rate of reaction into the appropriate design equation (level ⑨).

For gas-phase reactions in packed beds where there is a pressure drop, we need to proceed to level ⑦ to evaluate the pressure ratio p (i.e., $(p = P / P_0)$) in the concentration term using the Ergun equation (Section 5.5). In level ⑧, we combine the equations for pressure drop in level ⑦ with the information in levels ④ and ⑤ to proceed to level ⑨, where the equations are then evaluated in the appropriate manner (i.e., analytically using a table of integrals, or numerically using an ODE solver). Although this structure emphasizes the determination of a reaction time or reactor volume for a specified conversion, it can also readily be used for other types of reactor calculations, such as determining the conversion for a specified volume. Different manipulations can be performed in level ⑨ to answer the different types of questions mentioned here.

The structure shown in [Figure 5-1](#) allows one to develop a few basic concepts and then to arrange the parameters (equations) associated with each concept in a variety of ways. Without such a structure, one is faced with the possibility of choosing or perhaps memorizing the correct equation from a *multitude of equations* that can arise for a variety of different combinations of reactions, reactors, and sets of conditions. The challenge is to put everything together in an orderly and logical fashion so that we can arrive at the correct equation for a given situation.

Fortunately, by using the algorithm to formulate CRE problems shown in [Figure 5-2](#), which happens to be analogous to the algorithm for ordering dinner from a fixed-price menu in a fine French restaurant, we can eliminate virtually all memorization. In both of these algorithms, we must make **choices** in each category. For example, in ordering from a *Fix Pris* French menu,[†] we begin by choosing one dish from the *appetizers* listed. Analogous to the French menu, in Step 1 of the CRE algorithm shown in [Figure 5-2](#), we begin by choosing the appropriate mole balance for one of the three types of reactors. After making our reactor choice (e.g., PFR), we go to the small oval ready to make our second choice in Step 2, Rate Laws. In Step 2 we choose the rate law (*entrée*), and in Step 3 we specify whether the reaction is gas or liquid phase (*cheese* or *dessert*). Finally, in Step 4 we combine Steps 1, 2, and 3 and either obtain an analytical solution or solve the equations using an ODE solver.

French Menu
Analogy
Choices

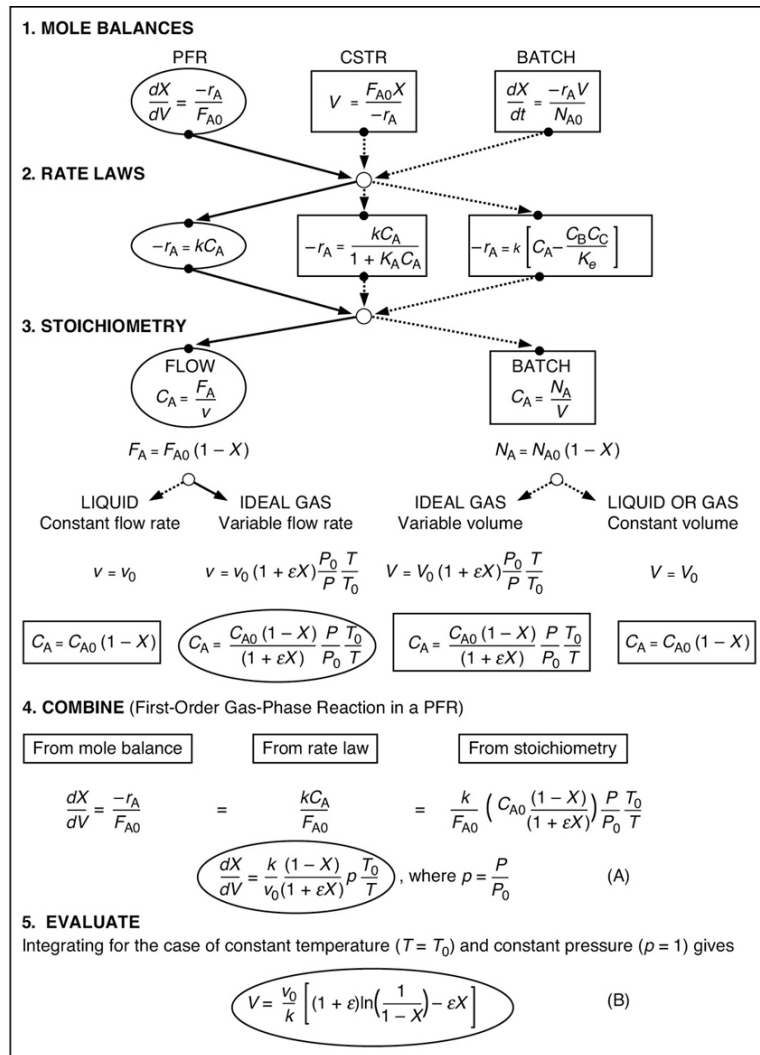


Figure 5-2 Algorithm for isothermal reactors.

† View the full French menu at

(<http://www.umich.edu/~elements/6e/05chap/summary-french.html>).

The Algorithm

1. Mole balance
2. Rate law
3. Stoichiometry
4. Combine
5. Evaluate

We now will apply this algorithm to a specific situation. Suppose that we have, as shown in [Figure 5-2](#), mole balances for three reactors, three rate laws, and the equations for concentrations for both liquid and gas phases. In [Figure 5-2](#), we see how the algorithm is used to formulate the equation to calculate the *PFR reactor volume for a first-order gas-phase reaction*. The pathway to arrive at this equation is shown by the ovals connected to the dark lines through the algorithm. The dashed lines and the boxes represent other pathways for solutions to other situations. The algorithm for the pathway shown in [Figure 5-2](#) is

1. **Mole balances**, choose species A reacting in a PFR
2. **Rate laws**, choose the irreversible first-order reaction
3. **Stoichiometry**, choose the gas-phase concentration
4. **Combine** steps 1, 2, and 3 to arrive at Equation A
5. **Evaluate**. The combine step can be evaluated either
 1. Analytically ([Appendix A.1](#))
 2. Graphically ([Chapter 2](#))
 3. Numerically ([Appendix A.4](#))
 4. Via software (e.g., Polymath, Wolfram, Python, MATLAB)

In [Figure 5-2](#), we chose to integrate Equation A for constant temperature and pressure to find the volume necessary to achieve a specified conversion (or calculate the conversion that can be achieved in a specified reactor volume). Unless the parameter values are zero, we typically **do not** (please trust me when I say *do not*) substitute numerical values for parameters in the combine step until the very end, that is Step 5 *Evaluate*.

Substitute parameter values in Steps 1–4 *only* if they are zero.

For the case of isothermal operation with no pressure drop, we were able to obtain an analytical solution, given by Equation B in [Figure 5-2](#), which gives the reactor volume necessary to achieve a conversion X for a first-order gas-phase reaction carried out isothermally in a PFR. However, in the majority of situations, analytical solutions to the ordinary differential equations appearing in the combine step are not possible. Consequently, we include Polymath, or some other ODE solver such as MATLAB, Wolfram, or Python in our menu in that it makes obtaining solutions to the differential equations much more palatable.

We can solve the equations in the **combine** step either

1. Analytically ([Appendix A.1](#))
2. Graphically ([Chapter 2](#))
3. Numerically ([Appendix A.4](#))
4. Using software (e.g., Polymath).

5.2 BATCH REACTORS (BRS)

One of the jobs in which chemical engineers are involved is the scale-up of laboratory experiments to pilot-plant operation or to full-scale production. In the past, a pilot plant would be designed based on laboratory data. In this section, we show how to analyze a laboratory-scale batch reactor in which a liquid-phase reaction of known order is being carried out.

In modeling a batch reactor, we assume there is no inflow or outflow of material and that the reactor is well mixed. For most liquid-phase reactions, the density change with reaction is usually small and can be neglected (i.e., $V = V_0$). In addition,

for *gas-phase* reactions in which the batch reactor volume remains constant, we also have $V = V_0$.

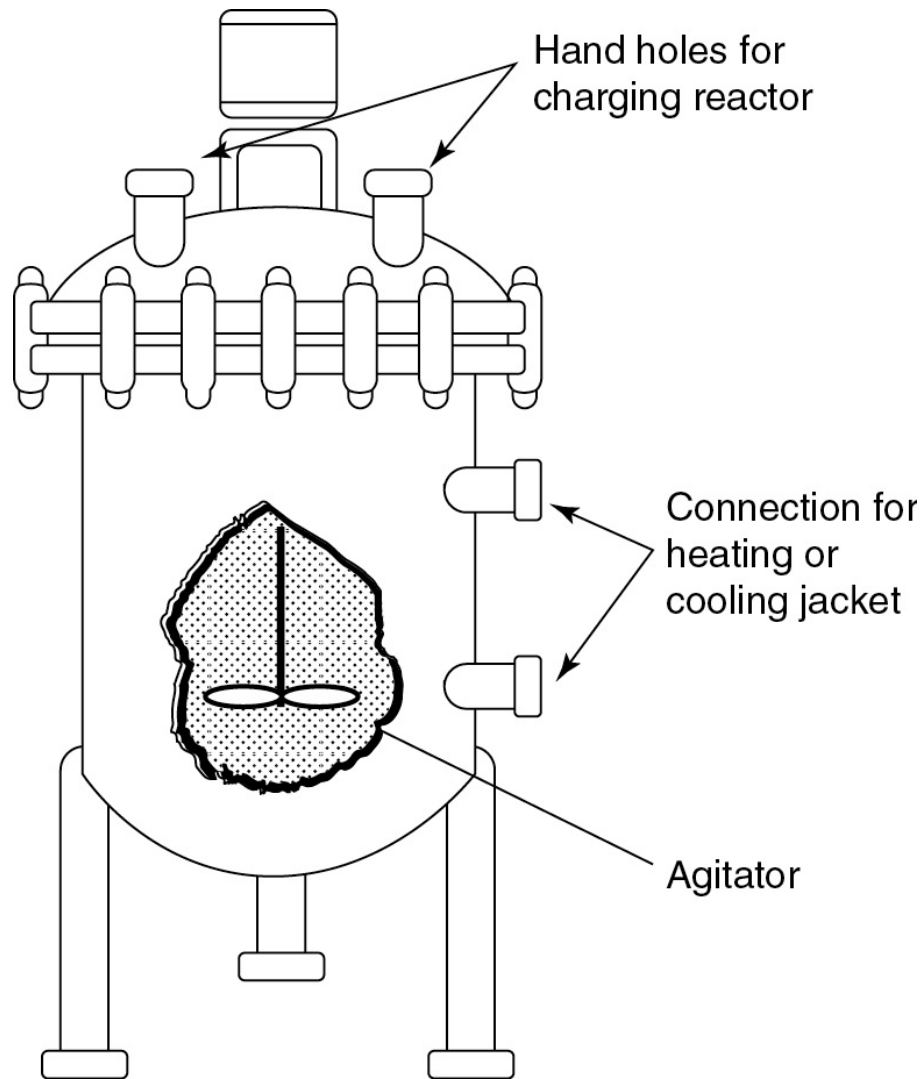


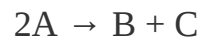
Figure 5-3 Batch reactor.

(<http://encyclopedia.che.engin.umich.edu/Pages/Reactors/Batch/Batch.html>)

5.2.1 Batch Reaction Times

The time necessary to achieve a specific conversion depends on how fast the reaction takes place, which in turn is dependent on the rate constant and the reactant concentrations.

To get a feel of how long it takes to carry a batch reaction, we shall calculate the batch reaction times for different values of the reaction rate constant, k , for a first- and second-order reaction. First, let's solve for the time to achieve a conversion X for the second-order reaction:



The Algorithm

1. The **mole balance** on a constant-volume, $V = V_0$, batch reactor is

$$N_{A0} \frac{dX}{dt} = -r_A V_0 \quad (2-6)$$

Mole Balance

Dividing by N_{A0} and recognizing $C_{A0} = N_{A0}/V_0$ we obtain

$$\frac{dX}{dt} = -\frac{r_A}{C_{A0}} \quad (5-1)$$

2. The **rate law** is

$$-r_A = k_2 C_A^2 \quad (5-2)$$

Rate Law

3. From **stoichiometry** for a constant-volume batch reactor, we obtain

$$C_A = \frac{N_A}{V} = \frac{N_A}{V_0} = \frac{N_{A0}}{V_0} (1 - X) = C_{A0} (1 - X) \quad (4-12)$$

Stoichiometry

4. **Combining** the **mole balance**, **rate law**, and **stoichiometry** we obtain

$$-r_A = k_2 C_{A0}^2 (1 - X)^2$$

Next, we substitute for $-r_A$ in Equation (5-1)

$$\frac{dX}{dt} = k_2 C_{A0} (1 - X)^2 \quad (5-3)$$

Combine

5. To **evaluate**, we separate the variables and integrate

$$\frac{dX}{(1-X)^2} = k_2 C_{A0} dt$$

Initially, if $t = 0$, then $X = 0$. If the reaction is carried out isothermally, k will be constant; we can integrate this equation (see [Appendix A.1](#) for a table of integrals used in CRE applications) to obtain

$$\int_0^t dt = \frac{1}{k_2 C_{A0}} \int_0^X \frac{dX}{(1-X)^2}$$

Evaluate

$$t_R = \frac{1}{k_2 C_{A0}} \left(\frac{X}{1-X} \right) \quad (5-4)$$

Second-order, isothermal, constant-volume batch reactor

This time is the reaction time t (i.e., t_R) needed to achieve a conversion X for a second-order reaction in a batch reactor. In a similar fashion, we can apply the CRE algorithm to a first-

order reaction to obtain the reaction time, t_R , needed to achieve a conversion X

$$t_R = \frac{1}{k_1} \ln \frac{1}{1-X} \tag{5-5}$$

First-order isothermal constant-volume batch reactor

It is important to have a grasp of the order of magnitudes of batch reaction times, t_R , to achieve a given conversion, say 90%, for different values of the product of specific reaction rate, k , and initial concentration, C_{A0} . Table 5-1 shows the algorithm to find the batch reaction times, t_R , for both first- and second-order reactions carried out isothermally. We can obtain these estimates of t_R by considering the first- and second-order irreversible reactions of the form

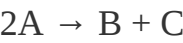


TABLE 5-1 ALGORITHM TO ESTIMATE REACTION TIMES

Material Balance	$\frac{dX}{dt_R} = \frac{-r_A}{N_{A0}} V$	
	Rate Law	
	First-Order $-r_A = k_1 C_A$	Second-Order $-r_A = k_2 C_A^2$
$C_A = \frac{N_A}{V_0} = C_{A0} (1 - X)$		

St
oic
hio
me
try
(V
=
 V_0)

Co
m
bi
ne
 $\frac{dX}{dt_R} = k_1(1 - X)$

$$\frac{dX}{dt_R} = k_2 C_{A0}(1 - X)^2$$

Ev
alu
ate
 $t_R = \frac{1}{k_1} \ln \frac{1}{1-X}$

$$t_R = \frac{X}{k_2 C_{A0}(1-X)}$$

(In
teg
rat
e)

Constant Volume $V = V_0$

For *first-order reactions*, the reaction time to reach 90% conversion (i.e., $X = 0.9$) in a constant-volume batch reactor scales as

$$t_R = \frac{1}{k_1} \ln \frac{1}{1-X} = \frac{1}{k_1} \ln \frac{1}{1-0.9} = \frac{2.3}{k_1}$$

If $k_1 = 10^{-4} \text{ s}^{-1}$,

$$t_R = \frac{2.3}{10^{-4} \text{ s}^{-1}} = 23000 \text{ s} = 6.4 \text{ h}$$

The time necessary to achieve 90% conversion in a batch reactor for an irreversible first-order reaction in which the specific reaction rate, k_1 , is (10^{-4} s^{-1}) is 6.4 h.

For *second-order reactions*, we have

$$t_R = \frac{1}{k_2 C_{A0}} \frac{X}{1-X} = \frac{0.9}{k_2 C_{A0}(1-0.9)} = \frac{9}{k_2 C_{A0}}$$

If $k_2 C_{A0} = 10^{-3} \text{ s}^{-1}$,

$$t_R = \frac{9}{10^{-3} \text{ s}^{-1}} = 9000 \text{ s} = 2.5 \text{ h}$$

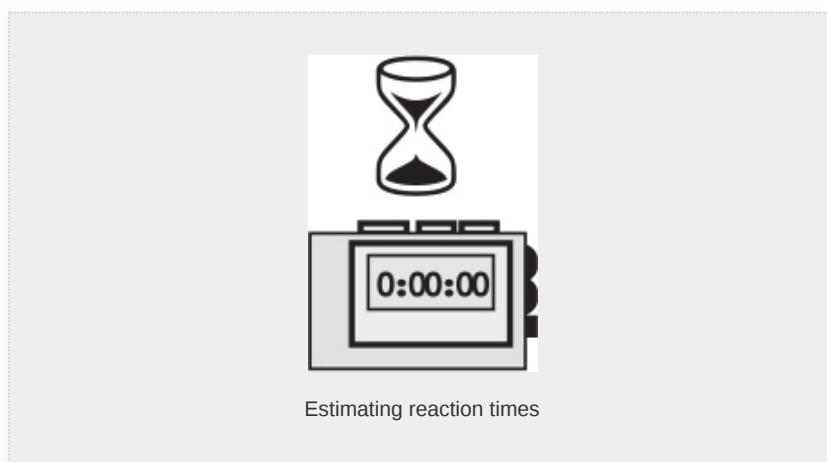
We note that if 99% conversion had been required for this value of kC_{A0} , the reaction time, t_R , would jump to 27.5 h.

Table 5-2 gives the *order of magnitude* of time to achieve 90% conversion for first- and second-order irreversible batch reactions. Flow reactors would be used for reactions with *characteristic reaction times*, t_R , of minutes or less.

TABLE 5-2 BATCH REACTION TIMES

First-Order Second-Order Reaction Time		
$k_1 \text{ (s}^{-1}\text{)}$	$k_2 C_{A0} \text{ (s}^{-1}\text{)}$	t_R
10^{-4}	10^{-3}	Hours
10^{-2}	10^{-1}	Minutes

1	10	Seconds
1000	10000	Milliseconds



The times in Table 5-2 are the reaction time to achieve 90% conversion (i.e., to reduce the concentration from C_{A0} to $0.1 C_{A0}$). The total cycle time in any batch operation is often, considerably longer than the reaction time, t_R , as one must account for the time necessary to fill (t_f) and heat (t_e) the reactor together with the time necessary to clean the reactor between batches, t_c . In some cases, the reaction time calculated from Equations (5-4) and (5-5) may be only a small fraction of the total cycle time, t_t .

$$t_t = t_f + t_e + t_c + t_R$$

Typical cycle times for a batch polymerization process are shown in Table 5-3. Batch polymerization reaction times, t_R , may vary between 5 and 60 hours. Clearly, decreasing the

reaction time with a 24-hour reaction, as is the case in Example 13-2, is a promising endeavor. As the reaction time is reduced (e.g., 2.5 hours for a second-order reaction with $k_2C_{A0} = 10^{-3} \text{ s}^{-1}$), it becomes important to use large lines and pumps to achieve rapid transfers and to utilize efficient sequencing to minimize the cycle time.

TABLE 5-3 TYPICAL CYCLE TIME FOR A BATCH
POLYMERIZATION PROCESS

Activity	Time (h)
1. Charge feed to the reactor and agitate, t_f	0.5–2.0
2. Heat to reaction temperature, t_e	0.5–2.0
3. Carry out reaction, t_R	(varies)
4. Empty and clean reactor, t_c	1.5–3.0
<hr/>	
Total time excluding reaction	2.5–7.0

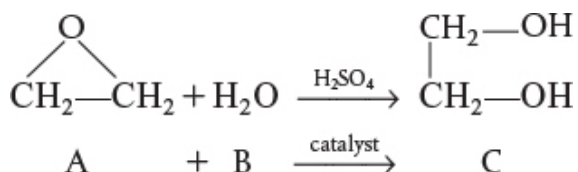
Batch operation times

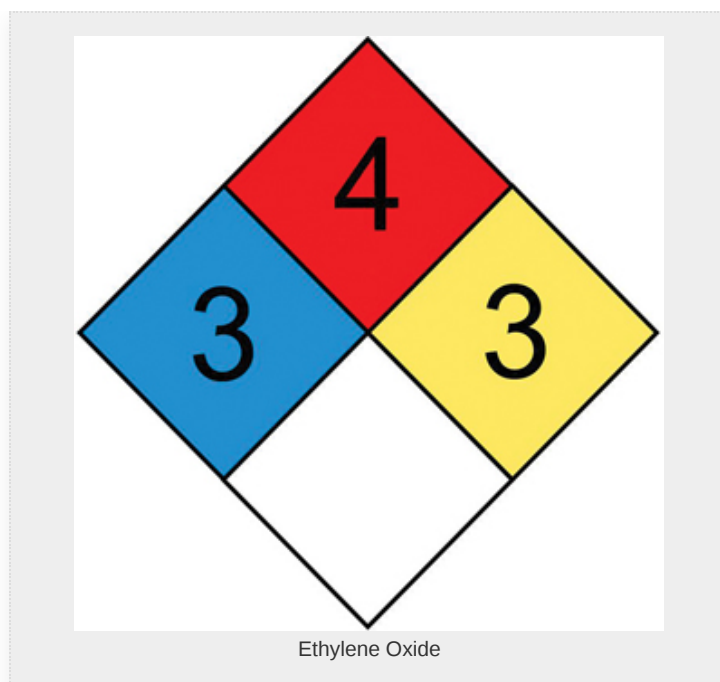
Usually, one has to optimize the reaction time with the processing times listed in Table 5-3 to produce the maximum number of batches (i.e., pounds or kilograms of product) in a day.

In the next four examples, we will describe the various reactors needed to produce 200 million pounds per year of ethylene glycol from a feedstock of ethane. We begin by finding the rate constant, k , for the hydrolysis of ethylene oxide to form ethylene glycol.

Example 5–1 Determining k from Batch Data

It is desired to design a CSTR to produce 200 million pounds of ethylene glycol per year by hydrolyzing ethylene oxide. However, before the design can be carried out, it is necessary to perform and analyze a batch-reactor experiment to determine the specific reaction-rate constant, k . Because the reaction will be carried out isothermally, the specific reaction rate will need to be determined only at the reaction temperature of the CSTR. At temperatures above 80°C, there is a significant by-product formation, while at temperatures below 40°C, the reaction does not proceed at a significant rate; consequently, a temperature of 55°C has been chosen. Because water is present in excess, its concentration (55.5 mol/dm³) may be considered constant during the course of the reaction. The reaction is first-order in ethylene oxide.





In the laboratory experiment, 500 mL of a 2 M solution (2 kmol/m^3) of ethylene oxide (A) in water was mixed with 500 mL of water (B) containing 0.9 wt % sulfuric acid, which is a catalyst. The temperature was maintained at 55°C . The concentration of ethylene glycol (C) was recorded as a function of time (Table E5-1.1).

1. Derive an equation for the concentration of ethylene glycol as a function of time.
2. Rearrange the equation derived in (a) to obtain a linear plot of a function concentration versus time.
3. Using the data in Table E5-1.1, determine the specific reaction rate, k , at 55°C .

TABLE E5-1.1 CONCENTRATION–TIME DATA

Time (min) Concentration of Ethylene Glycol (C) (kmol/m^3)*	
0.0	0.000

0.5	0.145
-----	-------

1.0	0.270
-----	-------

1.5	0.376
-----	-------

2.0	0.467
-----	-------

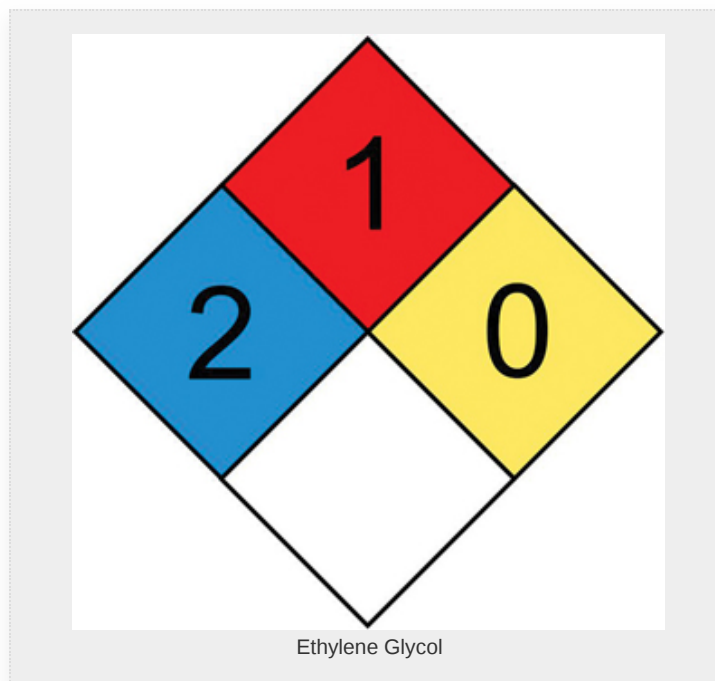
3.0	0.610
-----	-------

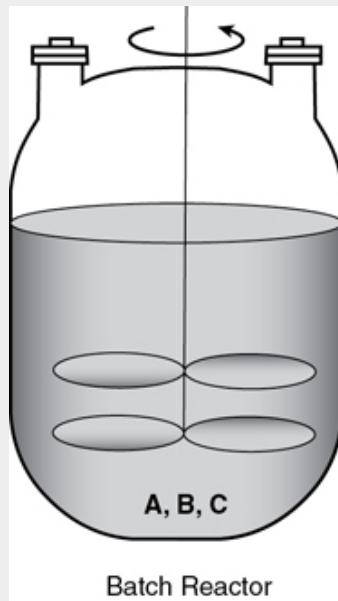
4.0	0.715
-----	-------

6.0	0.848
-----	-------

10.0	0.957
------	-------

* $1 \text{ kmol/m}^3 = 1 \text{ mol/dm}^3 = 1 \text{ mol/L}$.





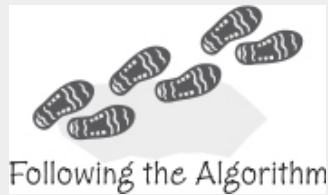
Check 10 types of homework problems on the CRE Web site for more solved examples using this algorithm.
(<http://www.umich.edu/~elements/6e/probsolv/totypes/index.htm>)

Solution

Part (a)

1. The **mole balance** on ethylene oxide (A) given in Equation (1-5) for a constant volume, V_0 , well-mixed batch reactor can be written as

$$\frac{1}{V_0} \frac{dN_A}{dt} = r_A \quad (\text{E5-1.1})$$

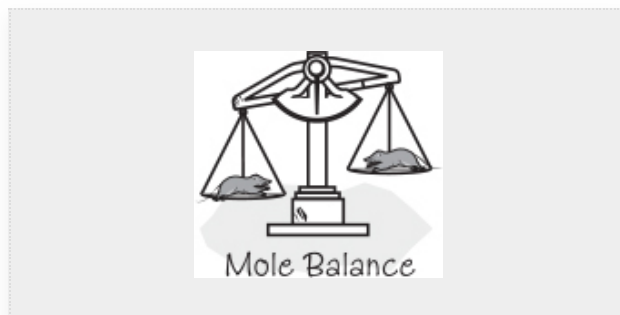


Taking V_0 inside the differential and recalling that the concentration is

$$C_A = \frac{N_A}{V_0}$$

then the differential mole balance becomes

$$\frac{d(N_A/V_0)}{dt} = \frac{dC_A}{dt} = r_A \quad (\text{E5-1.2})$$



2. The **rate law** for the ethylene oxide hydrolysis is

$$-r_A = kC_A \quad (\text{E5-1.3})$$



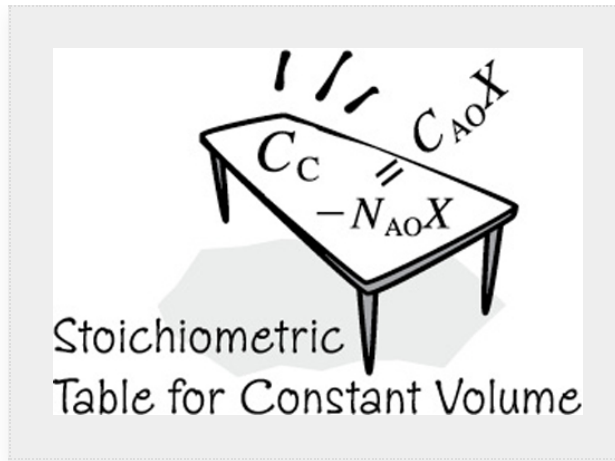
Because water is present in such excess, the concentration of water at any time t is virtually the same as the initial concentration, and the rate law is independent of the concentration of H_2O ($C_B \cong C_{B0} = 55.5$ moles per dm^3).[†]

[†] The reaction is actually pseudo first order because B is in excess so that $-r_A = k_2 C_A C_B \cong k_2 C_{B0} C_A = k C_A$ where $k = k_2 C_{B0}$.

3. **Stoichiometry.** Liquid phase, no volume change, $V = V_0$ (Table E5-1.2):

TABLE E5-1.2 STOICHIOMETRIC TABLE

Species	Symbol	Initial	Change	Remaining	Concentration
CH ₂ CH ₂ O	A	N _{A0}	-N _{A0} X	N _A = N _{A0} (1 - X)	C _A = C _{A0} (1 - X)
H ₂ O	B	Θ _B N _{A0}	-N _{A0} X	N _B = N _{A0} (Θ _B - X)	C _B = C _{A0} (Θ _B - X) C _B ≈ C _{A0} Θ _B = C _{B0}
(CH ₂ OH) ₂	C	0	N _{A0} X	N _C = N _{A0} X	C _C = C _{A0} X = C _{A0} - C _A
		N _{T0}	N _T = N _{T0} - N _{A0} X		



Recall that Θ_B is the ratio of the initial number of moles of B to moles of A (i.e., $\Theta_B = \frac{N_{B0}}{N_{A0}} = \frac{C_{B0}}{C_{A0}}$).

For species B, that is, water,

$$C_B = C_{A0}(\Theta_B - X)$$

We quickly see that water is in excess, as the molarity of water is 55 moles per liter. The initial concentration of A after mixing the two volumes together is 1 molar. Therefore,

$$\Theta_B = \frac{C_{B0}}{C_{A0}} = \frac{55 \text{ mol/dm}^3}{1 \text{ mol/dm}^3} = 55$$

The maximum value of X is 1, and $\Theta_B \gg 1$, therefore C_B is virtually constant

$$C_B \cong C_{A0} \Theta_B = C_{B0}$$

For species C, that is, ethylene glycol, the concentration is

$$C_C = \frac{N_C}{V_0} = \frac{N_{A0}X}{V_0} = \frac{N_{A0} - N_A}{V_0} = C_{A0} - C_A \quad (\text{E5-1.4})$$

4. **Combining** the rate law and the mole balance, we have

$$-\frac{dC_A}{dt} = kC_A \quad (\text{E5-1.5})$$

5. **Evaluate.** For isothermal operation, k is constant, so we can integrate this equation (E5-1.5)

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^t k dt = k \int_0^t dt$$



Combining mole balance, rate law, and stoichiometry

using the initial condition that

when $t = 0$, then $C_A = C_{A0} = 1 \text{ mol/dm}^3 = 1 \text{ kmol/m}^3$.

Integrating yields

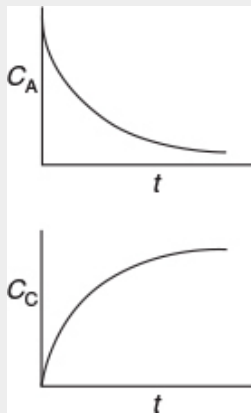
$$\ln \frac{C_{A0}}{C_A} = kt \quad (\text{E5-1.6})$$

The concentration of *ethylene oxide* (A) at any time t is

$$C_A = C_{A0}e^{-kt} \quad (\text{E5-1.7})$$

The concentration of *ethylene glycol* (C) at any time t can be obtained from the reaction stoichiometry, that is, Equation (E5-1.4)

$$C_C = C_{A0} - C_A = C_{A0} (1 - e^{-kt}) \quad (\text{E5-1.8})$$



Part (b)

We are now going to rearrange Equation (E5-1.8) for the concentration of ethylene glycol in such a manner that we can easily use the data in Table E5-1.1 to determine the rate constant k . Rearranging Equation (E5-1.8) to

$$(C_{A0} - C_C) = C_{A0}e^{-kt} \quad (\text{E5-1.9})$$

then dividing by C_{A0} and taking the natural log of both sides of Equation (E5-1.9) one obtains

$$\ln \frac{C_{A0} - C_C}{C_{A0}} = -kt \quad (\text{E5-1.10})$$

Part (c)

We see that a plot of $\ln[(C_{A0} - C_C)/C_{A0}]$ as a function of t will be a straight line with a slope $-k$. Using Table E5-1.1, we can construct Table E5-1.3 and use Excel to plot $\ln(C_{A0} - C_C)/C_{A0}$ as a function of t .

TABLE E5-1.3 PROCESSED DATA

t (min)	C_C (kmol/m ³)	$\frac{C_{A0}-C_C}{C_{A0}}$	$\ln\left(\frac{C_{A0}-C_C}{C_{A0}}\right)$
0.0	0.000	1.000	0.0000
0.5	0.145	0.855	-0.1570
1.0	0.270	0.730	-0.3150
1.5	0.376	0.624	-0.4720
2.0	0.467	0.533	-0.6290
3.0	0.610	0.390	-0.9420
4.0	0.715	0.285	-1.2550
6.0	0.848	0.152	-1.8840
10.0	0.957	0.043	-3.1470

From the slope of a plot of $\ln[(C_{A0} - C_C)/C_{A0}]$ versus t , we can find k , as shown in the Excel plot in [Figure E5-1.1](#).

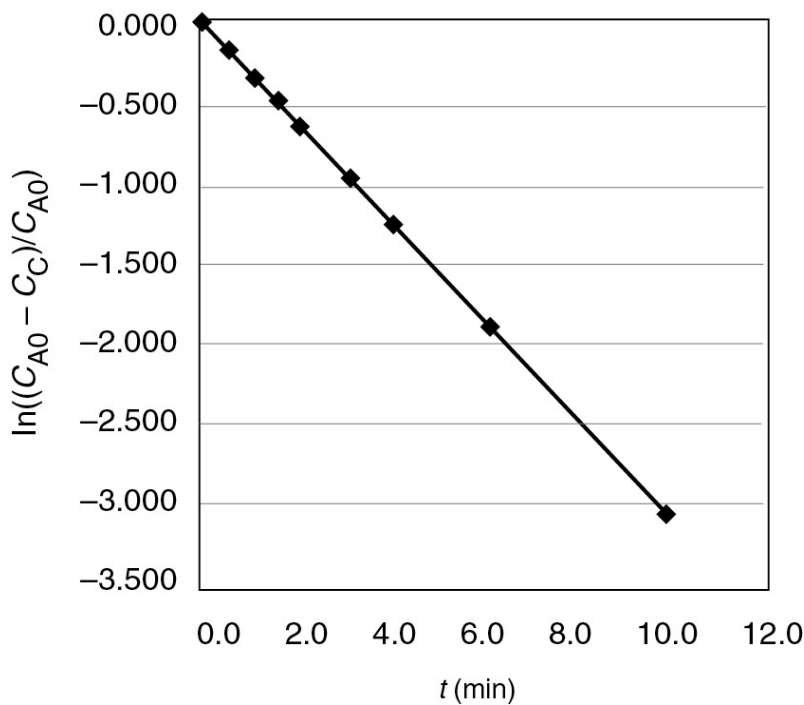


Figure E5-1.1 Excel plot of data.

Evaluating the specific reaction rate from *batch-reactor* concentration–time data

$$\text{Slope} = -k = -0.311 \text{ min}^{-1}$$

$$k = 0.311 \text{ min}^{-1}$$

The rate law becomes

$$-r_A = 0.311 \text{ min}^{-1} C_A \quad (\text{E5-1.11})$$

The rate law can now be used in the design of an industrial CSTR. For those who prefer to find k using semi-log graph paper, this type of analysis can be found at www.physics.uoguelph.ca/tutorials/GLP. Tutorials are also given in the *Summary Notes* for [Chapter 3](#) (last example) and [Chapter 7](#) (Excel).



Analysis: In this example, we used our CRE algorithm

**(mole balance → rate law → stoichiometry →
combine)**

to calculate the concentration of species C , C_C , as a function of time, t . We then used experimental batch data of C_C versus t to verify the reaction as a pseudo first-order reaction and to determine the *pseudo* first-order specific reaction-rate constant, k (s^{-1}).

5.3 CONTINUOUS-STIRRED TANK REACTORS (CSTRS)

Continuous-stirred tank reactors (CSTRs), such as the one shown here schematically in Figure 5-4, are typically used for liquid-phase reactions.

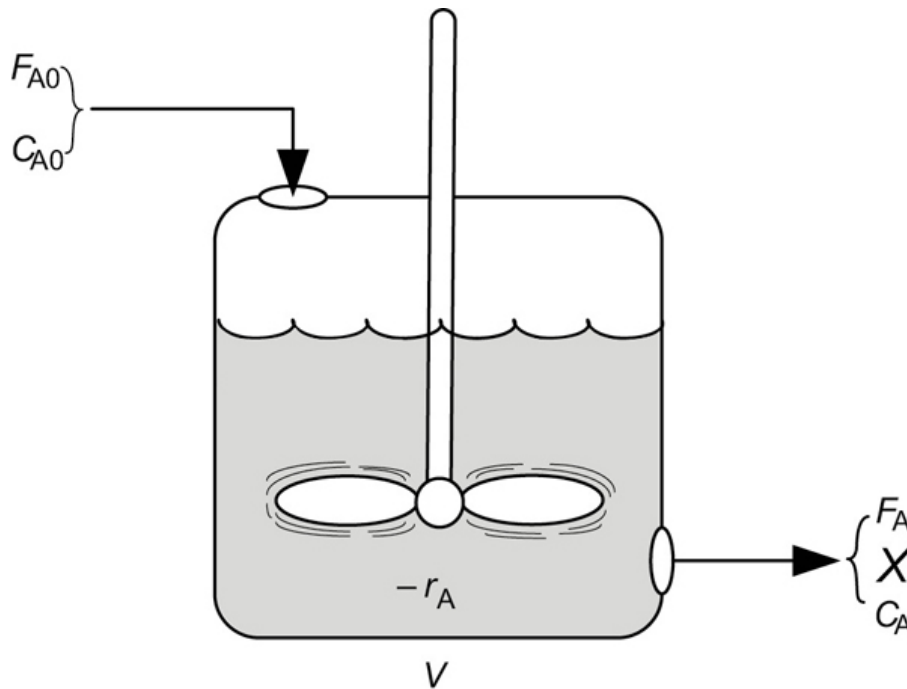


Figure 5-4 CSTR.

(<http://encyclopedia.che.engin.umich.edu/Pages/Reactors/CSTR/CSTR.html>)

In Chapter 2, we derived the following design equation for a CSTR

$$V = \frac{F_{A0}X}{(-r_A)_{\text{exit}}} \quad (2-13)$$

Mole Balance

which gives the volume V necessary to achieve a conversion X . As we saw in Chapter 2, the space time, τ , is a characteristic time of a reactor. To obtain the space time, τ , as a function of conversion, we first substitute for $F_{A0} = v_0 C_{A0}$ in Equation (2-13)

$$V = \frac{v_0 C_{A0} X}{(-r_A)_{\text{exit}}} \quad (5-6)$$

and then divide by v_0 to obtain the space time, τ , to achieve a conversion X in a CSTR

$$\tau = \frac{V}{v_0} = \frac{C_{A0}X}{(-r_A)_{\text{exit}}} \quad (5-7)$$

This equation applies to a single CSTR or to the first reactor of CSTRs connected in series.

5.3.1 A Single CSTR

5.3.1.1 First-Order Reaction in a CSTR

Let's consider a first-order irreversible reaction for which the rate law is

$$-r_A = kC_A$$

Rate Law

For liquid-phase reactions, there is no volume change during the course of the reaction, so we can use Equation (4-12) to relate concentration and conversion

$$C_A = C_{A0}(1 - X) \quad (4-12)$$

Stoichiometry

We can combine the mole balance equation (5-7), the rate law, and the concentration equation (4-12) to obtain

$$\tau = \frac{1}{k} \left(\frac{X}{1-X} \right)$$

Combine

Rearranging

$$X = \frac{\tau k}{1 + \tau k} \quad (5-8)$$

CSTR relationship between space time and conversion for a first-order liquid-phase reaction

A plot of conversion as a function of τk using Equation (5-8) is shown in Figure 5-5.

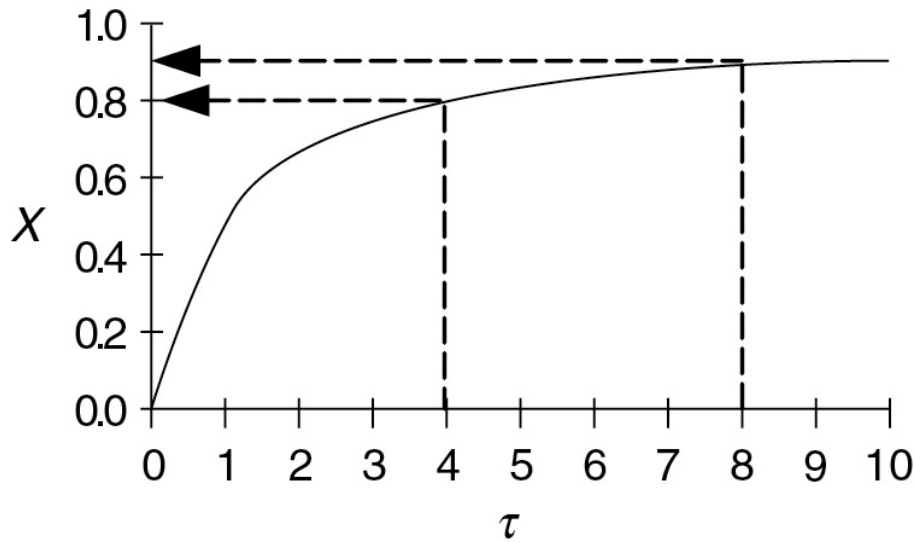


Figure 5-5 First-order reaction in a CSTR.

We can increase τk by either increasing the temperature to increase k or increasing the space time τ by increasing the volume V or decreasing the volumetric flow rate v_0 . For example, when we increase the reactor volume, V , by a factor of 2 (or decrease the volumetric flow rate v_0 by a factor of 2) as we go from $\tau k = 4$ to $\tau k = 8$, the conversion only increases from 0.8 to 0.89. Do you think it is worth the additional cost of a larger reactor to increase the conversion by only 0.09 or can you think of a better way to increase τk or the conversion?

We could also combine Equations (4-12) and (5-8) to find the exit reactor concentration of A, C_A ,

$$C_A = \frac{C_{A0}}{1+\tau k} \quad (5-9)$$

5.3.1.2 A Second-Order Reaction in a CSTR

For an irreversible second-order liquid-phase reaction, for example,

$$-r_A = kC_A^2$$

being carried out in a CSTR, the **combination** of the second-order **rate law** and the **design equation** (i.e., combined mole balance Equation (2-13) and rate law) yields

$$V = \frac{F_{A0}X}{-r_A} = \frac{F_{A0}X}{kC_A^2}$$

Using our stoichiometric table for constant density $v = v_0$, $C_A = C_{A0}(1 - X)$, and $F_{A0}X = v_0 C_{A0}X$, then

$$V = \frac{v_0 C_{A0}X}{kC_{A0}^2(1-X)^2}$$

Dividing both sides of the combined rate law and design equation for a second-order reaction by v_0 gives

$$\tau = \frac{V}{v_0} = \frac{X}{kC_{A0}(1-X)^2} \quad (5-10)$$

We solve Equation (5-10) for the conversion X

$$\begin{aligned} X &= \frac{\left(1+2\tau kC_{A0}\right) - \sqrt{\left(1+2\tau kC_{A0}\right)^2 - (2\tau kC_{A0})^2}}{2\tau kC_{A0}} \\ &= \frac{\left(1+2\tau kC_{A0}\right) - \sqrt{1+4\tau kC_{A0}}}{2\tau kC_{A0}} \end{aligned}$$

$$X = \frac{(1+2Da_2) - \sqrt{1+4Da_2}}{2Da_2} \quad (5-11)$$

Conversion for a second-order liquid-phase reaction in a CSTR

The minus sign must be chosen in the quadratic equation because X cannot be greater than 1. Conversion is plotted as a function of the Damköhler parameter for a second-order reaction, $Da_2 = \tau k C_{A0}$, in Figure 5-6. Observe from this figure that at high conversions (say 67%), a 10-fold increase in the reactor volume (or increase in the specific reaction rate by raising the temperature) will only increase the conversion up to 88%. This observation is a consequence of the fact that the CSTR operates under the condition of the lowest reactant concentration (i.e., the exit concentration), and consequently the smallest value of the rate of reaction.

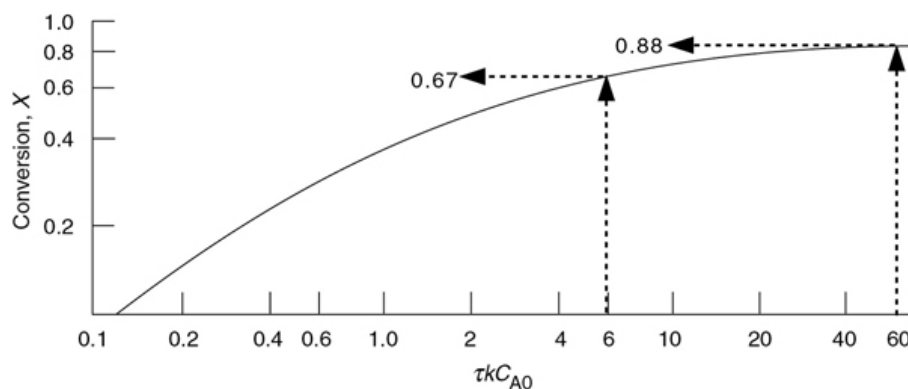


Figure 5-6 Conversion as a function of the Damköhler number ($Da_2 = \tau k C_{A0}$) for a second-order reaction in a CSTR.

5.3.1.3 The Damköhler Number

For a first-order reaction, the product τk is often referred to as the reaction **Damköhler number**, Da_1 , which is a dimensionless number that can give us a quick estimate of the

degree of conversion that can be achieved in continuous-flow reactors. The Damköhler number is the ratio of the rate of reaction of A to the rate of convective transport of A evaluated at the entrance to the reactor.

$$Da = \frac{-r_{A0}V}{F_{A0}}$$

$$Da = \frac{-r_{A0}V}{F_{A0}} = \frac{\text{Rate of reaction at entrance}}{\text{Entering flow rate of A}} = \frac{\text{"A reaction rate"}}{\text{"A convection rate"}}$$

The Damköhler number for a first-order irreversible reaction is

$$Da_1 = \frac{-r_{A0}V}{F_{A0}} = \frac{k_1 C_{A0} V}{v_0 C_{A0}} = \tau k_1$$

The Damköhler number for a second-order irreversible reaction is

$$Da_2 = \frac{-r_{A0}V}{F_{A0}} = \frac{k_2 C_{A0}^2 V}{v_0 C_{A0}} = \tau k_2 C_{A0}$$

It is important to know what values of the Damköhler number, Da , give high and low conversion in continuous-flow reactors. For irreversible reactions, a value of $Da = 0.1$ or less will usually give less than 10% conversion, and a value of $Da = 10.0$ or greater will usually give greater than 90% conversion; that is, the rule of thumb is

$$\begin{array}{l} \text{if } Da < 0.1, \text{ then } X < 0.1 \\ \text{if } Da > 10, \text{ then } X > 0.9 \end{array}$$

$$0.1 \leq Da \leq 10$$



Equation (5-8) for a first-order liquid-phase reaction in a CSTR can also be written in terms of the Damköhler number

$$X = \frac{Da_1}{1 + Da_1} \quad (5-12)$$

5.3.2 CSTRs in Series

A first-order reaction with no change in the volumetric flow rate ($v = v_0$) is to be carried out in two CSTRs placed in series (Figure 5-7).

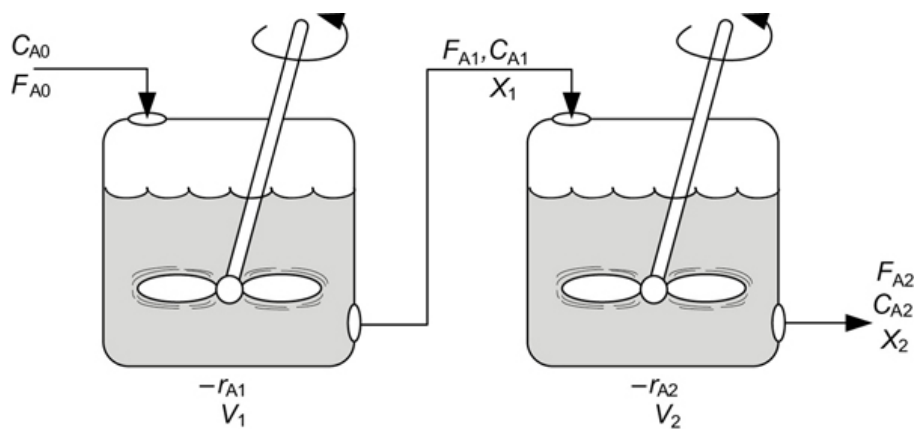


Figure 5-7 Two CSTRs in series.

The effluent concentration of reactant A from the first CSTR can be found using Equation (5-9)

$$C_{A1} = \frac{C_{A0}}{1 + \tau_1 k_1}$$

with $\tau_1 = V_1/v_0$. From a mole balance on reactor 2 one obtains

$$V_2 = \frac{F_{A1} - F_{A2}}{-r_{A2}} = \frac{v_0(C_{A1} - C_{A2})}{k_2 C_{A2}}$$

Solving for C_{A2} , the concentration exiting the second reactor, we obtain

$$C_{A2} = \frac{C_{A1}}{1 + \tau_2 k_2} = \frac{C_{A0}}{(1 + \tau_2 k_2)(1 + \tau_1 k_1)} \quad (5-13)$$

First-order reaction

If both reactors are of equal size ($\tau_1 = \tau_2 = \tau$) and operate at the same temperature ($k_1 = k_2 = k$), then

$$C_{A2} = \frac{C_{A0}}{(1 + \tau k)^2}$$

If, instead of two CSTRs in series, we had n equal-sized CSTRs connected in series ($\tau_1 = \tau_2 = \dots = \tau_n = \tau_i = (V_i/v_0)$) operating at the same temperature ($k_1 = k_2 = \dots = k_n = k$), the concentration leaving the last reactor would be

$$C_{An} = \frac{C_{A0}}{(1 + \tau k)^n} = \frac{C_{A0}}{(1 + Da_1)^n} \quad (5-14)$$

Substituting for C_{An} in terms of conversion

$$C_{A0}(1 - X) = \frac{C_{A0}}{(1 + Da_1)^n}$$

CSTRs in series

and rearranging, the conversion for these identical n tank reactors in series will be

$$X = 1 - \frac{1}{(1+Da_1)^n} \equiv 1 - \frac{1}{(1+\tau k)^n} \quad (5-15)$$

Conversion as a function of the number of tanks in series

Recall from Chapter 2, Figure 2-6, that as the number of tanks n becomes large, the conversion approaches that of a PFR.

A plot of the conversion as a function of the number of CSTRs (i.e., tanks) in series for a first-order reaction is shown in Figure 5-8 for various values of the Damköhler number τk . Observe from Figure 5-8 that when the product of the space time and the specific reaction rate is relatively large, say, $Da_1 \geq 1$, approximately 90% conversion is achieved in two or three reactors;

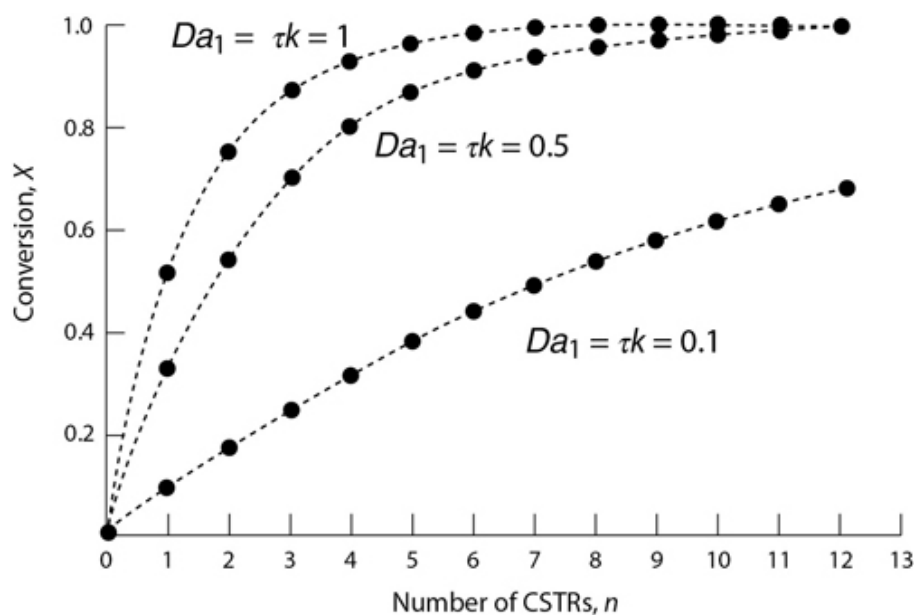


Figure 5-8 Conversion as a function of the number of CSTRs (i.e., tanks) in series for different Damköhler numbers for a first-order reaction.

Economics

thus, the cost of adding subsequent reactors might not be justified. When the product τk is small, $Da_1 \sim 0.1$, the conversion continues to increase significantly with each reactor added.

The rate of disappearance of A in the n th reactor is

$$-r_{An} = kC_{An} = k \frac{C_{A0}}{(1+\tau k)^n} \quad (5-16)$$

Example 5–2 Producing 200 Million Pounds per Year in a CSTR

Globally, close to 60 billion pounds of ethylene glycol (EG) were produced in 2016. It previously ranked as the 26th most produced chemical in the nation on a total pound basis. About one-half of the ethylene glycol is used for *antifreeze*, while the other half is used in the manufacture of polyesters. In the polyester category, 88% was used for fibers and 12% for the manufacture of bottles and films. The 2017 selling price for ethylene glycol was \$0.43 per pound.

Uses and economics

It is desired to produce 200 million pounds per year of EG. The reactor is to be operated isothermally. A 16.1 mol/dm^3 solution of ethylene oxide (EO) in water is mixed (see Figure E5-2.1) with an equal volumetric solution of water containing 0.9 wt % of the catalyst H_2SO_4 and fed to a CSTR. The *pseudo* first-order specific reaction-rate constant is 0.311 min^{-1} , as determined in Example 5-1. Practical guidelines for reactor scale-up are given by Mukesh.¹

1. If 80% conversion is to be achieved, determine the necessary CSTR volume.
2. If two 800-gal reactors were arranged in parallel with the feed equally divided, what would be the corresponding conversion?
3. If two 800-gal reactors were arranged in series, what would be the corresponding conversion?

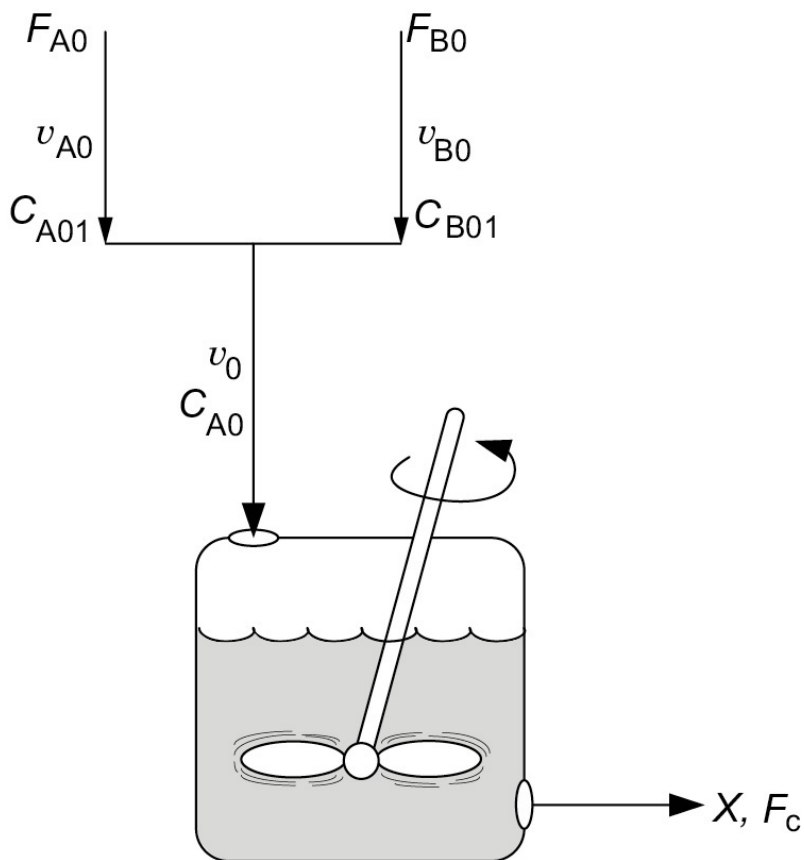
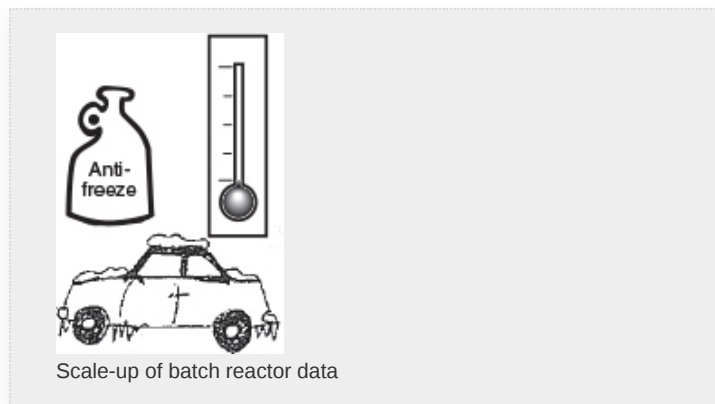


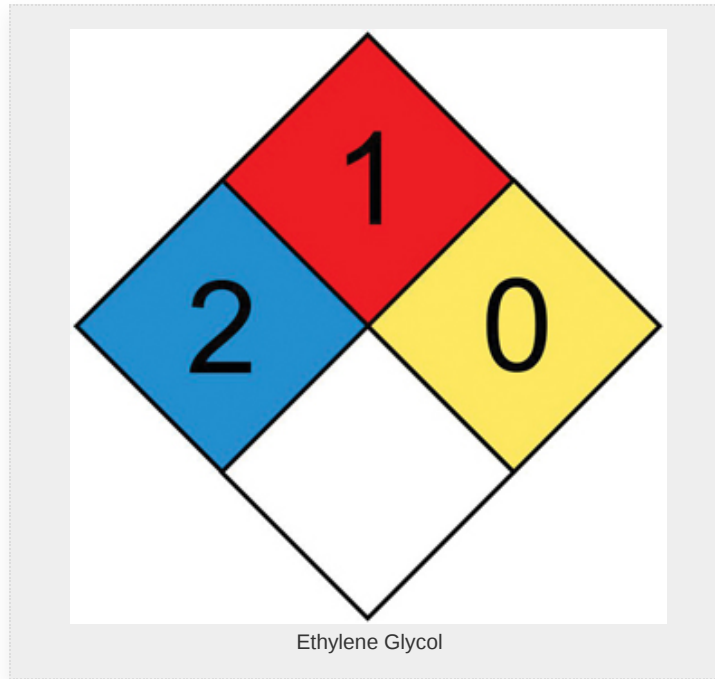
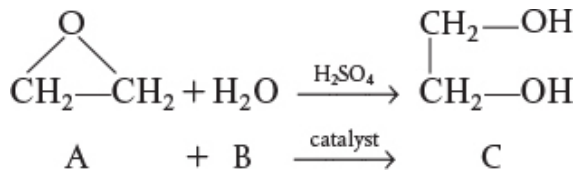
Figure E5-2.1 Single CSTR.



¹ D. Mukesh, *Chemical Engineering*, 46 (January 2002),
www.CHE.com.

Solution

Assumption: Ethylene glycol (EG) is the only reaction product formed.



First let's calculate the molar feed rate, F_{A0} , required to produce the ethylene glycol required.

The specified ethylene glycol (EG) production rate in mol/s is

$$F_C = 2 \times 10^8 \frac{\text{lb}_m}{\text{yr}} \times \frac{1 \text{ yr}}{365 \text{ days}} \times \frac{1 \text{ day}}{24 \text{ h}} \times \frac{1 \text{ h}}{3600 \text{ s}} \times \frac{454 \text{ g}}{\text{lb}_m} \times \frac{1 \text{ mol}}{62 \text{ g}} = 46.4 \frac{\text{mol}}{\text{sec}}$$

From the reaction stoichiometry

$$F_C = F_{A0} X$$

we find the required molar flow rate of ethylene oxide for 80% conversion to be

Answer

$$F_{A0} = \frac{F_C}{X} = \frac{46.4 \text{ mol/s}}{0.8} = 58.0 \text{ mol/s}$$

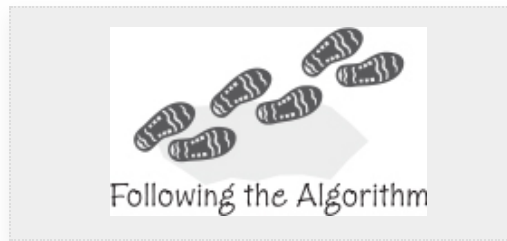
1. We now calculate the single CSTR volume to achieve 80% conversion using the **CRE algorithm**.

1. CSTR Mole Balance:

$$V = \frac{F_{A0}X}{-r_A} \quad (\text{E5-2.1})$$

2. Rate Law:

$$-r_A = kC_A \quad (\text{E5-2.2})$$



3. Stoichiometry: Liquid phase ($v = v_0$):

$$C_A = \frac{F_A}{v_0} = \frac{F_{A0}(1-X)}{v_0} = C_{A0}(1-X) \quad (\text{E5-2.3})$$

4. Combining:

$$V = \frac{F_{A0}X}{kC_{A0}(1-X)} = \frac{v_0X}{k(1-X)} \quad (\text{E5-2.4})$$

5. Evaluate:

The entering volumetric flow rate of stream A, with $C_{A01} = 16.1 \text{ mol/dm}^3$ before mixing, is

$$v_{A0} = \frac{F_{A0}}{C_{A01}} = \frac{58 \text{ mol/s}}{16.1 \text{ mol/dm}^3} = 3.6 \frac{\text{dm}^3}{\text{s}}$$

From the problem statement $v_{B0} = v_{A0}$

$$F_{B0} = v_{B0}C_{B01} = 3.62 \frac{\text{dm}^3}{\text{s}} \times \left[\frac{1000 \text{ g}}{\text{dm}^3} \times \frac{1 \text{ mol}}{18 \text{ g}} \right] = 201 \frac{\text{mol}}{\text{s}}$$

The total entering volumetric flow rate of liquid is

$$v_0 = v_{A0} + v_{B0} = 3.62 \frac{\text{dm}^3}{\text{s}} + 3.62 \frac{\text{dm}^3}{\text{s}} = 7.2 \frac{\text{dm}^3}{\text{s}}$$

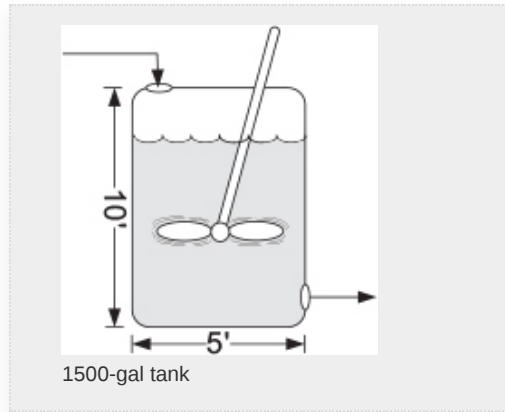
Substituting in Equation (E5-2.4), recalling that $k = 0.311 \text{ min}^{-1}$, yields

$$k_1 = \frac{0.311}{\text{min}} \times \frac{1 \text{ min}}{60 \text{ s}} = \frac{0.0052}{\text{s}}$$

$$V = \frac{v_0X}{k(1-X)} = \frac{7.2 \text{ dm}^3/\text{s}}{\frac{0.0052}{\text{s}} \cdot 1-0.8} = 5538 \text{ dm}^3$$

$$V = 5.538 \text{ m}^3 = 197 \text{ ft}^3 = 1463 \text{ gal}$$

A tank 5 ft in diameter and approximately 10 ft tall is necessary to achieve 80% conversion.



2. **CSTRs in parallel.** Can you guess what would happen if two 800-gal CSTRs arranged in parallel, as shown in Figure E5-2.2, had a volumetric flow rate $v_0 = 3.62 \text{ dm}^3/\text{s}$ fed to each reactor?

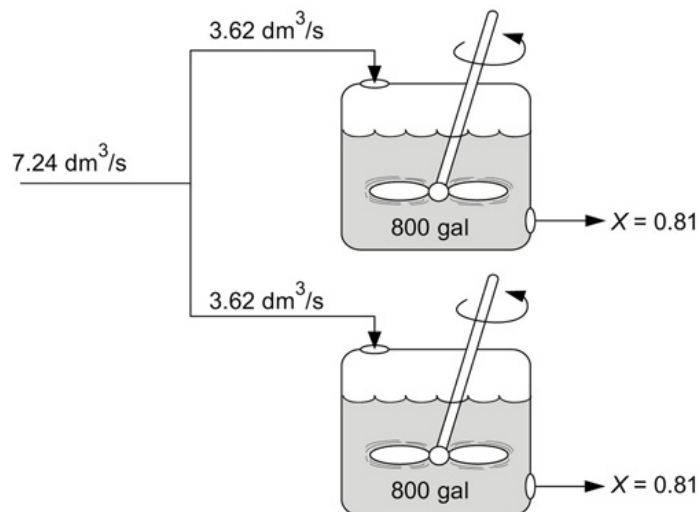


Figure E5-2.2 CSTRs in parallel.

Would the conversion increase, decrease, or remain the same?

To find out, let's begin by rearranging Equation (E5-2.4)

$$\frac{V}{v_0}k = \tau k = \frac{X}{1-X}$$

to obtain

$$X = \frac{\tau k}{1 + \tau k} \quad (\text{E5-2.5})$$

where

$$\tau = \frac{V}{v_0/2} = 800 \text{ gal} \times \frac{3.785 \text{ dm}^3}{\text{gal}} \frac{1}{3.62 \text{ dm}^3/\text{s}} = 836.5 \text{ s}$$

The **Damköhler number** for a first-order reaction is

$$Da_1 = \tau k = 836.5 \text{ s} \times 0.0052 \text{ s}^{-1} = 4.35$$

Substituting into Equation (E5-2.5) gives us

$$X = \frac{Da_1}{1 + Da_1} = \frac{4.35}{1 + 4.35} = 0.81$$

The conversion exiting both of the CSTRs in parallel is 81%.

Question Q5-6B asks you to generalize the result for n equal-size reactors V_i in parallel with equal feed rates (F_{A0}/n) and show that the conversion would also be the same if everything were fed to one big reactor of volume $V = nV_i$.

3. **CSTRs in series.** Recalling what we found in Chapter 2 when we sequenced reactors, can you guess what will happen to the conversion in Part (a) if the reactors are placed in series? Will it increase or decrease? If the 800-gal reactors are arranged in series as shown in Figure E5-2.3, the conversion in the *first* reactor (cf. Equation (E5-2.5)) is

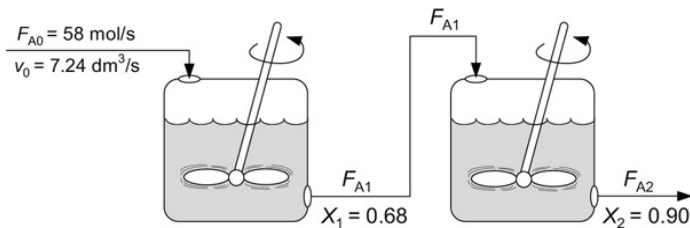


Figure E5-2.3 CSTRs in series.

$$X_1 = \frac{\tau_1 k}{1 + \tau_1 k} \quad (\text{E5-2.6})$$

where

$$\tau = \frac{V_1}{v_0} = \left(800 \text{ gal} \times \frac{3.785 \text{ dm}^3}{\text{gal}} \right) \times \frac{1}{7.24 \text{ dm}^3/\text{s}} = 418.2 \text{ s}$$

The Damköhler number for the first CSTR is

$$Da_1 = \tau_1 k = 418.2 \text{ s} \times \frac{0.0052}{\text{s}} = 2.167$$

First CSTR

the corresponding conversion in the first CSTR is

$$X_1 = \frac{2.167}{1 + 2.167} = \frac{2.167}{3.167} = 0.684$$

To calculate the conversion exiting the second reactor, we recall that $V_1 = V_2 = V$ and $v_{01} = v_{02} = v_0$; then

$$\tau_1 = \tau_2 = \tau$$

Conversion in the series arrangement is greater than in parallel for CSTRs. From our discussion of reactor staging in Chapter 2, we could have predicted that the series arrangement would have given the higher conversion.

A mole balance on the *second reactor* is

$$\text{In} - \text{Out} + \text{Generation} = 0$$

$$\widehat{F}_{A1} - \widehat{F}_{A2} + \widehat{r_{A2}V} = 0$$

Basing the conversion on the total number of moles reacted up to a point per mole of A fed to the first reactor

$$F_{A1} = F_{A0}(1 - X_1) \text{ and } F_{A2} = F_{A0}(1 - X_2)$$

Second CSTR

Rearranging

$$V = \frac{F_{A1} - F_{A2}}{-r_{A2}} = F_{A0} \frac{X_2 - X_1}{-r_{A2}}$$

$$-r_{A2} = kC_{A2} = k \frac{F_{A2}}{v_0} = \frac{kF_{A0}(1 - X_2)}{v_0} = kC_{A0}(1 - X_2)$$

Combining the mole balance on the second reactor (cf. Equation (2-24)) with the rate law, we obtain

$$V = \frac{F_{A0}(X_2 - X_1)}{-r_{A2}} = \frac{C_{A0}v_0(X_2 - X_1)}{kC_{A0}(1 - X_2)} = \frac{v_0}{k} \left(\frac{X_2 - X_1}{1 - X_2} \right) \quad (\text{E5-2.7})$$

Solving Equation (E5-2.7) for the conversion exiting the second reactor yields

$$X_2 = \frac{X_1 + Da_1}{1 + Da_1} = \frac{X_1 + \tau k}{1 + \tau k} = \frac{0.684 + 2.167}{1 + 2.167} = 0.90$$

The same result could have been obtained from Equation (5-15)

$$X_2 = 1 - \frac{1}{(1 + \tau k)^n} = 1 - \frac{1}{(1 + 2.167)^2} = 0.90$$

Over two hundred million pounds of EG per year can be produced using two 800-gal (3.0-m³) reactors in series.

Analysis: The CRE algorithm was applied to a first-order irreversible liquid-phase reaction carried out

isothermally in a single CSTR, two CSTRs in series, and also two CSTRs in parallel. The equations were solved algebraically for each case. When the entering molar flow rate was equally divided between the two CSTRs in parallel, the overall conversion was the same as that for a single CSTR. For two CSTRs in series, the overall conversion was greater than that of a single CSTR. This result will always be the case for isothermal reactions with power-law rate laws with reaction orders greater than zero.

Safety Considerations

We can find information online about the safety of ethylene glycol and other chemicals from [Table 5-4](#). One source is the Vermont Safety Information Resources, Inc., Web site (Vermont SIRI, www.siri.org). For example, we can learn from the *Control Measures* that we should use neoprene gloves when handling the material, and that we should avoid breathing the vapors. If we click on “Dow Chemical USA” and scroll the *Reactivity Data*, we would find that ethylene glycol will ignite in air at 413°C.

Safety information MSDS



TABLE 5-4 ACCESSING SAFETY INFORMATION

1. Type in: <https://us.vwr.com/store/search/searchMSDS.jsp>

2. When the first screen appears, type in the chemical you need to find in the Keyword box and click on the Search button.

Example: Keyword **Ethylene Glycol**

3. The next page shows the list of Manufacturers (e.g., Alfa Aesar, MilliporeSigma) along with catalog number that provide the data on chemical you entered.

ETHYLENE GLYCOL*99% 2.5KG	 View SDS	AAA11591-0E	Alfa Aesar
ETHYLENE GLYCOL ANHYDROUS 4L	 View SDS	EM-EX0566-4	MilliporeSigma

Click on “View SDS” under the **SDS** column for Alfa Aesar to see the material safety Data Sheet that will appear in a .pdf format

4. Scroll down for information you desire:

1. Identification

2. Hazard(s) Identification (GHS Pictographs)

3. Composition/Information on Ingredients

4. 4. First Aid Measures

5. 5. Fire Fighting Measures

6. 6. Accidental Release Measures

7. 7. Handling and Storage

8. 8. Exposure Controls/Personal Protection

9. 9. Physical and Chemical Properties

10. 10. Stability and Reactivity

11. 11-16. Information such as Toxicological, Ecological,
Disposal Considerations, Transport, Regulatory and
Other Information

For ethylene oxide go to *Cameo Chemicals*
(<https://cameochemicals.noaa.gov/chemical/694>).

5.4 TUBULAR REACTORS

Gas-phase reactions are carried out primarily in tubular reactors where the flow is generally turbulent. By assuming that there is no dispersion and there are no radial gradients in either temperature, velocity, concentration, or reaction rate, we can model the flow in the reactor as plug flow.²

² Laminar flow reactors (LFRs) and dispersion effects are discussed in [Chapter 17](#). As a general rule, the conversion calculated for a PFR will not be significantly different than that for an LFR. For example, from [Table E17-1.1](#) in [Chapter 17](#), we see on page 895 that when $\tau k = 0.1$ then $X_{\text{PFR}} = 0.095$ and $X_{\text{LFR}} = 0.09$, when $\tau k = 2.0$ then $X_{\text{PFR}} = 0.865$ and $X_{\text{LFR}} = 0.78$ and when $\tau k = 4$, then $X_{\text{PFR}} = 0.98$ and $X_{\text{LFR}} = 0.94$.

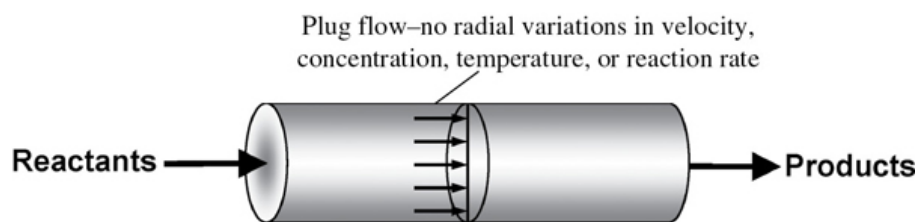


Figure 1-9 (Revisited) tubular reactor.

(<http://encyclopedia.che.engin.umich.edu/Pages/Reactors/PBR/PBR.html>)

The *differential form* of the PFR design equation such as

$$F_{A0} \frac{dX}{dV} = -r_A \quad (2-15)$$

Use this differential form of the PFR/PBR **mole balances** when there is ΔP or heat effects.

must be used when there is a pressure drop in the reactor or heat exchange between the PFR and the surroundings.

In the absence of pressure drop or heat exchange, the integral form of the *plug-flow design* equation can be used,

$$V = F_{A0} \int_0^X \frac{dX}{-r_A} \quad (2-16)$$



As an example, consider the elementary reaction



for which the rate law is

$$-r_A = kC_A^2$$

Rate Law

We shall first consider the reaction to take place as a liquid-phase reaction and then as a gas-phase reaction. For the gas phase, we will have to specify the products to learn whether there is a change in the total number of moles in order to calculate δ .

5.4.1 Liquid-Phase Reactions in a PFR $\therefore v = v_0$

The combined PFR mole balance and rate law is

$$\frac{dX}{dV} = \frac{kC_A^2}{F_{A0}}$$

If the reaction is carried out in the liquid phase, the concentration of A is

$$C_A = C_{A0} (1 - X)$$

Stoichiometry (liquid phase)

and for isothermal operation, we can bring k outside the integral

$$V = \frac{F_{A0}}{kC_{A0}^2} \int_0^X \frac{dX}{(1-X)^2} = \frac{v_0}{kC_{A0}} \left(\frac{X}{1-X} \right)$$

Combine

This equation gives the reactor volume to achieve a conversion X . Dividing by v_0 ($\tau = V/v_0$) and solving for conversion, we find

$$X = \frac{\tau k C_{A0}}{1 + \tau k C_{A0}} = \frac{Da_2}{1 + Da_2}$$

Evaluate

where Da_2 is the Damköhler number for a second-order reaction, that is, $\tau k C_{A0}$.

5.4.2 Gas-Phase Reactions in a PFR [$v = v_0 (1 + \varepsilon X)$ (T/T_0)(P_0/P)]

For constant-temperature ($T = T_0$) and constant-pressure ($P = P_0$) *gas-phase reactions*, the concentration in [Table 4-3](#) is expressed as a function of conversion

$$C_A = \frac{F_A}{v} = \frac{F_A}{v_0(1+\varepsilon X)} = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} = C_{A0} \frac{(1-X)}{(1+\varepsilon X)} \quad (\text{E4-3.1})$$

Stoichiometry (gas phase)

and then combining the PFR mole balance, rate law, and stoichiometry

$$V = F_{A0} \int_0^X \frac{(1+\varepsilon X)^2}{kC_{A0}^2(1-X)^2} dX$$

Combine

The entering concentration C_{A0} can be taken outside the integral sign since it is not a function of conversion. Because the reaction is carried out isothermally, the specific reaction-rate constant, k , can also be taken outside the integral sign.

$$V = \frac{F_{A0}}{kC_{A0}^2} \int_0^X \frac{(1+\varepsilon X)^2}{(1-X)^2} dX$$

For an isothermal reaction, k is constant.

From the integral equations in [Appendix A.1](#), we find that

$$V = \frac{v_0}{kC_{A0}} \left[2\varepsilon(1+\varepsilon) \ln(1-X) + \varepsilon^2 X + \frac{(1+\varepsilon)^2 X}{1-X} \right] \quad (\text{E5-17})$$

Evaluate

Reactor volume for a second-order gas-phase reaction

5.4.3 Effect of ε on Conversion

We now look at the effect of the change in the total number of moles in the **gas phase** on the relationship between conversion

and volume. For constant temperature and pressure, Equation (4-23) becomes

$$v = v_0 (1 + \epsilon X)$$

$$\begin{aligned} T &= T_0 \\ P &= P_0 (\because p = 1) \end{aligned}$$

Let's now consider three types of reactions, one in which $\epsilon = 0$ (i.e., $\delta = 0$), one in which $\epsilon < 0$ ($\delta < 0$), and one in which $\epsilon > 0$ ($\delta > 0$). When there is no change in the number of moles with reaction (e.g., $A \rightarrow B$), $\delta = 0$ and therefore $\epsilon = 0$, then the fluid moves through the reactor at a constant volumetric flow rate ($v = v_0$) as the conversion increases.

When there is a decrease in the number of moles ($\delta < 0$, $\epsilon < 0$) in the gas phase, the volumetric gas flow rate decreases and the conversion increases. For example, when pure A enters for the reaction $2A \rightarrow B$, and taking A as the basis of calculation, then $A \rightarrow B/2$ and we have $\epsilon = y_{A0}\delta = 1 \left(\frac{1}{2} - 1 \right) = -0.5$

$$v = v_0(1 - 0.5X)$$

Consequently, the gas molecules will spend more time in the reactor than they would if the flow rate were constant, $v = v_0$. As a result, this longer residence time would result in a higher conversion than if the flow rate, v , were constant at v_0 .

On the other hand, if there is an increase in the total number of moles ($\delta > 0$, $\epsilon > 0$) in the gas phase, then the volumetric flow rate, v , will increase as the conversion increases. For example, for the reaction $A \rightarrow 2B$, then $\epsilon = y_{A0}\delta = 1 (2 - 1) = 1$

$$v = v_0(1 + X)$$

and the molecules will spend less time in the reactor than they would if the volumetric flow rate were constant. As a result of this smaller residence time in the reactor, the conversion will be less than what would result if the volumetric flow rate, v , were constant at v_0 .

The importance of changes in volumetric flow rate (i.e., $\varepsilon \neq 0$) with reaction

Figure 5-9 shows the volumetric flow rate profiles for the three cases just discussed. We note that for the numbers chosen here we see that at the end of the reactor, virtually complete conversion has been achieved.

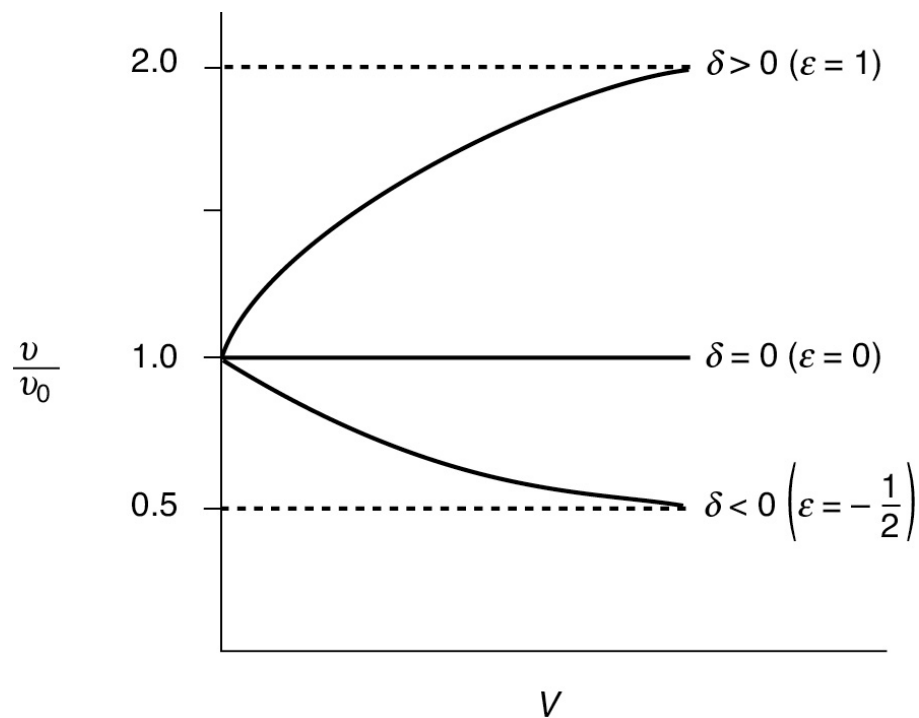


Figure 5-9 Change in gas-phase volumetric flow rate down the length of the reactor.

Example 5–3 Producing 300 Million Pounds per Year of Ethylene in a Plug-Flow Reactor: Design of a Full-Scale Tubular Reactor

Ethylene ranks first in the United States in total pounds of organic chemicals produced each year, and it is the number one organic chemical produced each year. Over 60 billion pounds were produced in 2016, and it sold for \$0.28 per pound. Sixty percent of the ethylene produced is used in the manufacture of polyethylene, 15% for ethylene oxide, 10% for ethylene dichloride, 6% for ethyl benzene, and 9% for other products.

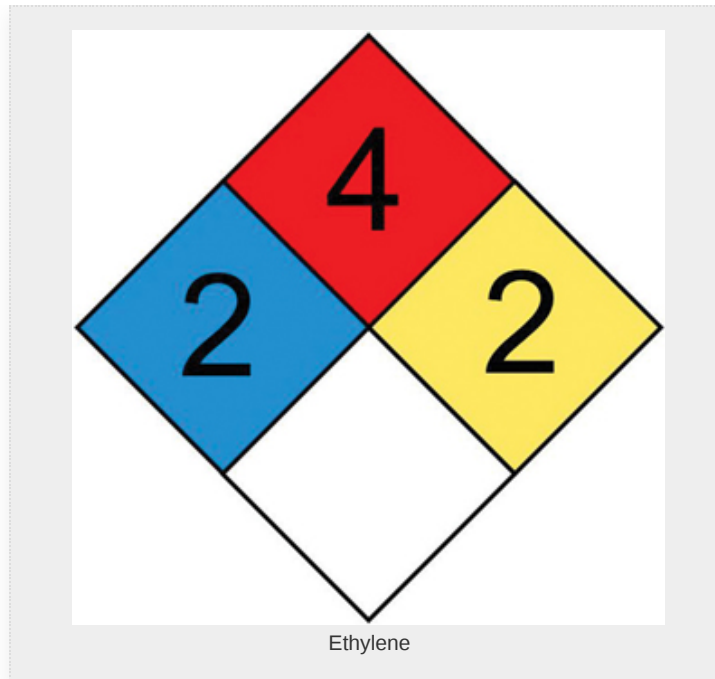
The economics

The uses

Determine the plug-flow reactor volume necessary to produce 300 million pounds of ethylene per year by cracking a feed stream of pure ethane. The reaction is irreversible and follows an elementary rate law. We want to achieve 80% conversion of ethane, operating the reactor isothermally at 1100 K and at a pressure of 6 atm. The specific reaction rate at 1000 K is 0.072 s^{-1} and the activation energy is 82000 cal/mol.

Solution





Let $A = C_2H_6$, $B = C_2H_4$, and $C = H_2$. In symbols,



Because we want the reader to be familiar with both metric units **and** English units, we will work a few of the examples using English units. Trust me, a number of companies still use concentrations in lb-mol/ft^3 . To help you relate English and metric units, the corresponding metric units will be given in parenthesis next to the English units. The only step in the algorithm that is different is the evaluation step.

The molar flow rate of ethylene exiting the reactor is

$$\begin{aligned}
 F_B &= 300 \times 10^6 \frac{\text{lb}_m}{\text{yr}} \times \frac{1 \text{ yr}}{365 \text{ days}} \times \frac{1 \text{ day}}{24 \text{ h}} \times \frac{1 \text{ h}}{3600 \text{ s}} \times \frac{\text{lb-mol}}{28 \text{ lb}_m} \left(\frac{454 \text{ g}}{\text{lb}_m} \times \frac{1 \text{ mol}}{28 \text{ g}} \right) \\
 &= 0.340 \frac{\text{lb-mol}}{\text{s}} \left(F_B = 154.2 \frac{\text{mol}}{\text{s}} \right)
 \end{aligned}$$

Next, calculate the molar feed rate of ethane, F_{A0} , to produce 0.34 lb mol/s of ethylene when 80% conversion is achieved,

Answer

$$F_B = F_{A0}X$$

$$F_{A0} = \frac{0.34 \text{ lb mol/s}}{0.8} = 0.425 \frac{\text{lb-mol}}{\text{s}} \quad (F_{A0} = 193 \text{ mol/s})$$



1. Plug-Flow Mole Balance:

$$F_{A0} \frac{dX}{dV} = -r_A \quad (2-15)$$

Mole Balance

Rearranging and integrating for the case of **no pressure drop** and isothermal operation yields

$$V = F_{A0} \int_0^X \frac{dX}{-r_A} \quad (\text{E5-3.1})$$

2. Rate Law³:

$$-r_A = kC_A \quad \text{with } k = 0.072 \text{ s}^{-1} \text{ at } 1000 \text{ K} \quad (\text{E5-3.2})$$

Rate Law

The activation energy is 82 kcal/mol.

³ *Ind. Eng. Chem. Process Des. Dev.*, 14, 218 (1975); *Ind. Eng. Chem.*, 59(5), 70 (1967).

3. **Stoichiometry:** For isothermal operation and negligible pressure drop, the concentration of ethane is calculated as follows:

The gas-phase volumetric flow rate at constant T and P is

$$v = v_0 \frac{F_T}{F_{T0}} = v_0 (1 + \varepsilon X)$$

Stoichiometry

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} = C_{A0} \left(\frac{1-X}{1+\varepsilon X} \right) \quad (\text{E5-3.3})$$

$$C_C = \frac{C_{A0}X}{(1+\varepsilon X)} \quad (\text{E5-3.4})$$

4. **Combine** Equations (E5-3.1)–(E5-3.3) to obtain

$$\begin{aligned} V &= F_{A0} \int_0^X \frac{dX}{kC_{A0}(1-X)/(1+\varepsilon X)} = F_{A0} \int_0^X \frac{(1+\varepsilon X)dX}{kC_{A0}(1-X)} \\ &= \frac{F_{A0}}{C_{A0}} \int_0^X \frac{(1+\varepsilon X)dX}{k(1-X)} \end{aligned} \quad (\text{E5-3.5})$$

Combining the design equation, rate law, and stoichiometry

5. **Evaluate:**

Since the reaction is carried out isothermally, we can take k outside the integral sign and use [Appendix A.1](#) to carry out our integration.

$$V = \frac{F_{A0}}{kC_{A0}} \int_0^X \frac{(1+\varepsilon X)dX}{1-X} = \frac{F_{A0}}{kC_{A0}} \left[(1+\varepsilon) \ln \frac{1}{1-X} - \varepsilon X \right] \quad (\text{E5-3.6})$$

Analytical Solution

6. Parameter Evaluation:

$$C_{A0} = y_{A0} C_{T0} = \frac{y_{A0} P_0}{RT_0} = (1.0) \left(\frac{6 \text{ atm}}{(0.73 \text{ ft}^3 \cdot \text{atm} / \text{lb-mol} \cdot \text{R}) \times (1980^\circ \text{R})} \right)$$

$$= 0.00415 \frac{\text{lb-mol}}{\text{ft}^3} (0.066 \text{ mol/dm}^3)$$

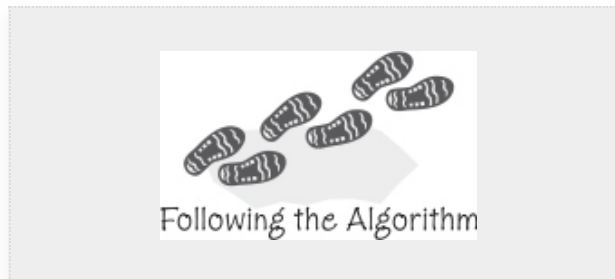
$$\varepsilon = y_{A0} \delta = (1)(1 + 1 - 1) = 1$$

Evaluate

Oops! The rate constant k is given as 0.072 s^{-1} **but** that is at 1000 K, and we need to calculate k at reaction conditions, which is 1100 K.

$$\begin{aligned} k(T_2) &= k(T_1) \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right] \\ &= k(T_1) \exp \left[\frac{E}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \right] \quad (\text{E5-3.7}) \\ &= \frac{0.072}{\text{s}} \exp \left[\frac{82000 \text{ cal/mol} (1100 - 1000) \text{ K}}{1.987 \text{ cal/(mol} \cdot \text{K)} (1000 \text{ K}) (1100 \text{ K})} \right] \\ &= 3.07 \text{ s}^{-1} \end{aligned}$$

Answer



Substituting F_{A0} , k , C_{A0} , ε and into Equation (E5-3.6) yields

$$\begin{aligned} V &= \frac{0.425 \text{ lb mol/s}}{(3.07/\text{s})(0.00415 \text{ lb-mol/ft}^3)} \left[(1 + 1) \ln \frac{1}{1-X} - (1) X \right] \\ &= 33.36 \text{ ft}^3 \left[2 \ln \left(\frac{1}{1-X} \right) - X \right] \quad (\text{E5-3.8}) \end{aligned}$$

For $X = 0.8$,

$$\begin{aligned} V &= 33.36 \text{ ft}^3 \left[2 \ln \left(\frac{1}{1-0.8} \right) - 0.8 \right] \\ &= 80.7 \text{ ft}^3 = (2280 \text{ dm}^3 = 2.28 \text{ m}^3) \end{aligned}$$

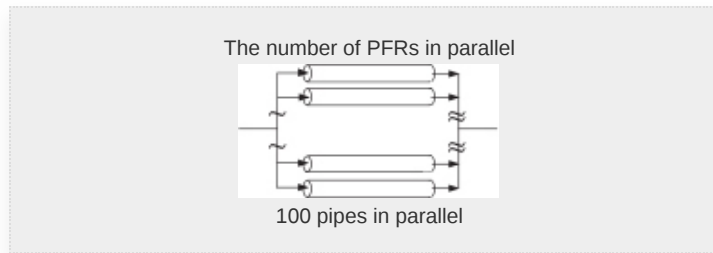
Answer

It was decided to use a bank of 2-in. schedule-80 pipes in parallel that are 40 ft in length. For schedule-80 pipe, the cross-sectional area, A_C , is 0.0205 ft^2 . The number of pipes, n , necessary is

$$n = \frac{\text{Reactor volume}}{\text{Volume of 1 pipe}} = \frac{80.7 \text{ ft}^3}{(0.0205 \text{ ft}^2)(40 \text{ ft})} = 98.4 \quad (\text{E5-3.9})$$

To determine the concentration and conversion profiles down the length of the reactor, z , we divide the volume equation (E5-3.8) by the cross-sectional area, A_C ,

$$z = \frac{V}{A_C} \quad (\text{E5-3.10})$$



Equation (E5-3.9) was used along with the volume of one pipe, 0.81 ft^3 , the cross-sectional area of one pipe $A_C = 0.0205 \text{ ft}^2$, and Equations (E5-3.8) and (E5-3.3) to obtain Figure E5-3.1. Using a bank of 100 pipes will give us the reactor volume necessary to make 300 million pounds per year of ethylene from ethane. The concentration and conversion profiles down any one of the pipes are shown in Figure E5-3.1.

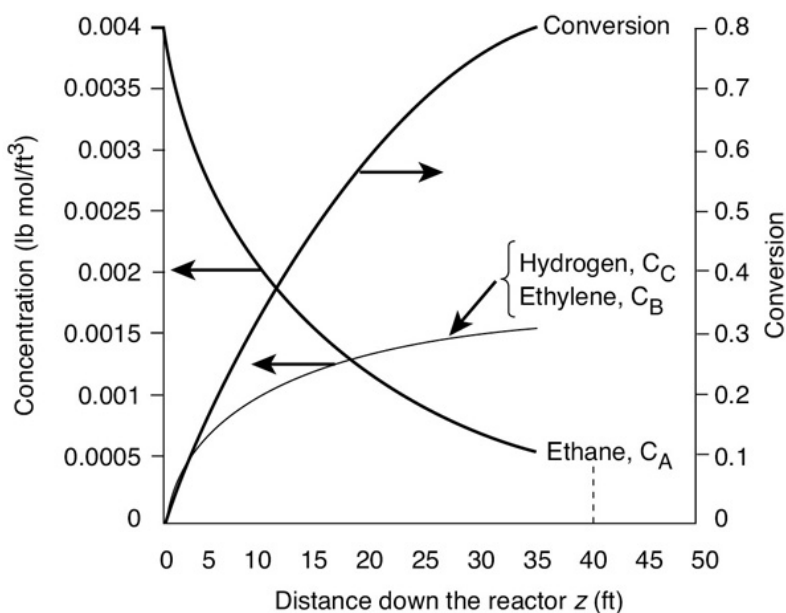


Figure E5-3.1 Conversion and concentration profiles.

Analysis: The CRE algorithm was applied to a gas-phase reaction that had a change in the total number of moles during the reaction. A bank of 100 PFRs in parallel, each with a volume of 0.81 ft^3 , will give the same conversion as 1 PFR with a volume of 81 ft^3 . The conversion and concentration profiles are shown in Figure E5-3.1. You will note that the profiles change more rapidly near the entrance to the reactor where the reactant concentrations are high and then change more slowly near the exit where most of the reactants have been consumed, resulting in a smaller rate of reaction.

We will also solve this problem using Polymath, Python, and Wolfram in order to turn it into a Living Example Problem (LEP). To view .cdf files, all you need is **Wolfram CDF Player**, which can be downloaded for free at <http://www.wolfram.com/cdf-player/>. We will use the m, kg, s units and the values

shown above in parenthesis (e.g., $C_{A0} = 0.066$ mol/dm³) in the LEP. The reader should use the “sliders” in Wolfram or Python for this LEP on the CRE Web site (<http://www.umich.edu/~elements/6e/05chap/live.html>) to vary the parameters and determine their effect on the conversion X .

5.5 PRESSURE DROP IN REACTORS

In liquid-phase reactions, the concentration of reactants is insignificantly affected by even relatively large changes in the total pressure. Consequently, we can totally ignore the effect of pressure drop on the rate of reaction when sizing liquid-phase chemical reactors. However, in gas-phase reactions, the concentration of the reacting species is proportional to the total pressure; therefore, proper accounting for the effects of pressure drop on the reaction system can, in many instances, be a key factor in the success or failure of the reactor operation. This fact is especially true in microreactors packed with solid catalyst. Here, the microfluidic channels are so small (see Problem 5-21B) that pressure drop can limit the throughput and conversion for gas-phase reactions.

Pressure drop is ignored for liquid-phase kinetics calculations.

5.5.1 Pressure Drop and the Rate Law

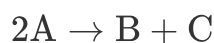
We now focus our attention on accounting for the pressure drop in the rate law. For an ideal gas, we recall Equation (4-25) to write the concentration of reacting species i as

$$C_i = C_{A0} \left(\frac{\Theta_i + v_i X}{1 + \varepsilon X} \right) \frac{P}{P_0} \frac{T_0}{T} \quad (5-18)$$

For gas-phase reactions, pressure drop may be very important.

where $\Theta_i = \frac{F_{i0}}{F_{A0}}$, $\varepsilon = y_{A0}\delta$, $\varepsilon = y_{A0}\delta$, and v_i is the stoichiometric coefficient (e.g., $v_A = -1$, $v_B = -b/a$). We now must determine the pressure ratio ($p = P/P_0$) as a function of the PFR reactor volume, V , or the PBR catalyst weight, W , to account for pressure drop. We then can combine the concentration, rate law, and PBR mole balance. However, whenever accounting for the effects of pressure drop, *the differential form of the mole balance (design equation) must be used.*

If, for example, the second-order reaction



is being carried out in a packed-bed reactor, the **differential form of the mole balance** equation in terms of catalyst weight is

$$F_{A0} \frac{dX}{dW} = -r'_A \left(\frac{\text{Gram moles}}{\text{Gram catalyst} \cdot \text{min}} \right) \quad (2-17)$$

When $P \neq P_0$, one **must** use the differential forms of the PFR/PBR design equations.

The **rate law** is

$$-r'_A = kC_A^2 \quad (5-19)$$

From **stoichiometry** for gas-phase reactions (Table 3-5)

$$C_A = \frac{C_{A0}(1-X)}{1+\varepsilon X} p \frac{T_0}{T}$$

and the rate law can be written as

$$-r'_A = k \left[\frac{C_{A0}(1-X)}{1+\varepsilon X} p \frac{T_0}{T} \right]^2 \quad (5-20)$$

Note from Equation (5-20) that the larger the pressure drop (i.e., the smaller the value of p) from frictional losses, the smaller the reaction rate!

Combining Equation (5-20) with the mole balance (2-17) and assuming isothermal operation ($T = T_0$) gives

$$F_{A0} \frac{dX}{dW} = k \left[\frac{C_{A0}(1-X)}{1+\varepsilon X} \right]^2 p^2$$

Dividing by F_{A0} (i.e., $v_0 C_{A0}$) yields

$$\frac{dX}{dW} = \frac{k C_{A0}}{v_0} \left(\frac{1-X}{1+\varepsilon X} \right)^2 p^2$$

For isothermal operation ($T = T_0$), the right-hand side is a function of only conversion and pressure

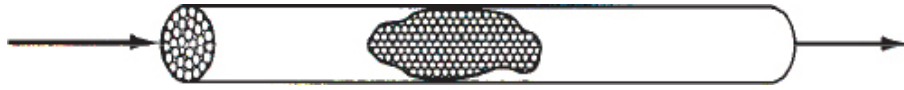
$$\frac{dX}{dW} = F_1(X, p) \quad (5-21)$$

Another equation is needed (e.g., $p = f(W)$).

We now need to relate the pressure drop to the catalyst weight in order to determine the conversion as a function of catalyst weight (i.e., catalyst mass).

5.5.2 Flow Through a Packed Bed

The majority of gas-phase reactions are catalyzed by passing the reactant through a packed bed of catalyst particles.



The equation used most often to calculate pressure drop in a packed porous bed is the **Ergun equation**^{4,5}:

$$\frac{dP}{dZ} = -\frac{G}{\rho g_c D_P} \left(\frac{1-\phi}{\phi^3} \right) \left[\overbrace{\frac{150(1-\phi)\mu}{D_P}}^{\text{Term 1}} + \overbrace{1.75G}^{\text{Term 2}} \right] \quad (5-22)$$

⁴ R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, 2nd ed. New York: Wiley, 2002, p. 191.

⁵ A slightly different set of constants for the Ergun Equation (e.g., 1.8G instead of 1.75G) can be found in *Ind. Eng. Chem. Fundamentals*, 18 (1979), p. 199.

Ergun equation

Term 1 is dominant for laminar flow, and Term 2 is dominant for turbulent flow, where

P = pressure (lb_f/ft², (bar), or (kPa))

ϕ = porosity = $\frac{\text{Volume of void}}{\text{total bed volume}}$ = void fraction

$1 - \phi$ = $\frac{\text{Volume of solid}}{\text{total bed volume}}$

g_c = 32.174 lb_m · ft/s² · lb_f conversion factor

= 4.17 × 10⁸ lb_m · ft/h² · lb_f

(Recall that for the metric system $g_c = 1.0$)

D_P = diameter of particle in the bed, ft or (m)

μ = viscosity of gas passing through the bed, (lb_m/ft·h) or (kg/m · s)

z = length down the packed bed of pipe, (ft) or (m)

u = superficial velocity = volumetric flow rate ÷ cross-sectional area of pipe, (ft/h) or (m/s)

ρ = gas density, (lb_m/ft³) or (kg/m³)

G = ρu = superficial mass velocity, (lb_m/ft² · h) or (kg/m² · s)

In calculating the pressure drop using the Ergun equation, the only parameter that varies with pressure on the right-hand side of Equation (5-22) is the gas density, ρ . We are now going to calculate the pressure drop through a packed-bed reactor.

Because the PBR is operated at steady state, the mass flow rate at any point down the reactor, \dot{m} (kg/s), is equal to the entering mass flow rate, \dot{m}_0 (i.e., equation of continuity)

$$\dot{m}_0 = \dot{m}$$

$$\rho_0 v_0 = \rho v$$

Recalling Equation (4-16), we have

$$v = v_0 \frac{P_0}{P} \left(\frac{T}{T_0} \right) \frac{F_T}{F_{T0}} \quad (4-16)$$

$$\rho = \rho_0 \frac{v_0}{v} = \rho_0 \frac{P}{P_0} \left(\frac{T_0}{T} \right) \frac{F_{T0}}{F_T} \quad (5-23)$$

Combining Equations (5-22) and (5-23) gives

$$\frac{dP}{dz} = - \underbrace{\frac{G(1-\phi)}{\rho_0 g_c D_P \phi^3} \left[\frac{150(1-\phi)\mu}{D_P} + 1.75G \right]}_{\beta_0} \frac{P_0}{P} \left(\frac{T}{T_0} \right) \frac{F_T}{F_{T0}}$$

Simplifying yields

$$\boxed{\frac{dP}{dz} = -\beta_0 \frac{P_0}{P} \left(\frac{T}{T_0} \right) \frac{F_T}{F_{T0}}} \quad (5-24)$$

where β_0 is a constant that depends only on the properties of the packed bed (ϕ , D_P) and the fluid properties at the entrance conditions (i.e., μ , G , ρ_0 , T_0 , P_0). Typical units of β_0 are (atm/ft), (bar/m), or (kPa/m).

$$\boxed{\beta_0 = \frac{G(1-\phi)}{\rho_0 g_c D_P \phi^3} \left[\frac{150(1-\phi)\mu}{D_P} + 1.75G \right] \left(\text{e. g., } \frac{\text{kPa}}{\text{m}}, \frac{\text{atm}}{\text{ft}} \right)} \quad (5-25)$$

For tubular packed-bed reactors, we are more interested in catalyst weight rather than the distance z down the reactor. The catalyst weight up to a distance of z down the reactor is

$$\begin{aligned} W &= (1-\phi)A_c z \times \rho_c \\ \overbrace{\left[\text{Weight of catalyst} \right]} &= \overbrace{\left[\text{Volume of solids} \right]} \times \overbrace{\left[\text{Density of solid catalyst} \right]} \end{aligned} \quad (5-26)$$

$$\boxed{z = \frac{W}{(1-\phi)A_c \rho_c}}$$

where A_c is the cross-sectional area. The *bulk density* of the catalyst, ρ_b (mass of catalyst per volume of reactor bed), is just the product of the density of the solid catalyst particles, ρ_c , and the fraction of solids, $(1 - \phi)$:

$$\rho_b = \rho_c (1 - \phi)$$

Bulk density

Using the relationship between z and W (Equation (5-26)), we can change our variables to express the Ergun equation in terms of catalyst weight:

$$\frac{dP}{dW} = - \frac{\beta_0}{A_c(1-\phi)\rho_c} \frac{P_0}{P} \left(\frac{T}{T_0} \right) \frac{F_T}{F_{T0}}$$

Use this form for multiple reactions and membrane reactors.

Further simplification yields

$$\frac{dP}{dW} = - \frac{\alpha}{2} \frac{T}{T_0} \frac{P_0}{P/P_0} \left(\frac{F_T}{F_{T0}} \right) \quad (5-27)$$

Again, let $p = (P/P_0)$, then

$$\boxed{\frac{dp}{dW} = - \frac{\alpha}{2p} \frac{T}{T_0} \frac{F_T}{F_{T0}}} \quad (5-28)$$

Used for multiple reactions

where

$$\boxed{\alpha = \frac{2\beta_0}{A_c\rho_c(1-\phi)P_0}} \quad (5-29)$$

and where typical units of α might be (kg^{-1}) or (lb_m^{-1}) .

We will use Equation (5-28) when multiple reactions are occurring or when there is pressure drop in a membrane reactor. However, for single reactions in packed-bed reactors, it is more convenient to express the Ergun equation in terms of the conversion X . Recalling Equation (4-20) for F_T ,

$$\frac{F_T}{F_{T0}} = 1 + \varepsilon X \quad (4-20)$$

Differential form of Ergun equation for the pressure drop in packed beds

where, as before

$$\varepsilon = y_{A0}\delta = \frac{F_{A0}}{F_{T0}}\delta \quad (4-22)$$

Substituting for the ratio (F_T/F_{T0}) , Equation (5-28) can now be written as

$$\frac{dp}{dW} = -\frac{\alpha}{2p} (1 + \varepsilon X) \frac{T}{T_0} \quad (5-30)$$

Use for single reactions

We note that when ε is negative, the pressure drop ΔP will be less (i.e., higher pressure) than that for $\varepsilon = 0$. When ε is positive, the pressure drop ΔP will be greater (i.e., lower pressure) than when $\varepsilon = 0$.

For isothermal operation, Equation (5-30) is only a function of conversion and pressure

$$\frac{dp}{dw} = F_2(X, p) \quad (5-31)$$

Recalling Equation (5-21), for the combined mole balance, rate law, and stoichiometry

$$\frac{dX}{dW} = F_1(X, p) \quad (5-21)$$

Two coupled equations to be solved numerically

we see that we have two coupled first-order differential equations, (5-31) and (5-21), that must be solved simultaneously. A variety of software packages (e.g., Polymath) and numerical integration schemes are available for this purpose.

Analytical Solutions. If $\varepsilon = 0$, or if we can neglect (εX) with respect to 1.0 (i.e., $\varepsilon X \ll 1$), we can obtain an analytical solution to Equation (5-30) for iso-thermal operation (i.e., $T = T_0$). For isothermal operation with $\varepsilon = 0$, Equation (5-30) becomes

$$\frac{dp}{dW} = -\frac{\alpha}{2p} \quad (5-32)$$

Isothermal with $\varepsilon = 0$

Rearranging gives

$$\frac{2pdp}{dW} = -\alpha$$

Taking p inside the derivative, we have

$$\frac{dp^2}{dW} = -\alpha$$

Integrating with $p = 1$ ($P = P_0$) at $W = 0$ yields

$$p^2 = (1 - \alpha W)$$

Taking the square root of both sides gives

$$p = \frac{P}{P_0} = (1 - \alpha W)^{1/2} \quad (5-33)$$

Pressure ratio **only** for $\varepsilon = 0$ and isothermal

Be sure **not** to use this equation if $\varepsilon \neq 0$ **or** if the reaction is not carried out isothermally. The pressure-drop parameter α is



$$\alpha = \frac{2\beta_0}{A_c(1-\phi)\rho_c P_0} \left(\text{kg}^{-1} \text{ or } \text{lb}_m^{-1} \right) \quad (5-29)$$

Equation (5-33) can be used to substitute for the pressure in the rate law, in which case the mole balance can then be written solely as a function of conversion and catalyst weight. The resulting equation can readily be solved either analytically or numerically.

If we wish to express the pressure in terms of reactor length z , we can use Equation (5-26) to substitute for W in Equation (5-33). Then

$$p = \frac{P}{P_0} = \left(1 - \frac{2\beta_0 z}{P_0} \right)^{1/2} \quad (5-34)$$

from which one can plot the pressure along the length of the reactor.

5.5.3 Pressure Drop in Pipes

Normally, the pressure drop for gases flowing through pipes without packing can be neglected. For flow in pipes, the pressure drop along the length of the pipe can be approximated by

$$p = (1 - \alpha_p V)^{1/2} \quad (5-35)$$

where

$$\alpha_p = \frac{4f_F G^2}{A_c \rho_0 P_0 D} \quad (5-36)$$

and where f_F usually is the Fanning friction factor, D is the pipe diameter, and the other parameters are the same as previously defined.

For the flow conditions given in Example (5-4) in a 1000-ft length of 1½-in. schedule-40 pipe ($\alpha_p = 0.05 \text{ m}^{-3}$), the pressure drop is usually less than 5%. However, for high volumetric flow rates through microreactors, the pressure drop might be significant. See sample calculation on the Web site at <http://www.umich.edu/~elements/6e/05chap/pdf/alpha-P-calculation-Example-5-4.pdf>.

Example 5–4 Calculating Pressure Drop in a Packed Bed

Plot the pressure drop in a 60-ft length of 1½-in. schedule-40 pipe packed with catalyst pellets ¼ in. in diameter. There is 104.4 lb_m/h of gas passing through the bed. The temperature is constant along the length of pipe at 260°C. The void fraction is 45% and the properties of the gas are similar to those of air at this temperature. The entering pressure is 10 atm.

Solution

1. First let's calculate the total pressure drop.

At the end of the reactor, $z = L$, Equation (5-34) becomes

$$\frac{P}{P_0} = \left(1 - \frac{2\beta_0 L}{P_0}\right)^{1/2} \quad (\text{E5-4.1})$$

$$\beta_0 = \frac{G(1-\phi)}{g_c \rho_0 D_p \phi^3} \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right] \quad (5-25)$$

$$G = \frac{\dot{m}}{A_c} \quad (\text{E5-4.2})$$

Evaluating the pressure-drop parameters

We now look up the cross-sectional area for 1½-in. schedule-40 pipe, to find $A_c = 0.01414 \text{ ft}^2$

$$G = \frac{104.4 \text{ lb}_m/\text{h}}{0.01414 \text{ ft}^2} = 7383.3 \frac{\text{lb}_m}{\text{h} \cdot \text{ft}^2}$$

For air at 260°C and 10 atm we find

$$\mu = 0.0673 \text{ lb}_m/\text{ft} \cdot \text{h}$$

$$\rho_0 = 0.413 \text{ lb}_m/\text{ft}^3$$

$$v_0 = \frac{\dot{m}}{\rho_0} = \frac{104.4 \text{ lb}_m/\text{h}}{0.413 \text{ lb}_m/\text{ft}^3} = 252.8 \text{ ft}^3/\text{h} \quad (7.16 \text{ m}^3/\text{h})$$

Evaluating the parameters in the Ergun equation

From the problem statement

$$D_p = 1/4 \text{ in.} = 0.0208 \text{ ft}, \varphi = 0.45 \text{ and}$$

$$g_c = 4.17 \times 10^8 \frac{\text{lb}_m \cdot \text{ft}}{\text{lb}_f \cdot \text{h}^2}$$

Substituting these values into Equation (5-25) gives

$$\beta_0 = \left[\frac{7383.3 \text{ lb}_m / \text{ft}^2 \cdot \text{h} (1-0.45)}{(4.17 \times 10^8 \text{ lb}_m \cdot \text{ft} / \text{lb}_f \cdot \text{h}^2) (0.413 \text{ lb}_m \text{ ft}^3) (0.0208 \text{ ft}) (0.45)^3} \right] \quad (\text{E5-4.3})$$

$$\times \left[\frac{150(1-0.45)(0.0673 \text{ lb}_m / \text{ft} \cdot \text{h})}{0.0208 \text{ ft}} + 1.75 (7383.3) \frac{\text{lb}_m}{\text{ft}^2 \cdot \text{h}} \right]$$

$$\beta_0 = 0.01244 \frac{\text{lb}_f \cdot \text{h}}{\text{ft} \cdot \text{lb}_m} \left[\overbrace{266.9}^{\text{Term 1}} + \overbrace{12,920.8}^{\text{Term 2}} \right] \frac{\text{lb}_m}{\text{ft}^2 \cdot \text{h}} = 164.1 \frac{\text{lb}_f}{\text{ft}^3} \quad (\text{E5-4.4})$$



Tedious reading and calculations, but we gotta know how to do the nitty-gritty.

We note that the turbulent flow term, Term 2, is dominant

$$\beta_0 = 164.1 \frac{\text{lb}_f}{\text{ft}^3} \times \frac{1 \text{ ft}^2}{144 \text{ in.}^2} \times \frac{1 \text{ atm}}{14.7 \text{ lb}_f / \text{in.}^2}$$

$$\beta_0 = 0.0775 \frac{\text{atm}}{\text{ft}} = 25.8 \frac{\text{kPa}}{\text{m}} \quad (\text{E5-4.5})$$

$$\text{Unit conversion for } \beta_0 : \frac{1 \text{ atm}}{\text{ft}} = 333 \frac{\text{kPa}}{\text{m}}$$

We are now in a position to calculate the total pressure drop ΔP

$$p = \frac{P}{P_0} = \left(1 - \frac{2\beta_0 L}{P_0} \right)^{1/2} = \left(1 - \frac{\overbrace{2 \times 0.0775}^{0.155} \text{ atm/ft} \times 60 \text{ ft}}{10 \text{ atm}} \right)^{1/2} \quad (\text{E5-4.6})$$

$$p = 0.265$$

$$p = 0.265P_0 = 2.65 \text{ atm (268 kPa)} \\ \Delta P = P_0 - P = 10 - 2.65 = 7.35 \text{ atm (744 kPa)} \quad (\text{E5-4.7})$$

2. Now let's use Equation (E5-4.1) to plot the pressure and Equation (4-16) to plot the volumetric flow rate profiles. Recalling Equation (5-23) for the case $\varepsilon = 0$ and $T = T_0$

$$v = v_0 \frac{P_0}{P} = \frac{v_0}{p} \quad (\text{E5-4.8})$$

Equations (5-34) and (E5-4.8) were used in the construction of Table E5-4.1.

TABLE E5-4.1 P AND v PROFILES

z (ft)	0	10	20	30	40	50	60
P (atm)	10	9.2	8.3	7.3	6.2	4.7	2.65
v (ft ³ /h)	25 3	27 5	30 5	34 7	408	538	955

For $\rho_c = 120 \text{ lb}_m/\text{ft}^3$

$$\alpha = \frac{2\beta_0}{\rho_c(1-\varphi)A_c P_0} = \frac{2(0.0775)\text{atm/ft}}{120 \text{ lb}_m/\text{ft}^3 (1-0.45)(0.01414 \text{ ft}^2) 10 \text{ atm}}$$

$$\alpha = 0.0165 \text{ lb}_m^{-1} = 0.037 \text{ kg}^{-1} \quad (\text{E5-4.9})$$

Typical value of α

Equations (E5-4.1) and (E5-4.8), along with the values in Table E5-4.1, were used to obtain Figure E5-4.1.

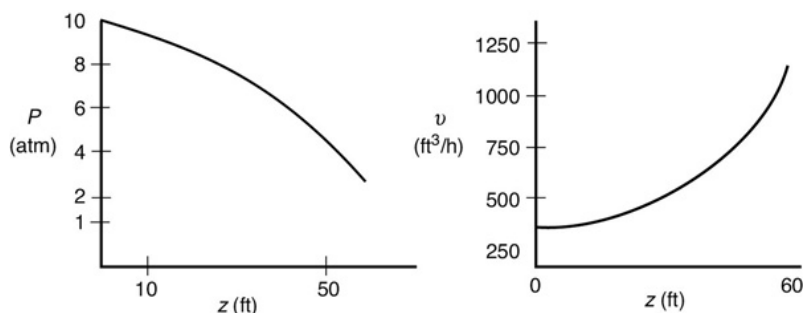


Figure E5-4.1 Pressure and volumetric flow rate profiles ($z = W/A_c \rho_c (1 - \phi)$).

Note how the volumetric flow rate increases dramatically as we move down the reactor. Visit LEP P5-4 on the CRE Web site and use Wolfram or Python to see how p and f change as one varies the pressure drop parameters in the Ergun Equation. Write three conclusions from your Wolfram or Python experiments.

$$p = \frac{P}{P_0}$$

$$f = \frac{v}{v_0}$$

Analysis: This example showed how to calculate the pressure drop and pressure-drop parameters (α and β_0) for a gas flowing through a packed-bed reactor. The pressure and volumetric flow rate profiles were then calculated as a function of z down the packed catalyst bed (i.e., catalyst weight), and shown in Figure E5-4.1. Recall from Equation (5-26) $W = [(1-\phi)A_c \rho_c]z$. One thing I bet you did not expect in this figure is how much the volumetric flow rate increases as the pressure decreases as one moves down the length of the PBR.

5.5.4 Analytical Solution for Reaction with Pressure Drop

Let's reason out how pressure drop affects our CRE algorithm. Figure 5-10 shows qualitatively the effects of pressure drop on reactor design. Starting with Figure 5-10(a), we see how the Ergun equation predicts the pressure decreases as the catalyst weight increases down the packed-bed reactor. The subsequent figures, (b)–(e), show this effect of pressure drop on concentration, reaction rate, conversion, and volumetric flow rate, respectively. Each of these figures compares the respective profiles when there is a pressure-drop with those profiles for *no* pressure drop. We see that when there is pressure drop in the reactor, the reactant concentrations, and thus reaction rate for reaction (for reaction orders greater than 0 order), will always be smaller than the case with no pressure drop. As a result of this smaller reaction rate, the conversion will be less with pressure drop than without pressure drop. Trust me on this next suggestion. Go to the CRE Web site, Chapter 5 YouTube videos (<http://www.umich.edu/~elements/6e/youtube/index.html>) and click on the funny video *Chemical Reaction Engineering Gone Wrong*. The students worked very hard on this video and if you don't like it, I will buy you a Little Mac sandwich at the AIChE Student Chapter meeting in 2021.

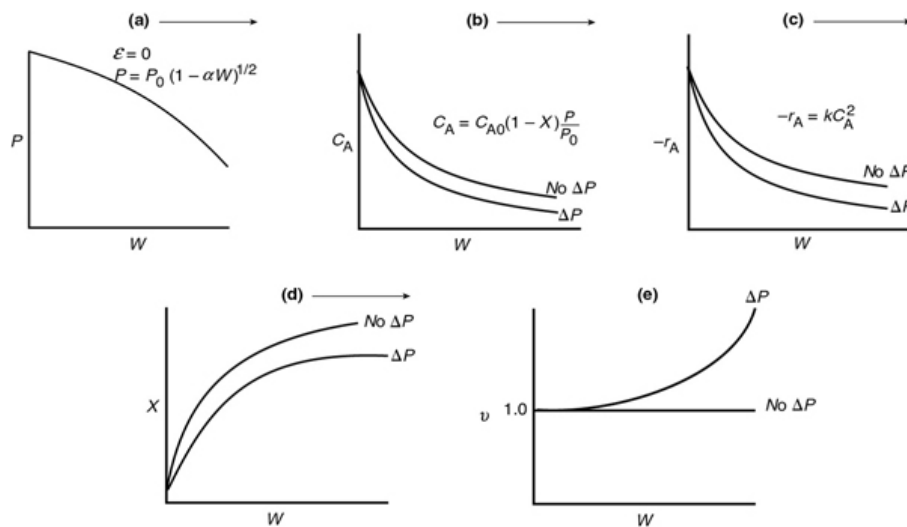
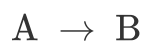


Figure 5-10 Effect of pressure drop on P (a), C_A (b), $-r_A$ (c), X (d), and v (e).

How will pressure drop, ΔP , affect our reactor calculations?

Second-Order Gas-Phase Reaction in a PBR with Pressure Drop

Now that we have expressed pressure as a function of catalyst weight (Equation (5-33) for $\varepsilon = 0$), we can return to the second-order isothermal reaction



to relate conversion and catalyst weight. Recall our mole balance, rate law, and stoichiometry.

1. Mole Balance:

$$F_{A0} \frac{dX}{dW} = -r'_A \quad (2-17)$$

2. Rate Law:

$$-r'_A = kC_A^2 \quad (5-19)$$

3. **Stoichiometry:** Gas-phase isothermal reaction ($T = T_0$) with $\varepsilon = 0$. From Equation (5-23), $v = v_0/p$

Only for $\varepsilon = 0$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v} = C_{A0}(1-X)P \quad (5-37)$$

$$p = \frac{P}{P_0} = (1 - \alpha W)^{1/2} \quad (5-33)$$

Using Equation (5-33) to substitute for p in terms of the catalyst weight, we obtain

$$C_A = C_{A0} (1 - X) (1 - \alpha W)^{1/2}$$



4. **Combining:**

$$\frac{dX}{dW} = \frac{kC_{A0}^2}{F_{A0}} (1 - X)^2 [(1 - \alpha W)^{1/2}]^2$$

5. **Separating Variables:**

$$\frac{F_{A0}}{kC_{A0}^2} \frac{dX}{(1-X)^2} = (1 - \alpha W)dW$$

Integrating with limits $X = 0$ when $W = 0$ and substituting for $F_{A0} = C_{A0}v_0$ yields

$$\frac{v_0}{kC_{A0}} \left(\frac{X}{1-X} \right) = W \left(1 - \frac{\alpha W}{2} \right)$$

We can solve the above equation to either find X at a given W , or find W necessary to achieve a given X .

6. **A Solving for conversion gives**

$$X = \frac{\frac{kC_{A0}W}{v_0} \left(1 - \frac{\alpha W}{2}\right)}{1 + \frac{kC_{A0}W}{v_0} \left(1 - \frac{\alpha W}{2}\right)} \quad (5-38)$$

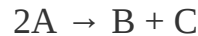
6. B Solving for the catalyst weight, we have

$$W = \frac{1 - \{1 - [(2v_0\alpha)/kC_{A0}][X/(1-X)]\}^{1/2}}{\alpha} \quad (5-39)$$

Catalyst weight for second-order reaction in PBR with ΔP

Example 5–5 Effect of Pressure Drop on the Conversion Profile

Reconsider the packed-bed reactor in [Example 5-4](#) for the case where a second-order reaction



is taking place in 20 m of a 1½-in. schedule-40 pipe packed with catalyst. The flow and packed-bed conditions in [Example 5-4](#) remain the same here except that they are converted to SI units; that is, $P_0 = 10 \text{ atm} = 1013 \text{ kPa}$, and

Entering volumetric flow rate: $v_0 = 7.15 \text{ m}^3/\text{h}$
(252 ft³/h)

Catalyst pellet size: $D_p = 0.006 \text{ m}$ (ca. ¼ in.)

Solid catalyst density: $\rho_c = 1923 \text{ kg/m}^3$ or (120 lb_m/ft³)

Cross-sectional area of 1½-in. schedule-40 pipe:
 $A_C = 0.0013 \text{ m}^2$

Pressure-drop parameter: $\beta_0 = 25.8 \text{ kPa/m}$

Reactor length: $L = 20 \text{ m}$

We need to be able to work either metric, SI, or English units.

We will vary the particle size to learn its effect on the conversion profile. However, we will assume that the specific reaction rate, k , is unaffected by particle size, an assumption that we know from [Chapters 14 and 15](#) is valid only for small particles.

1. First, calculate the conversion in the absence of pressure drop.
2. Next, calculate the conversion accounting for pressure drop.
3. Finally, determine how your answer to **(b)** would change if the catalyst particle diameter were doubled.

The entering concentration of A is 0.1 kmol/m^3 and the specific reaction rate is

$$k = \frac{12 \text{ m}^6}{\text{kmol} \cdot \text{kg-cat} \cdot \text{h}}$$

Solution

We use Equation (5-38) to calculate the conversion as a function of catalyst weight.

$$X = \frac{\frac{kC_{A0}W}{v_0} \left(1 - \frac{\alpha W}{2}\right)}{1 + \frac{kC_{A0}W}{v_0} \left(1 - \frac{\alpha W}{2}\right)} \quad (5-38)$$

First, let's evaluate the parameters. For the bulk catalyst density

$$\rho_b = \rho_c(1 - \phi) = (1923)(1 - 0.45) = 1058 \text{ kg/m}^3$$

The weight of catalyst in the 20 m of 1½-in. schedule-40 pipe is

$$W = A_c \rho_b L = \left(0.0013 \text{ m}^2\right) \left(1058 \frac{\text{kg}}{\text{m}^3}\right) (20 \text{ m})$$

$$W = 27.5 \text{ kg}$$

$$\frac{kC_{A0}W}{v_0} = \frac{12 \text{ m}^6}{\text{kmol} \cdot \text{kg-cat} \cdot \text{h}} \cdot 0.1 \frac{\text{kmol}}{\text{m}^3} \cdot \frac{27.5 \text{ kg}}{7.15 \text{ m}^3/\text{h}} = 4.6$$

1. Next, let's calculate the conversion for no pressure drop, $\Delta P = 0$ (i.e., $\alpha = 0$)

$$X = \frac{\frac{kC_{A0}W}{v_0}}{1 + \frac{kC_{A0}W}{v_0}} = \frac{4.6}{1 + 4.6} = 0.82 \quad (\text{E5-5.1})$$

$X = 0.82$

2. Next, calculate the conversion with pressure drop. Recalling Equation (5-29) and substituting the bulk density $\rho_b = (1 - \phi)\rho_c = 1058 \text{ kg/m}^3$.

In Equation (E5-4.9) in Example 5-4 on page 193, we calculated α to be

$$\alpha = \frac{2\beta_0}{P_0 A_c \rho_b} = 0.037 \text{ kg}^{-1} \quad (\text{E5-5.2})$$

then

$$\left(1 - \frac{\alpha W}{2}\right) = 1 - \frac{(0.037)(27.5)}{2} = 0.49 \quad (\text{E5-5.3})$$

$$X = \frac{\frac{kC_{A0}W}{v_0}\left(1 - \frac{\alpha W}{2}\right)}{1 + \frac{kC_{A0}W}{v_0}\left(1 - \frac{\alpha W}{2}\right)} = \frac{(4.6)(0.49)}{1 + (4.6)(0.49)} = \frac{2.26}{3.26} \quad (\text{E5-5.4})$$

$$X = 0.693$$

Watch out for under design!

Analysis: We see the predicted conversion dropped from 82.2% to 69.3% because of pressure drop. It would be not only embarrassing but also an economic disaster if we had neglected pressure drop and the actual conversion had turned out to be significantly smaller. This point is emphasized in the five-star (★★★★★) YouTube video *Chemical Engineering Gone Wrong* on the CRE Web site (<https://www.youtube.com/watch?v=S9mUAXmNqxs>).

The Wolfram sliders that can be used to explore this Living Example Problem (LEP) along with the conversion and pressure ratio profiles are shown in Figures E5-5.1 and E5-5.2.

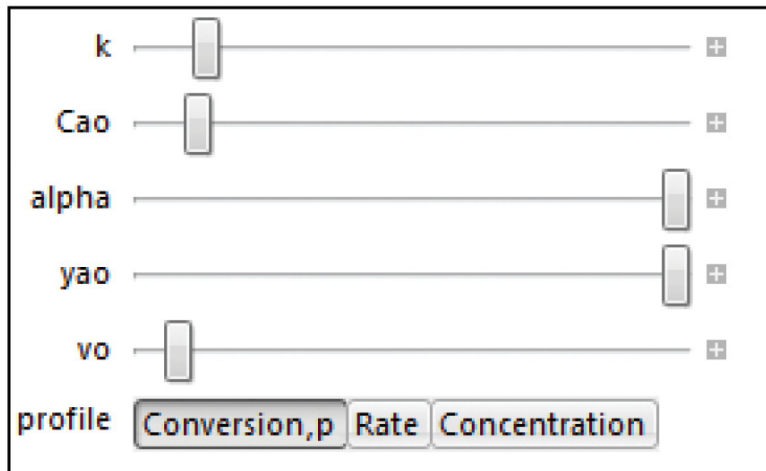


Figure E5-5.1 Wolfram sliders.

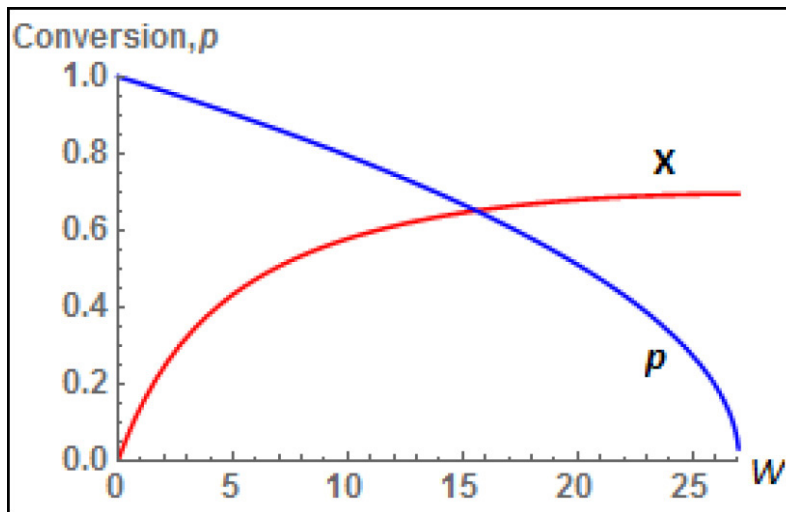


Figure E5-5.2 Wolfram profiles.

After going to the LEP and moving the sliders, be sure to explain why the profiles changed like they did and write three conclusions from your Wolfram or Python experiments.

5.5.5 Robert the Worrier Wonders: *What If...*

Robert is one of the most important members of our engineering team. He is always trying to anticipate changes and the effect of those changes on the process, not only

qualitatively, but quantitatively—a skill **all** engineers should try to hone. He uses basic engineering analysis to predict the new condition if a change is made or occurs unexpectedly.



Let's continue Example 5-6 where we now ask a couple of *What if...* questions. To illustrate engineering analysis, we will address Robert's worry... *What if we decrease the catalyst size by a factor of 4 and increase the entering pressure by a factor of 3?* Will the conversion (a) increase, (b) decrease, (c) remain the same, or (d) cannot tell?

Let's see if we can help Robert out.

First, we need to see how the pressure-drop parameter, α , varies with the system parameters. Combining Equations (5-29) and (5-25), we obtain

$$\alpha = \frac{2}{A_c(1-\phi)\rho_c P_0} \beta_0 = \frac{2}{A_c(1-\phi)\rho_c P_0} \left[\frac{G(1-\phi)}{\rho_0 g_c D_p \phi^3} \left[\frac{150(1-\phi)\mu}{D_p} + \frac{\text{Turbulent}}{1.75G} \right] \right] \quad (5-40)$$

Using an average molecular weight of the gas and the ideal gas law, we can express the entering density as

$$\rho_0 = \frac{(MW)P_0}{RT_0} \quad (5-41)$$

Next, substitute for ρ_0 in Equation (5-40) to obtain

$$\alpha = \frac{RT_0}{(MW)A_C\rho_c g_c P_0^2 D_p \phi^3} G \left[\frac{\frac{\text{Term 1}}{150(1-\phi)\mu}}{D_p} + \frac{\text{Term 2}}{1.75G} \right] \quad (5-42)$$

We are now going to consider a *What if...* analysis for laminar and turbulent flow separately. We will only consider changing the superficial mass flow rate, entering pressure, catalyst particle diameter, and cross-sectional area of the tube in which the catalyst is placed. We keep the catalyst pellet density, ρ_c and void fraction ϕ unchanged and in addition we will leave it as an exercise for the reader to change the temperature and analyze the results.

A. Laminar Flow Dominant (Term 1 \gg Term 2)

We see the pressure-drop parameter α varies as

$$\alpha \sim \frac{GT_0}{A_C D_p^2 P_0^2} \quad (5-43)$$

We now consider the original condition, Case 1, and the condition after a change is made, Case 2, and take the ratio of Case 2 to Case 1.

Case 1 / Case 2

$$\alpha_2 = \alpha_1 \left(\frac{G_2}{G_1} \right) \left(\frac{A_{C1}}{A_{C2}} \right) \left(\frac{D_{P1}}{D_{P2}} \right)^2 \left(\frac{P_{01}}{P_{02}} \right)^2 \left(\frac{T_{02}}{T_{01}} \right) \quad (5-44)$$

For constant mass flow rate for Case 1 and Case 2, we can substitute for G

$$G = \frac{\dot{m}}{A_C}$$

to obtain the pressure-drop parameter, α_2 , for Case 2, after a change in conditions has been made.

$$\alpha_2 = \alpha_1 \left(\frac{A_{C1}}{A_{C2}} \right)^2 \left(\frac{D_{P1}}{D_{P2}} \right)^2 \left(\frac{P_{01}}{P_{02}} \right)^2 \left(\frac{T_{02}}{T_{01}} \right) \quad (5-45)$$

α_2 for laminar flow

We now proceed for turbulent flow to learn how α varies with the system parameters.

B. Turbulent Flow Dominant ($Term\ 2 \gg Term\ 1$)

We see the pressure-drop parameter varies Taking the ratio of Case 1 to Case 2

$$\alpha \sim \frac{G^2 T_0}{A_c D_P P_0^2}$$

Taking the ratio of Case 1 to Case 2

$$\alpha_2 = \alpha_1 \left(\frac{G_2}{G_1} \right)^2 \left(\frac{A_{C1}}{A_{C2}} \right) \left(\frac{P_{01}}{P_{02}} \right)^2 \left(\frac{D_{P1}}{D_{P2}} \right) \left(\frac{T_{02}}{T_{01}} \right) \quad (5-46)$$

If the mass flow rate, \dot{m} , is the same for the two cases 1 and 2, we can substitute $G = \dot{m}/A_C$ to obtain

$$\alpha_2 = \alpha_1 \left(\frac{A_{C1}}{A_{C2}} \right)^3 \left(\frac{P_{01}}{P_{02}} \right)^2 \left(\frac{D_{P1}}{D_{P2}} \right) \left(\frac{T_{02}}{T_{01}} \right) \quad (5-47)$$

α_2 for turbulent flow

We observe that for turbulent flow the pressure-drop parameter α is more sensitive to changes to the cross-sectional area A_C and less sensitive to changes in the particle diameter D_P than that for laminar flow.

Example 5–6 Robert Worries What If...

How will the pressure-drop parameter (e.g., α) and conversion change if you decrease the particle diameter by a factor of 4 and increase entering pressure by a factor of 3, keeping everything else the same? To answer this question we need to consider each flow regime, laminar, and turbulent separately.



His friends sometimes call him "Robert What If."

For isothermal operation with $\delta = 0$, the relationship between the conversion, X , and the pressure-drop parameter is

$$X = \frac{\frac{kC_{A0}W}{v_0} \left(1 - \frac{\alpha W}{2}\right)}{1 + \frac{kC_{A0}W}{v_0} \left(1 - \frac{\alpha W}{2}\right)} \quad (5-38)$$

$$p = (1 - \alpha W)^{1/2} \quad (5-33)$$

- 1. Laminar Flow.** First, let's consider how the conversion would change if the flow were laminar.

$$\alpha_2 = \alpha_1 \left(\frac{A_{C1}}{A_{C2}}\right)^2 \left(\frac{D_{P1}}{D_{P2}}\right)^2 \left(\frac{P_{01}}{P_{02}}\right)^2 \left(\frac{T_{02}}{T_{01}}\right) \quad (5-44)$$

Here $G_1 = G_2$, $A_{C1} = A_{C2}$ and $T_{02} = T_{01}$, but

$$D_{P2} = \frac{1}{4} D_{P1} \text{ and } P_{02} = 3P_{01}$$

Substituting into Equation (5-44)

$$\alpha_2 = \alpha_1 \left(\frac{D_{P1}}{\frac{1}{4}D_{P1}} \right)^2 \left(\frac{P_{01}}{3P_{01}} \right)^2 = \frac{16}{9} \alpha_1 \quad (\text{E5-6.1})$$

Substitute α_2 into Equation (5-38)

$$\alpha = 0.037 \frac{16}{9} \text{kg}^{-1} = 0.066 \text{kg}^{-1}$$

$$\left(1 - \frac{\alpha W}{2} \right) = \left(1 - \frac{(0.066 \text{kg}^{-1})}{2} 27.5 \text{kg} \right) = 0.093$$

$$X = \frac{\frac{kC_{A0}W}{v_0} \left(1 - \frac{\alpha W}{2} \right)}{1 + \frac{kC_{A0}W}{v_0} \left(1 - \frac{\alpha W}{2} \right)} = \frac{(4.6)(0.096)}{1 + (4.6)(0.096)} = 0.31 \quad (\text{E5-6.2})$$

Oops!

The change was not such a good idea as we get much less conversion than before the change. Oops! Robert was indeed right to worry.

2. Turbulent Flow.

$$\alpha_2 = \alpha_1 \left(\frac{A_{C1}}{A_{C2}} \right)^3 \left(\frac{P_{01}}{P_{02}} \right)^2 \left(\frac{D_{P1}}{D_{P2}} \right) \left(\frac{T_{02}}{T_{01}} \right) \quad (5-47)$$

As above, $A_{C1} = A_{C2}$ and $T_{02} = T_{01}$, but $D_{P2} = \frac{1}{4}D_{P1}$ and $P_{02} = 3P_{01}$

$$\alpha_2 = \alpha_1 \left(\frac{D_{P1}}{\frac{1}{4}D_{P1}} \right) \left(\frac{P_{01}}{3P_{01}} \right)^2 = \frac{4}{9} \alpha_1 \quad (\text{E5-6.3})$$

Solving for our new α and then substituting into Equation (5-38)

$$\alpha_2 = 0.037 \frac{4}{9} = 0.0164 \text{kg}^{-1}$$

$$\left(1 - \frac{\alpha W}{2} \right) = \left(1 - \frac{(0.0164 \text{kg}^{-1})}{2} (27.5 \text{kg}) \right) = 0.77 \quad (\text{E5-6.4})$$

$$X = \frac{\frac{kC_{A0}W}{v_0} \left(1 - \frac{\alpha W}{2} \right)}{1 + \frac{kC_{A0}W}{v_0} \left(1 - \frac{\alpha W}{2} \right)} = \frac{(4.6)(0.77)}{1 + (4.6)(0.77)} = \frac{3.56}{4.56} = 0.78 \quad (\text{E5-6.5})$$

Analysis: The following table gives a summary of the conversion for the four cases presented in Example 5-5 for no pressure drop, and the base case and Example 5-6 for laminar and turbulent flow.

1. No pressure drop $X = 0.82$

2. Pressure drop (base case) $X = 0.69$

3. Pressure drop laminar flow $X = 0.31$

4. Pressure drop turbulent flow $X = 0.78$

In both laminar and turbulent flow, increasing the pressure, P_0 , decreases the pressure-drop parameter α . Decreasing the particle diameter D_p increases the pressure-drop parameter α for both laminar and turbulent flow, but more so for the laminar where $\alpha \sim 1/D_p^2$. The smaller the pressure-drop parameter, α , the smaller the pressure drop and thus the greater will be the conversion. For laminar flow, the negative effects of reducing the particle size by a factor of 4 are stronger than the effect of increasing pressure by a factor of 3.

Robert the Worrier, like the author of this book, thinks it is important to be able to carry out an *engineering analysis* using Case 1 and Case 2 and then take ratios to estimate the effect of changing parameters on conversion and reactor operation.

Additionally Noted: Because there is no change in the total number of moles during this isothermal gas-phase reaction occurring in a PBR, one can obtain an analytical solution to our CRE algorithm instead of using the Polymath software. Now let's look at what we could expect by changing the particle diameter of the catalyst pellets.

By increasing the particle diameter, we decrease the pressure-drop parameter and thus increase the reaction rate and the conversion. However, when the catalyst particles become large then interparticle diffusion effects could become important in the catalyst pellet. Consequently, this increase in conversion with increasing particle size to decrease pressure drop will not always be the case (cf. see [Figures 10-7, 10-8](#), [Equations \(15-54\) and \(15-57\)](#) and [Figure 15-4](#) in **Chapter 15**). For larger particles, it takes a longer time for a given number of reactant and product molecules to diffuse in and out of the catalyst particle where they undergo reaction (see [Figure 10-5](#)). Consequently, the specific reaction rate decreases with increasing particle size, that is, $k \sim 1/D_p$ (see [Chapter 15](#), [Equation \(15-33\)](#)), which in turn decreases the conversion.

Let's summarize these points for large and small particles sizes. At small particle diameters, the rate constant, k , is large and at its maximum value, but the pressure drop is also large, resulting in a low rate of reaction and low conversion. At large particle diameters, the pressure drop is small, but so is the rate constant, k , and the rate of reaction, resulting in low conversion. Thus, we see a low conversion at both

large and small particle diameters, consequently there is an optimum in between. This optimum is shown in Figure E5-6.1.

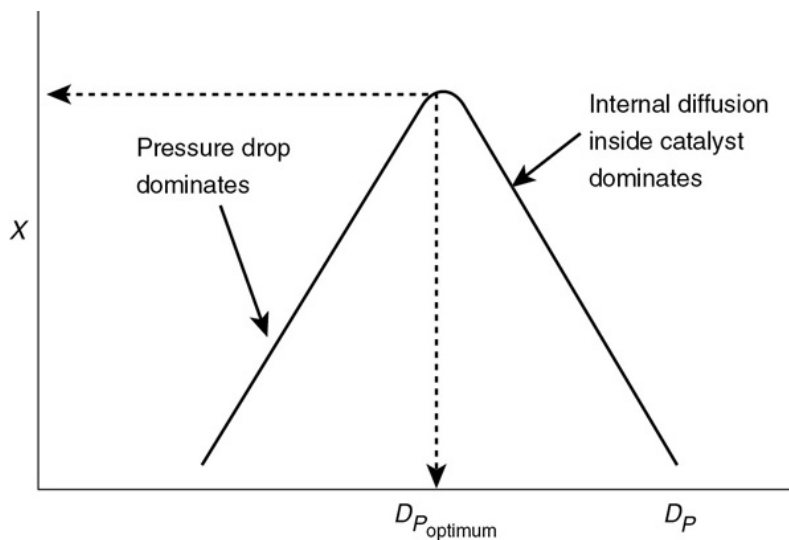
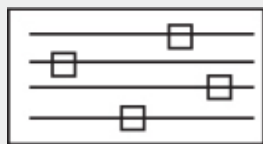


Figure E5-6.1 Finding the optimum particle diameter.

The variation $k \sim \frac{1}{D_p}$ is discussed in detail in [Chapter 15](#). Also, see [Chapter 5 Summary Notes](#).



LEP Sliders

One can now go to the LEP version of Example E5-6 and use the “sliders” in Wolfram to explore the effects of the PBR cross sectional area A_C , temperature, T , entering pressure, P_0 and the catalyst particle diameter, D_p .

If pressure drop is to be minimized, *why not pack the catalyst into a larger diameter tube* to decrease the superficial velocity, G , thereby reducing ΔP ? There are two reasons for *not* increasing the tube diameter: (1) There is an increased chance the gas could channel and bypass most of the catalyst, resulting in little conversion; (2) the ratio of the heat-transfer surface area to reactor volume (catalyst weight) will be decreased, thereby making heat transfer more difficult for highly exothermic and endothermic reactions.

Problems with large-diameter tubes

1. Bypassing of catalyst
2. Smaller heat-transfer area

We now proceed in Example 5-7 to combine pressure drop with reaction in a packed bed when we have volume change with reaction and therefore cannot obtain an analytical solution.⁶

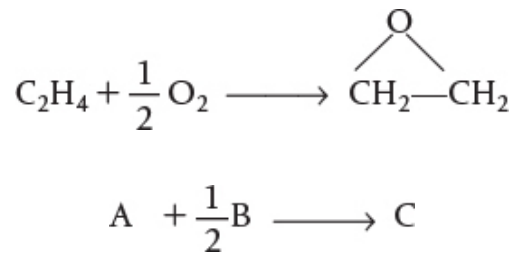
⁶ *Ind. Eng. Chem.*, 45, 234.

Example 5–7 Calculating X in a Reactor with Pressure Drop

Approximately 8.5 billion pounds of ethylene oxide were produced in the United States. The 2014 selling price was \$0.86 per pound, amounting to a commercial value of \$4.0 billion. Over 60% of the ethylene oxide produced is used to make ethylene glycol. The major end uses of ethylene oxide are antifreeze (30%), polyester (30%), surfactants (10%), and solvents (5%). We want to calculate the catalyst weight necessary to achieve 60% conversion when ethylene oxide is to be made by the vapor-phase catalytic oxidation of ethylene with air.

The economics

The uses



Ethylene and oxygen are fed in stoichiometric proportions to a packed-bed reactor operated isothermally at 260°C. Ethylene is fed at a rate of 136.21 mol/s at a pressure of 10 atm (1013 kPa_a). It is proposed to use 10 banks of 1-in. diameter schedule-40 tubes packed with catalyst with 100 tubes per bank. Consequently, the molar flow rate of ethylene to each tube is to be 0.1362 mol/s. The properties of the

reacting fluid are to be considered identical to those of air at this temperature and pressure. The density of the 1/4-in. catalyst particles is 1925 kg/m^3 , the bed void fraction is 0.45, and the gas density is 16 kg/m^3 . The rate law is

$$-r'_A = kP_A^{1/3}P_B^{2/3} \quad \text{mol/kgcat} \cdot \text{s}$$

with

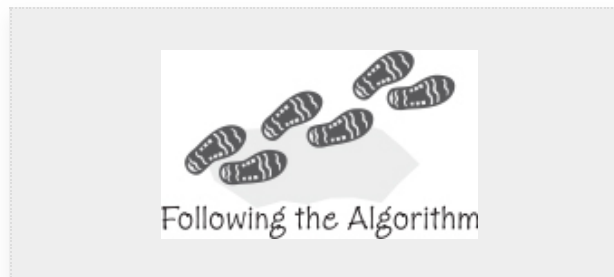
$$k = 0.00392 \frac{\text{mol}}{\text{atm} \cdot \text{kg-cat} \cdot \text{s}} \text{ at } 260^\circ \text{C}$$

The catalyst density, particle size, gas density, void fraction, pipe cross-sectional area, entering pressure, and superficial velocity are the same as in Example E5-4. Consequently we are in luck. Why are we in luck? We don't have to calculate the pressure-drop parameters β_0 and α because they are the same as those calculated in Example 5-4 and we will use these values, that is, $\beta_0 = 25.8 \text{ atm/m}$ and $\alpha = 0.0367 \text{ kg}^{-1}$ in this example.

Solution

1. Differential Mole Balance:

$$F_{A0} \frac{dX}{dW} = -r'_A \quad (\text{E5-7.1})$$



2. Rate Law:

$$-r'_A = kP_A^{1/3}P_B^{2/3} = k(C_A RT)^{1/3}(C_B RT)^{2/3} \quad (\text{E5-7.2})$$

$$= kRTC_A^{1/3}C_B^{2/3} \quad (\text{E5-7.3})$$

3. Stoichiometry: Gas-phase, isothermal $v = v_0(1 + \varepsilon X)(P_0/P)$:

$$C_A = \frac{F_A}{v} = \frac{C_{A0}(1-X)}{1+\varepsilon X} \left(\frac{P}{P_0} \right) = \frac{C_{A0}(1-X)p}{1+\varepsilon X} \quad \text{where } p = \frac{P}{P_0} \quad (\text{E5-7.4})$$

$$C_B = \frac{F_B}{v} = \frac{C_{A0}(\Theta_B - X/2)}{1+\varepsilon X} p \quad (\text{E5-7.5})$$

The algorithm

For stoichiometric feed $\Theta_B = \frac{F_{B0}}{F_{A0}} = \frac{1}{2}$

$$C_B = \frac{C_{A0}}{2} \frac{(1-X)}{(1+\varepsilon X)} p$$

For isothermal operation, Equation (5-30) becomes

$$\frac{dp}{dW} = -\frac{\alpha}{2p}(1 + \varepsilon X) \quad (\text{E5-7.6})$$

We can evaluate the **combine** step either

1. Analytically
2. Graphically
3. Numerically, or
4. Using software

4. Combining the rate law and concentrations

$$-r'_A = kRT_0 \left[\frac{C_{A0}(1-X)}{1+\varepsilon X} (p) \right]^{1/3} \left[\frac{C_{A0}(1-X)}{2(1+\varepsilon X)} (p) \right]^{2/3} \quad (\text{E5-7.7})$$

Factoring $\left(\frac{1}{2}\right)^{2/3}$ and recalling $P_{A0} = C_{A0} RT_0$, we can simplify Equation (E5-7.7) to

$$-r'_A = k' \left(\frac{1-X}{1+\varepsilon X} \right) p \quad (\text{E5-7.8})$$

where we have let $k' = kP_{A0} \left(\frac{1}{2}\right)^{2/3}$.

5. Parameter evaluation per tube (i.e., divide feed rates by 1000)

Evaluating k' , we have

$$k' = kP_{A0} \left(\frac{1}{2}\right)^{2/3} = 0.00392 \frac{\text{mol}}{\text{atm kg-cat}\cdot\text{s}} \times 3 \text{ atm} \times 0.63 = 0.0074 \frac{\text{mol}}{\text{kg-cat}\cdot\text{s}}$$

$$\text{Et} \quad F_{A0} = 0.1362 \text{ mol/s}$$

$$\text{O} \quad F_{B0} = 0.068 \text{ mol/s}$$

$$\text{In} \quad F_1 = 0.068 \text{ mol/s} \times \frac{79 \text{ mol N}_2}{21 \text{ mol O}_2} = 0.256 \frac{\text{mol}}{\text{s}}$$

$$\text{T} \quad F_{T0} = F_{A0} + F_{B0} + F_1 = 0.460 \frac{\text{mol}}{\text{s}}$$

Enter in g:

$$y_{A0} = \frac{F_{A0}}{F_{T0}} = \frac{0.1362}{0.460} = 0.30$$

$$\varepsilon = y_{A0}\delta = (0.3) \left(1 - \frac{1}{2} - 1\right) = -0.15$$

$$P_{A0} = y_{A0}P_0 = 3.0 \text{ atm}$$

As noted in the problem statement, $\beta_0 = 25.8 \text{ kPa/m}$ and $\alpha = 0.0367 \text{ kg}^{-1}$.

6. **Summary:** Combining Equations (E5-7.1) through (E5-7.8) and summarizing

$$\frac{dX}{dW} = \frac{-r'_A}{F_{A0}} \quad (\text{E5-7.9})$$

$$\frac{dp}{dW} = -\alpha \frac{(1+\varepsilon X)}{2p} \quad (\text{E5-7.10})$$

$$r'_A = -\frac{k'(1-X)}{1+\varepsilon X} p$$

$$k' = 0.0074 \left(\frac{\text{mol}}{\text{kg}\cdot\text{s}} \right) \quad (\text{E5-7.11})$$

$$F_{A0} = 0.1362 \left(\frac{\text{mol}}{\text{s}} \right) \quad (\text{E5-7.12})$$

$$\alpha = 0.0367 \left(\text{kg}^{-1} \right) \quad (\text{E5-7.13})$$

$$\varepsilon = -0.15 \quad (\text{E5-7.14})$$

To find W given X requires a short trial and error solution.

We will guess the final catalyst weight to achieve 60% conversion to be 27 kg and use this value as the integration end point in our Polymath program.

$$W_f = 27 \text{ kg of catalyst}$$

We have the boundary conditions $W = 0$, $X = 0$, $p = 1.0$, and $W_f = 27$ kg. Here, we are guessing an upper limit of the integration to be 27 kg, with the expectation that 60% conversion will be achieved *within* this catalyst weight. If 60% conversion is not achieved, we will guess a higher weight and redo the calculation.

Trial and Error Guess $W_f = 27$ kg

Living Example Problems (LEPs). As discussed in Section D.2, the LEPs are to be looked at as a piece of equipment on which you can run experiments on the reactor and reactions. With the advent of Wolfram and Python (which can be downloaded for free) this experimentation is a minor paradigm shift in the way we can assign homework problems. One simply moves the slider variable they want to study and observes the change in the reaction profile or trajectory, and then write a set of conclusions. In addition to the simulation experiments, there are a number of other homework problems and we recommend using the Polymath Software to solve these problems. With Polymath, one simply enters Equations (E5-7.9) and (E5-7.10) and the

corresponding parameter values (Equations (5-7.11)–(5-7.14)) into the computer with the boundary conditions, and they are solved and the results are displayed as shown in Figures E5-7.1(a) and E5-7.1(b). Equations (E5-7.9) and (E5-7.10) are entered as differential equations and the parameter values are set using explicit equations. The rate law may be entered as an explicit equation with Polymath's graphing function to generate a plot of the reaction rate as it changes down the length of the reactor. Consequently, one can download the Polymath program directly from the CRE Web site (<http://www.umich.edu/~elements/6e/05chap/live.html>), which has programmed Equations (E5-7.9)–(E5-7.14), and run the program for different parameter values.

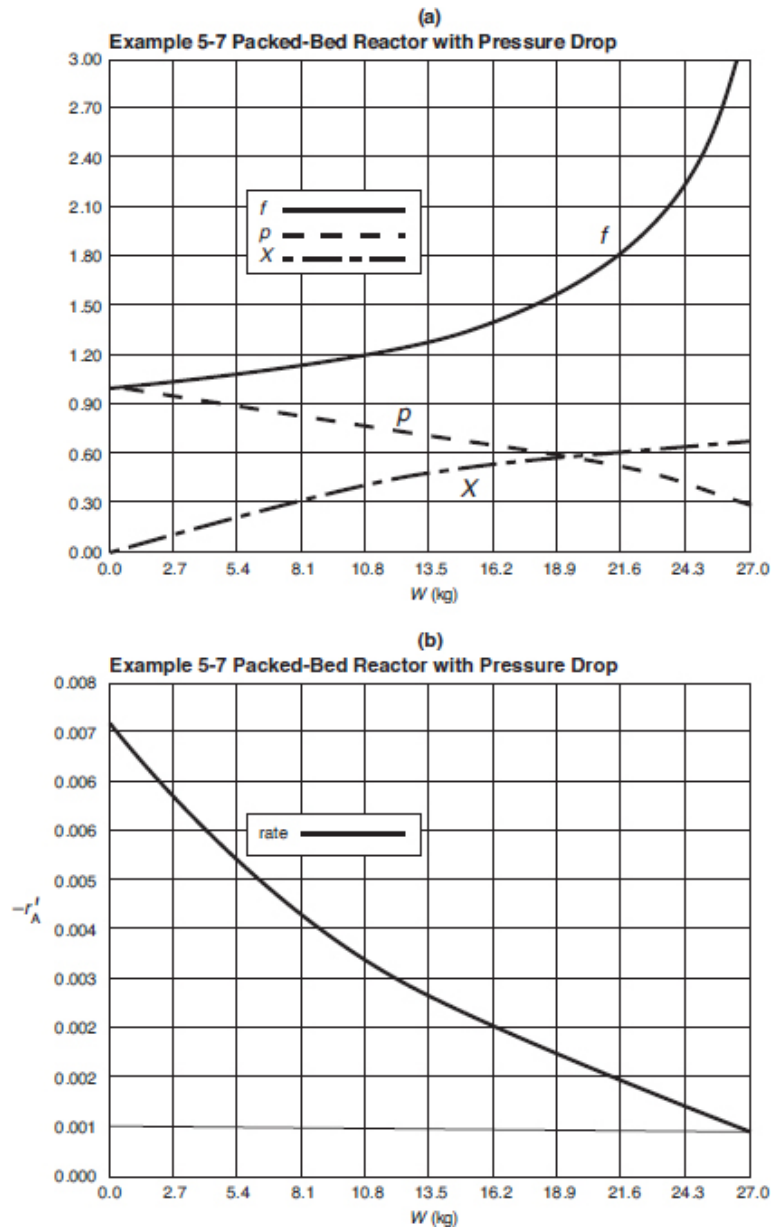


Figure E5-7.1 Output in graphical form from Polymath.

Polymath, MATLAB, Wolfram, and Python program examples can be downloaded from the CRE Web site (see the Introduction).

It is also interesting to learn what happens to the volumetric flow rate as the pressure decreases along the length of the reactor. Recalling Equation (4-23),

$$v = v_0 (1 + \varepsilon X) \frac{P_0}{P} \frac{T}{T_0} = \frac{v_0(1+\varepsilon X)(T/T_0)}{p} \quad (4-23)$$

We let f be the ratio of the volumetric flow rate, v , to the entering volumetric flow rate, v_0 , at any point down the reactor. For isothermal operation, Equation (4-23) becomes

$$f = \frac{v}{v_0} = \frac{1+\varepsilon X}{p} \quad (\text{E5-7.15})$$

Volumetric flow rate increases with increasing pressure drop.

The Polymath program and output are shown in Table E5-7.1.

TABLE E5-7.1 POLYMATH PROGRAM AND NUMERICAL OUTPUT

Differential equations

1. $d(X)/d(W) = -r_{\text{prime}}/F_{\text{ao}}$
2. $d(p)/d(W) = -\alpha(1+\varepsilon X)/2p$

Explicit equations

1. $\varepsilon = -0.15$
2. $k_{\text{prime}} = 0.0074$
3. $F_{\text{ao}} = 0.1362$
4. $\alpha = 0.0367$
5. $r_{\text{prime}} = -k_{\text{prime}}(1-X)/(1+\varepsilon X)^p$
6. $f = (1+\varepsilon X)/p$

7. rate = -raprime

POLYMATH Report

Ordinary Differential Equations

Calculated values of DEQ variables

Variable	Initial value	Final value
1	alpha	0.0367
2	eps	-0.15
3	f	1.
4	Fao	0.1362
5	kprime	0.0074
6	p	1.
7	raprime	-0.0074
8	rate	0.0074
9	W	0

10	X	0	0.6639461
----	---	---	-----------

Living Example Problem

For all Living Example Problems, Polymath, Python, Wolfram, can be loaded from the CRE Web site (see the Introduction).

(Information on how to obtain and load the Polymath software can be found in Appendix D. Tutorials can be found on the CRE Web site home page under Living Examples, Polymath.)

A Polymath Video Tutorial
 (<https://www.youtube.com/watch?v=nyJmt6cTiL4>)

Figure E5-7.1(a) shows X , p (i.e., $p = P/P_0$), and f (i.e., $f = 1/p$) down the length of the reactor. We see that both the conversion and the volumetric flow increase along the length of the reactor, while the pressure decreases. Figure E5-7.1(b) shows how the rate of reaction, $-r'_A$, decreases as we move down the reactor. For gas-phase reactions with orders greater than zero, the decrease in pressure will cause the reaction rate to be smaller than that in the case of no pressure drop.

From either the conversion profile (shown in Figure E5-7.1) or the Polymath table of results, we find 60% conversion is achieved with 20 kg catalyst in each tube.

We note from Figure E5-7.1 that the catalyst weight necessary to raise the conversion the last 1%, from 65% to 66% (0.9 kg), is 8.5 times more than that required to raise the conversion 1% at the reactor's entrance. Also, during the last 5% increase in conversion, the pressure decreases from 3.8 to 2.3 atm.

Effect of added catalyst on conversion

This catalyst weight of 20 kg/tube corresponds to a pressure drop of approximately 5 atm. **If** we had erroneously neglected pressure drop, the catalyst weight would have been found by integrating Equation (E5-7.9) with $p = 1$ to give

$$W = \frac{F_{A0}}{k'} \left[(1 + \varepsilon) \ln \left(\frac{1}{1-X} \right) \varepsilon X \right] \quad (\text{E5-7.16})$$

$$\begin{aligned} &= \frac{0.1362}{0.0074} \times \left[(1 - 0.15) \ln \frac{1}{1-0.6} - (-0.15)(0.6) \right] \quad (\text{E5-7.17}) \\ &= 16 \text{ kg of catalyst per tube (neglecting pressure drop)} \end{aligned}$$

Neglecting pressure drop results in poor design (here, 53% vs. 60% conversion)

But every chemical engineering student in Jofostan knew that!

$$\begin{aligned} f &= \frac{v}{v_0} \\ p &= \frac{P}{P_0} \end{aligned}$$

Analysis: If we had used this 16 kg per tube catalyst weight in our reactor instead of the required 27 kg per

tube, we would have had insufficient catalyst to achieve the desired conversion. For this 16 kg catalyst weight, Figure E5-7.1(a) shows that for the case of pressure drop, only 53% conversion would have been achieved and this would have been *embarrassing!*

Embarrassing!

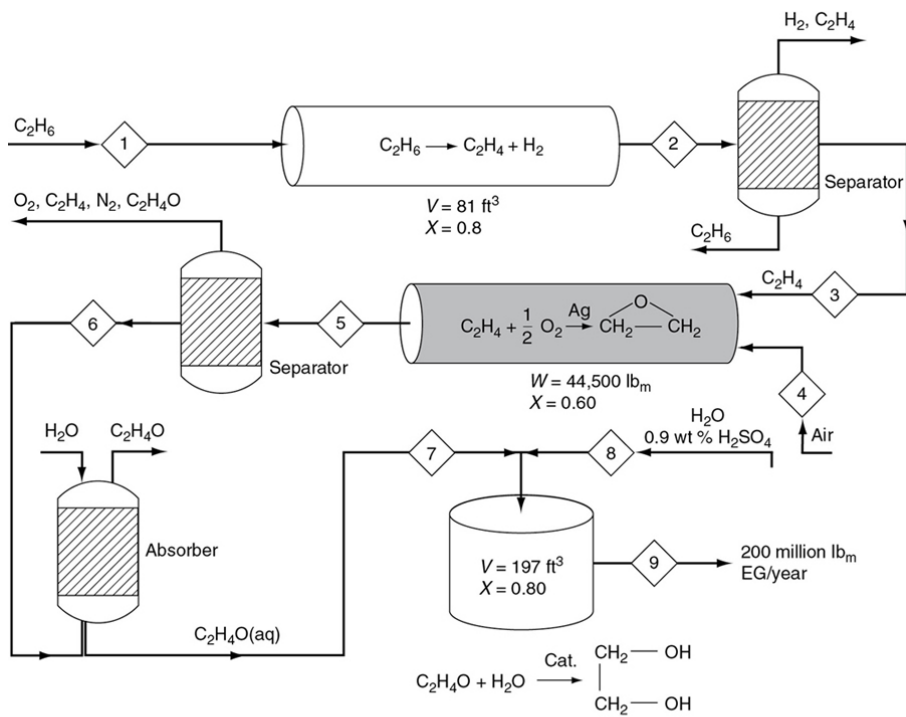
(To see just **how** embarrassing, you will need to watch a YouTube video. Go to the CRE Web site, Chapter 5 YouTube videos (<http://www.umich.edu/~elements/6e/youtube/index.html>) and click on the video *Chemical Reaction Engineering Gone Wrong*. This note is the second time I have recommended this video because I believe you'll enjoy it and also get the point.)

In arriving at this job-saving conclusion, we applied the CRE algorithm to a gas-phase reaction with a change in the total number of moles carried out in a PBR. The only small change from the previous example is that we had to use the ODE solver Polymath to combine and solve all the steps to obtain the profiles of the reaction rate ($-r_A$), conversion (X), pressure ratio (p), and volumetric flow rate ratio (f) as a function of catalyst weight down the length of the PBR.

5.6 SYNTHESIZING THE DESIGN OF A CHEMICAL PLANT

Careful study of the various reactions, reactors, and molar flows of the reactants and products used in the example

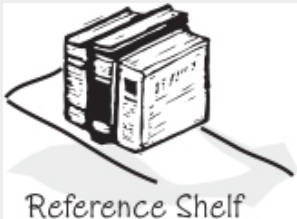
problems in this chapter reveals that they can be arranged to form a chemical plant to produce 200 million pounds of ethylene glycol from a feedstock of 402 million pounds per year of ethane. The flowsheet for the arrangement of the reactors, together with the molar flow rates, is shown in [Figure 5-11](#). Here, 0.425 lb mol/s of ethane is fed to 100 tubular plug-flow reactors connected in parallel; the total volume is 81 ft³ to produce 0.34 lb mol/s of ethylene (see [Example 5-3](#)). The reaction mixture is then fed to a separation unit where 0.04 lb mol/s of ethylene is lost in the separation process in the ethane and hydrogen streams that exit the separator. This process provides a molar flow rate of ethylene of 0.3 lb mol/s, which enters the packed-bed catalytic reactor together with 0.15 lb mol/s of O₂ and 0.564 lb mol/s of N₂. There are 0.18 lb mol/s of ethylene oxide (see [Example 5-6](#)) produced in the 1,000 pipes arranged in parallel and packed with silver-coated catalyst pellets. There is 60% conversion achieved in each pipe and the total catalyst weight in all the pipes is 44,500 lb_m. The effluent stream is passed to a separator where 0.03 lb mol/s of ethylene oxide is lost. The ethylene oxide stream is then contacted with water in a gas absorber to produce a 1-lb mol/ft³ solution of ethylene oxide in water. In the absorption process, 0.022 lb mol/s of ethylene oxide is lost. The ethylene oxide solution is fed to a 197-ft³ CSTR, together with a stream of 0.9 wt % H₂SO₄ solution, to produce ethylene glycol at a rate of 0.102 lb mol/s (see [Example 5-2](#)). This rate is equivalent to approximately 200 million pounds of ethylene glycol per year.



Stream	Component ^a	Flow Rate (lb mol/s)	Stream	Component ^a	Flow Rate (lb mol/s)
1	C_2H_6	0.425	6	EO	0.150
2	C_2H_4	0.340	7	EO	0.128
3	C_2H_4	0.300	8	H_2O	0.443
4	Air	0.714	9	EG	0.102
5	EO	0.180			

^aEG, ethylene glycol; EO, ethylene oxide.

Figure 5-11 Production of ethylene glycol.



Synthesizing a chemical plant

Always challenge the assumptions, constraints, and boundaries of the problem.

The profit from a chemical plant will be the difference between income from sales and the cost to produce the chemicals. An approximate formula might be

$$\text{Profit} = \text{Value of products} - \text{Cost of reactants} \\ - \text{Operating costs} - \text{Separation costs}$$

The operating costs include such costs as energy, labor, overhead, and depreciation of equipment. You will learn more about these costs in your senior design course. While most, if not all, of the streams from the separators could be recycled, let's consider what the profit might be if the streams were to go unrecovered. Also, let's conservatively estimate the operating and other expenses to be \$12 million per year and calculate the profit. Your design instructor might give you a better number. The 2006 prices of ethane, sulfuric acid, and ethylene glycol are \$0.17, \$0.15, and \$0.69 per pound, respectively. See www.chemweek.com for current U.S. prices.

For an ethane feed of 400 million pounds per year and a production rate of 200 million pounds of ethylene glycol per year, the profit is shown in [Table 5-5](#).

TABLE 5-5 PROFITS

$$\begin{aligned}
 \text{Profit} = & \left[\overbrace{\left(\frac{\$0.69}{\text{lb}_m} \times 2 \times 10^8 \frac{\text{lb}_m}{\text{year}} \right)}^{\text{Ethylene glycol value}} - \overbrace{\left(\frac{\$0.17}{\text{lb}_m} \times 4 \times 10^8 \frac{\text{lb}_m}{\text{year}} \right)}^{\text{Ethane cost}} \right. \\
 & - \overbrace{\left(\frac{\$0.15}{\text{lb}_m} \times 2.26 \times 10^6 \frac{\text{lb}_m}{\text{year}} \right)}^{\text{Sulfuric acid cost}} - \overbrace{\$12,000,000}^{\text{Operating cost}} \left. \right] \\
 = & \$138,000,000 - \$68,000,000 - 340,000 - \$12,000,000 \\
 \cong & \$57.7 \text{ million}
 \end{aligned}$$

You will learn more economics of chemical processing in your senior design class.

Using \$58 million per year as a rough estimate of the profit, you can now make different approximations about the conversion, separations, recycle streams, and operating costs to learn how they affect the profit.

5.7 AND NOW... A WORD FROM OUR SPONSOR—SAFETY 5 (AWFOS—S5 A SAFETY ANALYSIS OF THE INCIDENT ALGORITHM)

The Safety Analysis of the Incident is a type of algorithm to analyze an incident to help prevent future accidents. The Chemical Safety Board (CSB) has documented and made videos of a number of accidents that have occurred over the last 40 years. These videos and associated safety modules can be found on the safety website (<http://umich.edu/~safeche/>). For each safety module you are asked to (1) view the CSB video, (2) fill out the safety analysis algorithm, and (3) perform a few calculations specific to the module, and then fill out the NFPA and Bow Tie Diagrams. After viewing the video,

fill out the following *Safety Analysis of the Incident*. You need to brainstorm all the things that could go wrong and then plan the preventative and mitigating actions.

Safety Analysis of the Incident	
Activity:	-----
Hazard:	-----
Incident:	-----
Initiating Event:	-----
Preventative Actions and Safeguards:	-----
Contingency Plan/Mitigating Actions:	-----
Lessons Learned:	-----

Definitions

A The process, situation, or activity for which risk to people, property, or
cti the environment is being evaluated.
vi

ty
:

Hazard: A chemical or physical characteristic that has the potential to cause damage to people, property, or the environment.

Incident: What happened? Description of the event or sum of the events along with the steps that lead to one or more undesirable consequences, such as harm to people, damage to the property, to the environment, or asset/business.

Initiating event: The event that triggers the incident may be at the intersection of two or more failures, (e.g., failure of equipment, instrumentation and controller malfunction, human actions, flammable release). It could also include precursor events that precede the initiating event (e.g., no flow from pump, valve closed, inadvertent human action, ignition).
Event: The root cause of the sum events in causing the incident.

Preventive actions: Steps that can be taken to prevent the initiating event from occurring and becoming an incident that causes damage to people, property, or the environment. Brainstorm all potential problems and hazards that could go wrong. Next, brainstorm and list for each potential problem or hazard all the things that could cause that particular problem to occur (note there may be more than one cause for each potential problem). Finally, for each and every cause, list a preventative action that could be taken to prevent the cause from occurring.

guards:

Contingency Plan / Mitigating Actions: Brainstorm and list all the steps that reduce or mitigate the incident after the preventative action fails and the initiating event occurred.

Lessons Learned: What we have learned and can pass on to others that can prevent similar incidents from occurring

Example

As an example, the *Safety Analysis of the Incident* will be applied to the accident at Kayak Manufacturing, Material and Energy Balances Safety Module 2 ([http://umich.edu/~safeche/assets/pdf/courses/Problems/MaterialsAndEnergy/230Materials&EnergyModule\(2\)PS072219-WeldingDrum.pdf](http://umich.edu/~safeche/assets/pdf/courses/Problems/MaterialsAndEnergy/230Materials&EnergyModule(2)PS072219-WeldingDrum.pdf)) on the *Process Safety Across the Chemical Engineering Curriculum*.

What Happened: In January 2009, a worker at a Kayak Manufacturing Shop in Canada, was welding casters onto an empty acetone drum to make a shop cart. Prior to welding, they rinsed the drum with water and inverted it, but approximately one tablespoon of acetone residue remained in the drum. The worker's welding arc ignited the acetone and the explosion broke through the bottom of the inverted drum, killing the welder.

Now go ahead and watch the video (<https://www.youtube.com/watch?v=9DP5l9yYt-g>).

View the video and fill out the Safety Analysis of the Incident.

Solution:

Safety Analysis of the Incident

Activity: The activity in this incident is the hot work on storage drums that once held flammable chemicals. *Hot work* involves actions that could produce a spark or flame, such as welding, cutting, or grinding.

Hazard: The hazard in this incident is the flammability of acetone residue that was in the drums and its contact with tack welding which acted both as a heat and spark source.

Incident: The incident involved an employee trying to convert an empty acetone drum into a rolling shop cart. The employee rinsed the drum with water from an outdoor hose, agitated the drum, and inverted it to prepare for welding. Even though the drum was rinsed, it was estimated the inverted drum trapped vapor equivalent to approximately one tablespoon of acetone. Grinding the bottom of the drum to prepare for welding helped heat the acetone in the inverted drum. A tack weld perforated the surface and a second tack weld ignited the acetone, creating an explosion that killed a worker. This worker had no formal training in welding.

Initiating Event: The initiating event in this scenario was a spark that resulted from the grinding and welding of a drum that ignited the acetone vapors remaining in the drum.

Preventative Actions and Safeguards: Preventative actions or safeguards could have included safety procedures mandating employees properly dispose of flammable liquid drums and not reuse them, not perform hot work (e.g., grinding or welding) on or near flammable liquid drums (even when empty and rinsed). The manufacturer's material safety data sheet (MSDS) warnings and procedures for proper use and disposal of drums must be followed along with proper supervision of employees when welding and doing hot work. In addition, there should be proper training for employees who will be welding, education of all employees who use flammable substances on the proper, safe handling of drums and flammables, and having a safely designated welding area.

Contingency Plan/Mitigating Actions: Mitigating actions include training workers in emergency response and first aid procedures, as well as wearing personal protection equipment

(PPE) such as fire-resistant clothing and a full face shield or helmet.

Lessons Learned: The lesson learned from this incident is that one tablespoon of a flammable liquid combined with heat and a spark source is sufficient to kill someone. *Hot work* should not be done on or near flammable liquid containers, even if they have been rinsed with water. Empty flammable liquid containers must be disposed of properly according to manufacturer's guidelines and not reused.

Further reading on this incident involving acetone:

Acetone values obtained from NIST:

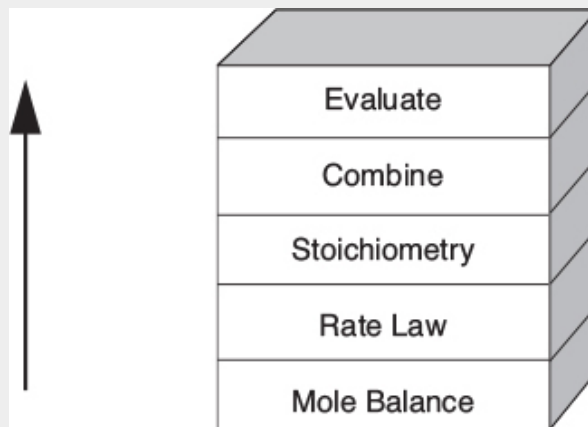
[https://webbook.nist.gov/cgi/cbook.cgi?](https://webbook.nist.gov/cgi/cbook.cgi?Name=acetone&Units=SI)

[Name=acetone&Units=SI](https://webbook.nist.gov/cgi/cbook.cgi?Name=acetone&Units=SI)

Antoine constants: $A = 4.42448$, $B = 1312.253$, $C = -32.445$

Molar heat of combustion: -1772 kJ/mol

Closure. This chapter presents the heart of chemical reaction engineering for isothermal reactors. After completing this chapter, the reader should be able to apply the algorithm building blocks



to any of the reactors discussed in this chapter: batch reactor, CSTR, PFR, and PBR. The reader should be able to account for pressure drop and describe the effects of the system variables such as catalyst particle size on the PBR

conversion, and explain why there is an optimum in the conversion when the catalyst particle size is varied. The reader should be able to use conversion to solve chemical reaction engineering problems. Finally, after completing this chapter, the reader should be able to work the California Professional Engineers' Exam Problems in approximately 30 minutes (cf. P5-15_B–P5-20_B) and to diagnose and troubleshoot malfunctioning reactors (cf. P5-8_B).

The CRE Algorithm

SUMMARY

1. Solution algorithm

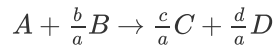
1. Mole balances (BR, CSTR, PFR, PBR):

$$N_{A0} \frac{dX}{dt} = -r_A V, \quad V = \frac{F_{A0} X}{-r_A}, \quad F_{A0} \frac{dX}{dV} = -r_A, \quad F_{A0} \frac{dX}{dW} = -r'_A \quad (\text{S5-1})$$

2. Rate law: For example,

$$-r'_A = kC_A^2 \quad (\text{S5-2})$$

3. Stoichiometry:



1. Liquid phase: $v = v_0$

$$C_A = C_{A0}(1 - X) \quad (\text{S5-3})$$

2. Gas phase:

$$v = v_0 (1 + \varepsilon X) \left(\frac{P_0}{P} \right) \left(\frac{T}{T_0} \right), \text{ where } \varepsilon = y_{A0} \delta = y_{A0} \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right)$$

$$p = \frac{P}{P_0}$$

$$f = v/v_0 \quad (\text{S5-4})$$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v} = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} \left(\frac{P}{P_0} \right) \frac{T_0}{T} = C_{A0} \left(\frac{1-X}{1+\varepsilon X} \right) p \frac{T_0}{T} \quad (\text{S5-5})$$

For a **PBR**

$$\frac{dp}{dW} = -\frac{\alpha(1+\varepsilon X)}{2p} \left(\frac{T}{T_0} \right) \quad (\text{S5-6})$$

$$\alpha = \frac{2\beta_0}{A_c(1-\phi)\rho_c P_0} \text{ and } \beta_0 = \frac{G(1-\phi)}{\rho_0 g_c D_p \phi^3} \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right]$$

Variable density with $\varepsilon = 0$ or $\varepsilon X \ll 1$ and isothermal operation:

$$\text{IFF } \varepsilon = 0 \quad p = \frac{P}{P_0} = (1 - \alpha W)^{1/2} \quad (\text{S5-7})$$

4. **Combining** the rate law and stoichiometry for isothermal operation in a PBR

$$\text{Liquid:} \quad -r'_A = kC_{A0}^2(1 - X)^2 \quad (\text{S5-8})$$

$$\text{Gas:} \quad -r'_A = kC_{A0}^2 \frac{(1-X)^2}{(1+\varepsilon X)^2} p^2 \quad (\text{S5-9})$$

5. **Solution** techniques:

1. Numerical integration—Simpson's rule
2. Table of integrals
3. Software packages
 1. Polymath
 2. MATLAB

An ODE solver (e.g., Polymath) will combine all the equations for you.

ODE SOLVER ALGORITHM

When using an ordinary differential equation (ODE) solver such as Polymath, MATLAB, or Wolfram, it is usually easier to leave the mole balances, rate laws, and concentrations as separate equations, rather than combining them into a single equation as we did to obtain an analytical solution. Writing the equations separately leaves it to the computer to combine them and produce a solution. The Polymath formulation for a packed-bed reactor with pressure drop is given in [Table 5-8.1](#) for an elementary reversible reaction carried out isothermally.

Living Example Problem 5-8: Algorithm for reversible gas-phase reaction



in a packed bed with pressure drop.

TABLE LEP 5-8.1 WOLFRAM, PYTHON, AND POLYMATH SIMULATIONS

<p>Mole Balance</p> $\frac{dX}{dW} = \frac{-r'_A}{F_{A0}}$ <p>Rate Law</p> $-r'_A = k \left[C_A C_B - \frac{C_C^3}{K_C} \right]$	<p>Stoichiometry</p> $C_A = C_{A0} \frac{1-X}{1+\varepsilon X} p$ $C_B = C_{A0} \frac{\theta_B - X}{1+\varepsilon X} p$ $C_C = \frac{3C_{A0}X}{(1+\varepsilon X)} p$ $\frac{dp}{dW} = -\frac{\alpha(1+\varepsilon X)}{2p}$ <p>(where $p = P/P_0$)</p>	<p>POLYMATH Report Ordinary Differential Equations Calculated values of DEQ variables</p> <table> <tr> <th>Variable</th><th>Initial value</th><th>Final value</th></tr> <tr> <td>1 alpha</td><td>0.01</td><td>0.01</td></tr> <tr> <td>2 Ca</td><td>0.01</td><td>0.0008947</td></tr> <tr> <td>3 Cao</td><td>0.01</td><td>0.01</td></tr> <tr> <td>4 Cb</td><td>0.020303</td><td>0.0031452</td></tr> <tr> <td>5 Cc</td><td>0</td><td>0.0038689</td></tr> <tr> <td>6 epsilon</td><td>0.33</td><td>0.33</td></tr> <tr> <td>7 Fao</td><td>15.</td><td>15.</td></tr> <tr> <td>8 k</td><td>5000.</td><td>5000.</td></tr> <tr> <td>9 Kc</td><td>0.05</td><td>0.05</td></tr> <tr> <td>10 p</td><td>1.</td><td>0.2609906</td></tr> <tr> <td>11 ra</td><td>-1.015152</td><td>-0.0082782</td></tr> <tr> <td>12 thetaB</td><td>2.030303</td><td>2.030303</td></tr> <tr> <td>13 vo</td><td>1500.</td><td>1500.</td></tr> <tr> <td>14 W</td><td>0</td><td>80.</td></tr> <tr> <td>15 X</td><td>0</td><td>0.590412</td></tr> <tr> <td>16 yao</td><td>0.33</td><td>0.33</td></tr> </table>	Variable	Initial value	Final value	1 alpha	0.01	0.01	2 Ca	0.01	0.0008947	3 Cao	0.01	0.01	4 Cb	0.020303	0.0031452	5 Cc	0	0.0038689	6 epsilon	0.33	0.33	7 Fao	15.	15.	8 k	5000.	5000.	9 Kc	0.05	0.05	10 p	1.	0.2609906	11 ra	-1.015152	-0.0082782	12 thetaB	2.030303	2.030303	13 vo	1500.	1500.	14 W	0	80.	15 X	0	0.590412	16 yao	0.33	0.33
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15 X	0	0.590412																																																			
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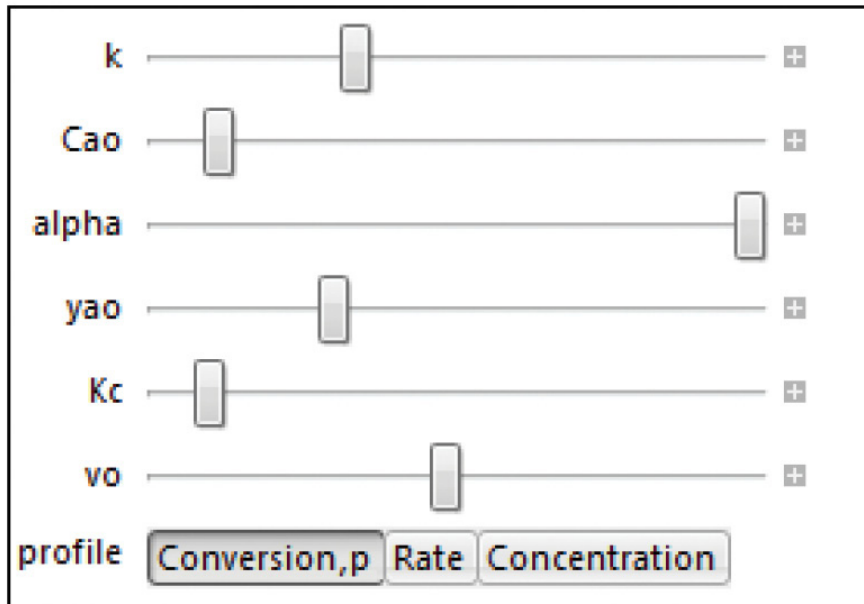


Figure E5-8.1 Wolfram sliders.

Go to this LEP on the Web site and use the “sliders” in Wolfram to explore this problem. You can download Wolfram

for free at <http://www.wolfram.com/cdf-player/>. Vary the parameters, k , α , and so on, to see how the conversion profile changes. A typical Wolfram output is shown in Figure E5-8.2. Describe the variations you see in the conversion and reaction rate profiles. However, **most importantly**, be able to explain why the variation is occurring and what causes it to occur.

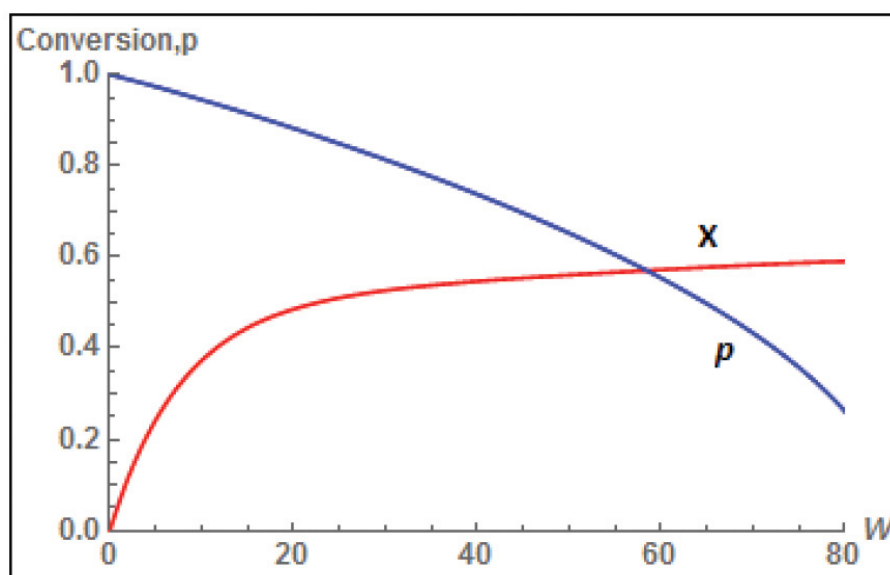


Figure E5-8.2 Wolfram X and p profiles.

CRE WEB SITE MATERIALS

(<http://umich.edu/~elements/6e/05chap/obj.html#/>)

Useful Links

Living
Example
Problems

Extra
Help

Additional
Materials

Professional
Reference
Shelf

Computer
Simulation
Problem
Statements

YouTube
Videos

Evaluation

Self Tests

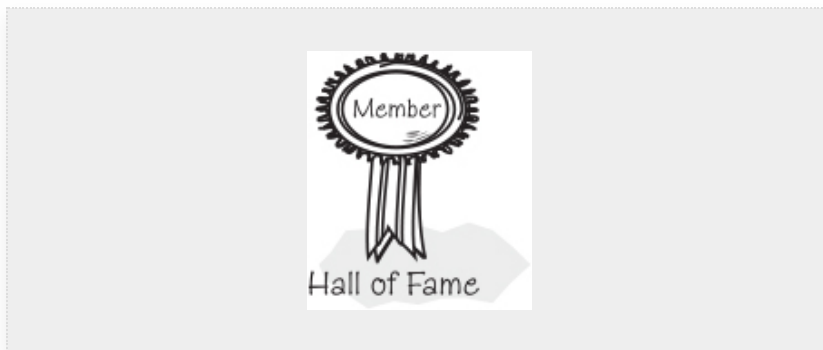
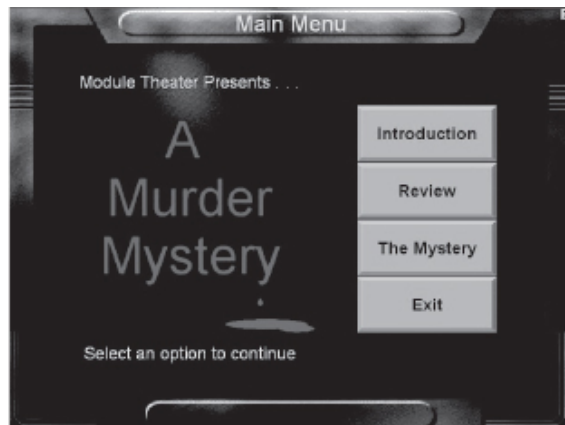
i>Clicker
Questions

Interactive Computer Games

(<http://umich.edu/~elements/6e/icm/index.html>)

Murder Mystery

(<http://umich.edu/~elements/6e/icm/murder.html>)



QUESTIONS, SIMULATIONS, AND PROBLEMS



The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$A = \bullet B = \blacksquare C = \blacklozenge D = \blacklozenge\blacklozenge$$

In each of the following questions and problems, rather than just drawing a box around your answer, write a sentence or two describing how you solved the problem, the assumptions you made, the reasonableness of your answer, what you learned, and any other facts that you want to include. To enhance the quality of your sentences, you may wish to refer to W. Strunk and E. B. White, *The Elements of Style*, 4th ed. New York: Macmillan, 2000, and Joseph M. Williams, *Style: Ten Lessons in Clarity & Grace*, 6th ed. Glenview, IL: Scott, Foresman, 1999.

Before solving the problems, state or sketch qualitatively the expected results or trends.

Questions

Q5-1A QBR (*Question Before Reading*). How do the steps in the design of a CSTR differ from those of a CSTR or a PFR with pressure drop?

Q5-2A i>clicker. Go to the Web site (http://www.umich.edu/~elements/6e/05chap/iclicker_ch5_q1.html) and view at least five i>clicker questions. Choose one that could be used as is, or a variation thereof, to be included on the next exam. You also could consider the opposite case: explain why the question should *not* be on the next exam. In either case, explain your reasoning.

Q5-3A Read through all the problems at the end of this chapter. Make up and solve an *original* problem based on the material in this chapter. **(a)** Use real data and

reactions from the literature. **(b)** Make up a reaction and data. **(c)** Use an example from everyday life (e.g., making toast or cooking spaghetti). In preparing your original problem, first list the principles you want to get across and why the problem is important. Ask yourself how your example will be different from those in the text or lecture. Other things for you to consider when choosing a problem are relevance, interest, impact of the solution, time required to obtain a solution, and degree of difficulty. Look through some of the journals for data, or to get some ideas for industrially important reactions, or for novel applications of reaction engineering principles (the environment, food processing, etc.). At the end of the problem and solution, describe the creative process used to generate the idea for the problem. **(d)** Write a question based on the material in this chapter that requires critical thinking. Explain why your question requires critical thinking. *Hint:* See Table P-2 discussed in the Complete Preface-Introduction on the Web site

(<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>) and apply it to this problem. **(e)** Listen to the audios on the CRE Web site

(www.umich.edu/~elements/6e/index.html) 

Lecture Notes, pick one, and describe how you might explain it differently.

Q5-4_A If it takes 11 minutes to cook spaghetti in Ann Arbor, Michigan, and 14 minutes in Boulder, Colorado, how long would it take in Cuzco, Peru? Discuss ways to make the spaghetti more tasty. If you prefer to make a creative spaghetti dinner for family or friends rather

than answering this question, that's OK, too; you'll get full credit—but **only if** you turn in your recipe and bring your instructor a taste.

Q5-5A Example 5-1. (1) What would be the error in k if the batch reactor were only 80% filled with the same concentrations of reactants, instead of being completely filled as in the example? (2) What generalizations can you draw from this example?

Q5-6B Example 5-2. (1) What conversion would be achieved if three 800-gal CSTRs were placed in series? (2) In parallel with the feed equally divided? (3) What are the advantages and disadvantages of adding this third reactor? (4) $F_{A0} = F_{A0}/n$, that conversion achieved in any one of the reactors will be identical to what would be achieved if the reactor were fed in one stream, $F_{A0} = nF_{Ai0}$, to one large reactor of volume $V = nV_i$.

Q5-7A Example 5-2. Describe how would your reactor volume and number of reactors change if you only needed 50% conversion to produce the 200 million pounds per year required?

Q5-8A Example 5-6. How would the pressure drop and pressure-drop parameters, α and β_0 , change if the particle diameter were reduced by 25%?

Q5-9A High Finance. (1) How would your profit/numbers change in Table 5-4 if you used the following 2010 prices? (2) Ethylene glycol \$0.54/kg, ethylene \$0.76/kg, ethylene oxide \$1.17/kg, ethane \$0.31/kg, sulfuric acid \$0.10/kg (98 wgt %), and propylene glycol \$1.70/kg. (3) What pops out at you?

Q5-10_A Can You Learn a New Dance? View the YouTube video titled *CSTR* to the tune of “It’s fun to stay at the YMCA” (<https://www.youtube.com/watch?v=AkM67QsTq3E>) made by the chemical reaction engineering students at the University of Alabama. You can also access it from the CRE Web site (<http://www.umich.edu/~elements/6e/index.html>); under “Additional Resources,” click on “Fun YouTube Videos.”

Q5-11_A Are there steps in the *Safety Analysis of the Incident* that should be removed or added? If so, what are they?

Q5-12_A Go to the five LearnChemE screencasts link for Chapter 5 (<http://www.umich.edu/~elements/6e/05chap/learn-cheme-videos.html>).

1. In the screencast of the PBR with pressure drop, is there a problem substituting for the volumetric flow rate when there is a change in the total number of moles, that is, $\delta \neq 0$?
2. View one of the other screencasts 5- to 6-minute video tutorials and list two of the most important points.
3. In the isothermal plug reactor screencast, how does the inert impact the reaction process?

Q5-13_A AWFOS–S5 View the CSB video (https://www.youtube.com/watch?v=-_ZLQkn7X-k) and then research the conclusion as to whether or not the safety analysis of the incident is complete.

Computer Simulations and Experiments

P5-1_B What if... you were asked to explore the example problems in this chapter to learn the effects of varying the different parameters? This sensitivity analysis can be carried out by downloading the examples from the

CRE Web site

(www.umich.edu/~elements/6e/index.html, under Living Example Problems (LEPs)). You can download **Wolfram** for free at <http://www.wolfram.com/cdf-player/>. For each of the example problems you investigate, write a paragraph describing your findings.

It is important to the learning process that you try to predict how the results change the answer or the shape of the conversion profile before moving a slider.

1. Example 5-3: Plug Flow Reactor

Wolfram and Python

1. Write down a conclusion about your variation of each slider and explain why the slider movement gave you the results it did.
2. What generalizations can you draw from this example?

2. Example 5-4: Pressure Drop in a Packed Bed

Wolfram and Python

1. Vary each of the parameters in the Ergun Equation and write a couple of sentences on the variable that changes the slope of p versus z the most, that is, what change increases the pressure drop the most?
2. What generalizations can you draw from this example?

3. Example 5-5: Effect of Pressure Drop on Conversion

Wolfram and Python

1. After varying each slider, write down a conclusion about the conversion and pressure profiles and explain why the slider movement gave you the results it did.
2. Why do C_A , C_B , and C_C all start to decrease at $W = 25$ kg?
3. What generalizations can you draw from this example?

4. Example 5-6: Robert Worries What If...

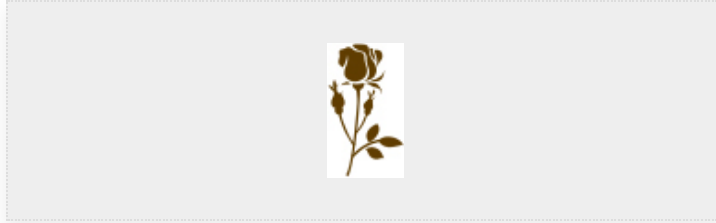
Wolfram and Python

1. Write down a conclusion about your variation of each slider and explain why the slider movement gave you the results it did.
2. How much would the catalyst weight change if the pressure were increased by a factor of 5 and the particle size decreased by a factor of 5? (Recall that α is also a function of P_0 .)
3. Use plots and figures to describe what you learned from this example and how it would apply to other situations.

5. Example 5-7: Calculating X in a Reactor with Pressure Drop

Wolfram and Python

This problem is a **Stop and Smell the Roses Simulation**. Explore this simulation to understand the interaction of pressure drop and conversion.



1. Explain what happens to X , p , and f as k' moves between its maximum and minimum values from its initial setting of $k' = 0.0035 \text{ s}^{-1}$.
 2. What happens to X , p , and f as α moves between its maximum and minimum?
 3. Write two conclusions from your slider experiments.
 4. After reviewing *Generating Ideas and Solutions* on the Web site ([http://www.umich.edu/~elements/6e/toc/SCPS,3rdEdBook\(Ch07\).pdf](http://www.umich.edu/~elements/6e/toc/SCPS,3rdEdBook(Ch07).pdf)), choose one of the brainstorming techniques (e.g., lateral thinking) to suggest two questions that should be included in this problem.
6. **Example 5-8: LEP.** Algorithm for $A + B = 3C$.

Wolfram and Python

1. Vary k' , C_{A0} , and K_C sliders individually between their maximum and minimum values. Write a set of conclusions and explain why the movement of the sliders changed the conversion and pressure drop profiles the way they did.
7. **AspenTech Example 5-3.** (1) Using $F_{A0} = 0.425 \text{ lb}_m \text{ mol/s}$, run the AspenTech simulation at 1000 K and at 1200 K and compare with the specified temperature of 1100 K. (2) Explore what a small change in activation energy can make in your results by changing E from 82 to 74 kcal/mol and then to 90 kcal/mol and compare your results with the base case of 82 kcal/mol.
8. **Download Reactor Lab (www.reactorlab.net)** onto your computer and call up *D1 Isothermal Reactors*. Detailed instructions with screen shots are given in *Chapter 4 Summary Notes*. (1) For **L1** Nth Order Reactions, vary the parameters n , E , T for a batch, CSTR, and PFR. Write a paragraph discussing the trends (e.g., first order vs. second order) and describe what you find. (2) Next, choose the “Quiz” at the top of the screen, find the reaction order, (3) and turn in your performance number. Performance number: _____

9. **Work the Chapter 5 Self-Tests in Summary Notes on the Web.** Write a question for this problem that involves critical thinking and explain *why* it involves critical thinking.

Interactive Computer Games

P5-2_B ICG—Mystery Theater—A real “who done it?” see *Pulp and Paper*, 25 (January 1993) and also *Pulp and Paper*, 9 (July 1993). The outcome of the murder trial is summarized in the December 1995 issue of *Papermaker*, page 12. You will use fundamental chemical engineering from Sections 5.1 to 5.3 to identify the victim and the murderer. #Really? Play the game and then record your performance number.

Performance number: _____



Who done it?

Problems

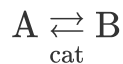
P5-3_A **OEQ** (*Old Exam Question*). **Multiple Choice.** In each case, you will need to explain the reason you chose the answer you did.

1. An irreversible, liquid-phase, second-order reaction, $A \rightarrow \text{Product(s)}$, proceeds to 50% conversion in a PFR operating isothermally, isobarically, and at steady state. What conversion would be obtained if the PFR operated at half the original pressure (with all else unchanged)?

- (1) >50% (2) <50% (3) 50% (4) Insufficient information to answer definitively
2. An irreversible, gas-phase, second-order reaction, $A \rightarrow \text{Product(s)}$, proceeds to 50% conversion in a PFR operating isothermally, isobarically, and at steady state. What conversion would be obtained if the PFR operated at half the original pressure (with all else unchanged)?
(1) >50% (2) <50% (3) 50% (4) insufficient information to answer definitively
3. The rate constant for an irreversible, heterogeneously catalyzed, gas-phase, second-order reaction, $A \rightarrow \text{Product(s)}$, was determined to be 0.234 from experimental data in a packed-bed reactor. The person analyzing the experimental data failed to include the large pressure drop in the reactor in his analysis. If the pressure drop were properly accounted for, the rate constant would be
(1) >0.234 (2) <0.234 (3) 0.234 (4) insufficient information to answer definitively

P5-4_B OEQ (Old Exam Question). Multiple Choice. In each of the cases below, **(a)** through **(e)**, you will need to explain why you chose the answer you did.

The elementary isomerization exothermic reaction



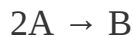
is carried out isothermally at 400 K in a PBR in which pressure drop plays a role, with $\alpha = 0.001 \text{ kg}^{-1}$. Currently, 50% conversion is achieved. The equilibrium constant at this temperature is 3.0.

- For a fixed mass flow rate \dot{m} , if the reactor diameter is increased by a factor of 4, the conversion will
(1) $X > 0.5$ (2) $X < 0.5$ (3) $X = 0.5$ (4) insufficient information to tell
- For a fixed mass flow rate \dot{m} , the equilibrium conversion is
(1) $X_e = 0.5$ (2) $X_e = 0.667$ (3) $X_e = 0.75$ (4) insufficient information to tell
- For a fixed mass flow rate \dot{m} , if the reactor diameter is increased by a factor of 2, the equilibrium conversion X_e will
(1) increase (2) decrease (3) remain the same (4) insufficient information to tell

4. For a fixed mass flow rate \dot{m} , if the particle size is increased, the equilibrium conversion will
(1) increase (2) decrease (3) remain the same (4) insufficient information to tell
5. For a fixed mass flow rate \dot{m} , if the particle size is increased, the conversion will
(1) increase (2) decrease (3) remain the same (4) insufficient information to tell

Question sets similar to Problems P5-3_A and P5-4_B that may help you prepare for exams can be found in **i>clickers** on the Chapter 5 Web site (<http://www.umich.edu/~elements/6e/05chap/obj.html>).

P5-5_A The elementary gas-phase reaction



is carried out in a constant-volume batch reactor where 50% conversion is achieved in 1 hour. Pure A is charged to the reactor at an initial concentration of 0.2 mol/dm^3 . If the same reaction is carried out in a CSTR, what volume would be necessary to achieve 50% conversion for a feed molar flow rate of 500 mol/h and an entering concentration of A of 0.2 mol/dm^3 ? (**Ans:** $V = 5000 \text{ dm}^3$)

P5-6_C A reversible liquid-phase isomerization $A \rightleftharpoons B$ is carried out *isothermally* in a 1000-gal CSTR. *The reaction is second order in both the forward and reverse directions.* The liquid enters at the top of the reactor and exits at the bottom. Experimental data taken in a batch reactor shows the CSTR conversion to be 40%. The reaction is reversible with $K_C = 3.0$ at 300 K, and $\Delta H_{RX}^\circ = -25,000 \text{ cal/mol}$. Assuming that the batch data taken at 300 K are accurate and that $E = 15000 \text{ cal/mol}$, what CSTR temperature do you recommend to obtain maximum conversion? *Hint:*

Read Appendix C and assume $\Delta C_P = 0$ in the Appendix Equation (C-9):

$$K_C(T) = K_C(T_0) \exp \left[\frac{\Delta H_{R_x}^\circ}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right]$$

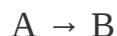
Use Polymath to make a plot of X versus T . Does it go through a maximum? If so, explain why.

P5-7_B OEQ (*Old Exam Question*). The irreversible gas-phase reaction



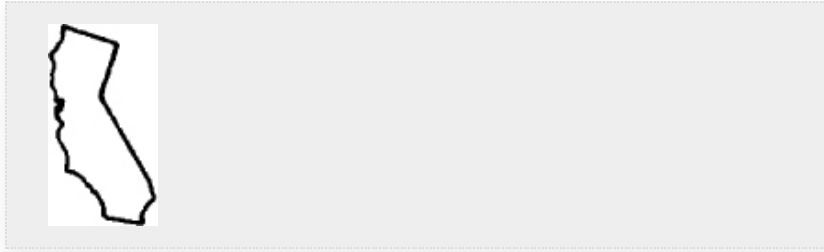
follows an elementary rate law and is to be carried out first in a PFR and then in a separate experiment in a CSTR. When pure A is fed to a 10 dm³ PFR at 300 K and a volumetric flow rate of 5 dm³/s, the conversion is 80%. When a mixture of 50% A and 50% inert (I) is fed to a 10 dm³ CSTR at 320 K and a volumetric flow rate of 5 dm³/s, the conversion is also 80%. What is the activation energy in cal/mol?

P5-8_B OEQ (*Old Exam Question*). The elementary gas-phase reaction



takes place isobarically and isothermally in a PFR where 63.2% conversion is achieved. The feed is pure A. It is proposed to put a CSTR of equal volume upstream of the PFR. Based on the entering molar flow rate of A to the first reactor, what will be the intermediate conversion from the CSTR, X_1 , and exit conversion from the PFR, X_2 , based on the feed to first reactor? The entering flow rates and all other variables remain the same as that for the

single PFR. Source: Modified California Registration Exam Problem. (**Ans:** $X_2 = 0.82$)



P5-9_A OEQ (*Old Exam Question*). The liquid-phase reaction



follows an elementary rate law and is carried out isothermally in a flow system. The concentrations of the A and B feed streams are each 2 M before mixing. The volumetric flow rate of each stream is 5 dm³/min, and the entering temperature is 300 K. The streams are mixed immediately before entering. Two reactors are available. One is a gray, 200.0-dm³ CSTR that can be heated to 77°C or cooled to 0°C, and the other is a white, 800.0-dm³ PFR operated at 300 K that cannot be heated or cooled but can be painted red or black. Note that $k = 0.07 \text{ dm}^3/\text{mol} \cdot \text{min}$ at 300 K and $E = 20 \text{ kcal/mol}$.

1. Which reactor and what conditions do you recommend? Explain the reason for your choice (e.g., color, cost, space available, weather conditions). Back up your reasoning with the appropriate calculations.
2. How long would it take to achieve 90% conversion in a 200-dm³ batch reactor with $C_{A0} = C_{B0} = 1 \text{ M}$ after mixing at a temperature of 77°C?
3. What would your answer to part (b) be if the reactor were cooled to 0°C? (**Ans:** 2.5 days)
4. What conversion would be obtained if the CSTR and PFR were operated at 300 K and connected in series? In parallel with 5 mol/min to each?
5. Keeping Table 4-3 in mind, what batch reactor volume would be necessary to process the same amount of species A per day as the flow reactors, while achieving 90% conversion? Referring to Table 1-1, estimate the cost of the batch reactor.

6. Write a couple of sentences describing what you learned from the problem and what you believe to be the point of the problem.
7. Apply one or more of the six ideas in Preface Table P-4, page xxvii, to this problem.

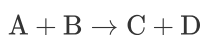
P5-10_B OEQ (*Old Exam Question*). Troubleshooting

1. A liquid-phase isomerization $A \rightarrow B$ is carried out in a 1000-gal CSTR that has a single impeller located halfway down the reactor. The liquid enters at the top of the reactor and exits at the bottom. The reaction is second order. Experimental data taken in a batch reactor predicted the CSTR conversion should be 50%. However, the conversion measured in the actual CSTR was 57%. Suggest reasons for the discrepancy and suggest something, for example, a model, that would give closer agreement between the predicted and measured conversions. Back your suggestions with calculations. P.S. It was raining *very* hard that day.
2. The liquid-phase reaction



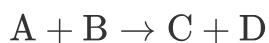
was carried out in a CSTR. For an entering concentration of 2 mol/dm^3 , the conversion was 40%. For the same reactor volume and entering conditions as the CSTR, the expected PFR conversion is 48.6%. However, the PFR conversion was, amazingly, 52.6% exactly. Brainstorm reasons for the disparity. Quantitatively show how these conversions came about (i.e., the expected conversion and the actual conversion). Part (b) is C-level difficulty. *#Really?*

3. The gas-phase reaction

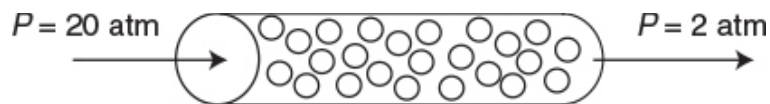


is carried out in a packed-bed reactor. When the particle size was decreased by 15%, the conversion remained unchanged. When the particle size was decreased by 20%, the conversion decreased. When the original particle size was increased by 15%, the conversion also decreased. In all cases, the temperature, the total catalyst weight, and all other conditions remained unchanged. What's going on here?

P5-11_B OEQ (*Old Exam Question*). The irreversible elementary gas-phase reaction

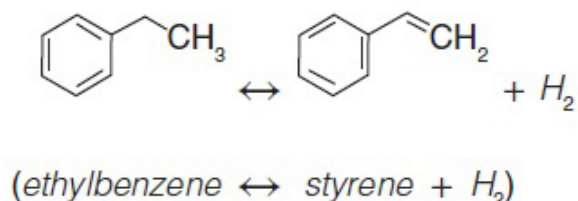


is carried out isothermally at 305 K in a packed-bed reactor with 100 kg of catalyst.



The entering pressure was 20 atm and the exit pressure is 2 atm. The feed is equal molar in A and B and the flow is in the turbulent flow regime, with $F_{A0} = 10 \text{ mol/min}$ and $C_{A0} = 0.4 \text{ mol/dm}^3$. Currently 80% conversion is achieved. What would be the conversion if the catalyst particle size were doubled and everything else remained the same? (**Ans:** $X = 0.83$)

P5-12_B The reversible gas-phase elementary reaction



is carried out in an isothermal CSTR with no pressure drop. The feed enters at a volumetric flow rate of $v_0 = 5000 \frac{\text{dm}^3}{\text{hr}}$. The feed consists of half ethyl benzene (i.e., A) and half inerts on a molar basis and is well mixed before it enters the reactor (I). The pressure in the reactor is 6 atm (so $P_{A0} = 3 \text{ atm}$ and $P_{I0} = 3 \text{ atm}$, making the entering concentration of ethyl benzene, A, $C_{A0} = 0.04 \frac{\text{mol}}{\text{dm}^3}$). The molar flow rate of A is $F_{A0} = 200 \frac{\text{mol}}{\text{hr}}$. At the reaction temperature of 640°C , the rate constant, k_A , is $5.92 \frac{\text{mol}}{\text{dm}^3 \cdot \text{hr} \cdot \text{atm}}$. The equilibrium constant, K_P , is 9 atm and the corresponding equilibrium conversion is $X_e = 0.84$.

Reference: Won Jae Lee and Gilbert F. Froment. *Ind. Eng. Chem. Res.*, 47, 9183–9194 (2008).

1. Write out each step of the algorithm.

2. Write the rate of reaction, $-r_A$, solely as a function of P_{A0} , X , K_P , and k .
3. Calculate the reactor volume necessary to achieve 90% of the equilibrium conversion, X_e .
4. How would the conversion from part (a) be affected if the reactor diameter increased and height decreased but total volume remained the same? Explain.

P5-13_B While on his way home from a concert by Ann Arbor's own Bob Seger at Pine Knob, during his visit to Michigan, world famous Inspector Sgt. Nigel Ambercromby was called in from Scotland Yard when the body of Ian Shoemaker, an English businessman, was discovered outside his home at 6 A.M. the morning of April 1st. Mr. Shoemaker was in the process of investigating why there was money missing from the chemical engineers' pension fund on March 31st. He met individually over coffee with each of the four employees who had access to the fund on March 31st, to confirm his suspicions before he pressed charges. However, the guilty one must have discovered Shoemaker's suspicions beforehand and wanted to keep their identity secret by murdering him.



Who done it?

During the autopsy the coroner determined Mr. Shoemaker was poisoned by a chemical known as Iocane powder. Iocane stops the heart from beating and is virtually

undetectable, but it decomposes in the blood to form the detectable compound Optoid, according to the reaction



Because of the high concentration of red blood cells, C_{RBC} , the rate law between Iocane and the red blood cells can be modeled as a pseudo first-order reaction in terms of the concentration of Iocane, C_A ,

$$-r_A = k'_A C_{\text{RBC}} C_A \cong k_A C_A$$

The coroner told Inspector Ambercromby that during the autopsy at 11 A.M. on April 1st, he found that the concentration of Optoid was 0.01 mol/dm^3 .

According to his calendar, Shoemaker had meetings the previous day, March 31st, at the following times:

1:30 P.M. (21.5 hours prior) with Mr. Gafhari

3:00 P.M. (20 hours prior) with Mr. Ross

5:00 P.M. (18 hours prior) with Ms. Patel

8:00 P.M. (15 hours prior) with Mr. Jenkins

These four individuals are now the prime suspects. Iocane is available over the counter as a rat poison in powder capsules, each containing 18 g (56.25 g/mol), and a capsule could have easily been put in Shoemaker's coffee.

Additional information:

Volume of blood: 5 dm^3

$k_A = 0.00944 \text{ hr}^{-1}$ at 310 K (body temperature)

$E = 20.5 \text{ kcal/mol}$

Assume the poison goes virtually immediately into the blood.

1. Calculate the initial concentration C_{A0} of Iocane in the blood in gmol/dm^3 after ingesting one capsule.
2. Knowing C_{A0} and the concentration of Optoid at 11 A.M., calculate the time Shoemaker was poisoned. Whom should Ambercromby arrest?
3. After calculating the time the poison was put in the coffee and arresting the alleged killer, Shoe-maker's wife mentioned that Shoemaker was running a fever of 311.7 K (101.4 F) that morning. Knowing Shoemaker had a fever, do you think Nigel arrested the right suspect? If not, whom should he arrest?

(Eric O'Neill, U of M, class of 2018)

P5-14_B The dehydration of butanol is carried out over a silica-alumina catalyst at 680 K.



The rate law is

$$-r'_{Bu} = \frac{kP_{Bu}}{(1 + K_{Bu}P_{Bu})^2}$$

with $k = 0.054 \text{ mol/gcat}\cdot\text{h}\cdot\text{atm}$ and $K_{Bu} = 0.32 \text{ atm}^{-1}$. Pure butanol enters a thin-tubed, packed-bed reactor at a molar flow rate of 50 kmol/hr and a pressure of 10 atm (1013•kPa).

1. What PBR catalyst weight is necessary to achieve 80% conversion in the absence of pressure drop? Plot and analyze X , p , f (i.e., (v/v_0)) and reaction rate, $-r'_A$, as a function of catalyst weight.
2. What "fluidized CSTR" catalyst weight is necessary to achieve 80% conversion?
3. Repeat (a) when there is pressure drop, with the pressure-drop parameter $\alpha = 0.0006 \text{ kg}^{-1}$. Do you observe a maximum in the rate of reaction, and if so, why? What catalyst weight is necessary to achieve 70% conversion? Compare this weight with that for no pressure drop to achieve the same conversion.
4. What generalizations can you make about this problem?
5. Write a question for this problem that requires critical thinking and then explain why your question requires critical thinking. *Hint:* See Preface Section G.2

P5-15_B OEQ (Old Exam Question). The gaseous reaction $A \rightarrow B$ has a unimolecular reaction rate constant of 0.0015 min^{-1} at 80°F . This reaction is to be carried out in *parallel tubes* 10 ft long and 1 in. inside diameter, under a pressure of 132 psig at 260°F . A production rate of 1000 lb/h of B is required. Assuming an activation energy of 25000 cal/mol, how many tubes are needed if the conversion of A is to be 90%? Assume perfect gas laws. A and B each have molecular weights of 58. Source: From California Professional Engineers' Exam.



P5-16_B OEQ (Old Exam Question).

1. The irreversible elementary reaction $2A \rightarrow B$ takes place in the gas phase in an *isothermal tubular (plug-flow) reactor*. Reactant A and a diluent C are fed in equimolar ratio, and conversion of A is 80%. If the molar feed rate of A is cut in half, what is the conversion of A assuming that the feed rate of C is left unchanged? Assume ideal behavior and that the reactor temperature remains unchanged. What was the point of this problem? Source: From California Professional Engineers' Exam.
2. Write a question that requires critical thinking, and explain why it involves critical thinking. (See Preface Section G.2.)



P5-17_B OEQ (Old Exam Question). Compound A undergoes a reversible isomerization reaction, $A \rightleftharpoons B$, over a supported metal catalyst. Under pertinent conditions, A and B are liquid, miscible, and of nearly identical density; the equilibrium constant for the reaction (in concentration units) is 5.8. In a *fixed-bed iso-thermal flow reactor* in which backmixing is negligible (i.e., plug flow), a feed of pure A undergoes a net conversion to B of 55%. The reaction is elementary. If a second, identical flow reactor at the same temperature is placed downstream from the first, what overall conversion of A would you expect if:

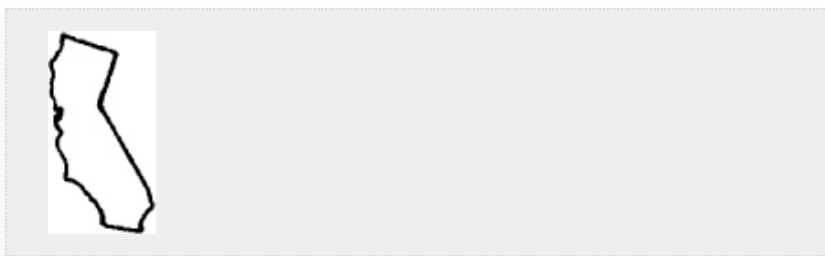
1. The reactors are directly connected in series? (**Ans:** $X = 0.74$)
2. The products from the first reactor are separated by appropriate processing and only the unconverted A is fed to the second reactor?
3. Apply to this problem one or more of the six ideas discussed in Table P-4 in the Complete Preface-Introduction on the Web Site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>).

P5-18_B OEQ (Old Exam Question). A total of 2500 gal/h of metaxylene is being isomerized to a mixture of orthoxylene, metaxylene, and paraxylene in a reactor containing 1000 ft³ of catalyst. The reaction is being carried out at 750°F and 300 psig. Under these conditions, 37% of the metaxylene fed to the reactor is isomerized. At a flow rate of 1667 gal/h, 50% of the metaxylene is isomerized at the same temperature and pressure. Energy changes are negligible.

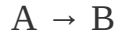


It is now proposed that a second plant be built to process 5500 gal/h of metaxylene at the same temperature and pressure as described earlier. What size reactor (i.e., what volume of catalyst) is required if conversion in the new plant is to be 46% instead of 37%? Justify any assumptions made for the scale-up calculation. (**Ans:** 2931 ft³ of catalyst) Make a list of the things you learned from this problem. Source: From California Professional Engineers' Exam.

P5-19_B OEQ (Old Exam Question). It is desired to carry out the gaseous reaction $A \rightarrow B$ in an existing *tubular reactor* consisting of 50 parallel tubes 40 ft long with a 0.75-in. inside diameter. Bench-scale experiments have given the reaction rate constant for this first-order reaction as 0.00152 s^{-1} at 200°F and 0.0740 s^{-1} at 300°F. At what temperature should the reactor be operated to give a conversion of A of 80% with a feed rate of 500 lb m/h of pure A and an operating pressure of 100 psig? A has a molecular weight of 73 Daltons. Departures from perfect gas behavior may be neglected, and the reverse reaction is insignificant at these conditions. (**Ans:** $T = 278^\circ\text{F}$) Source: From California Professional Engineers' Exam.

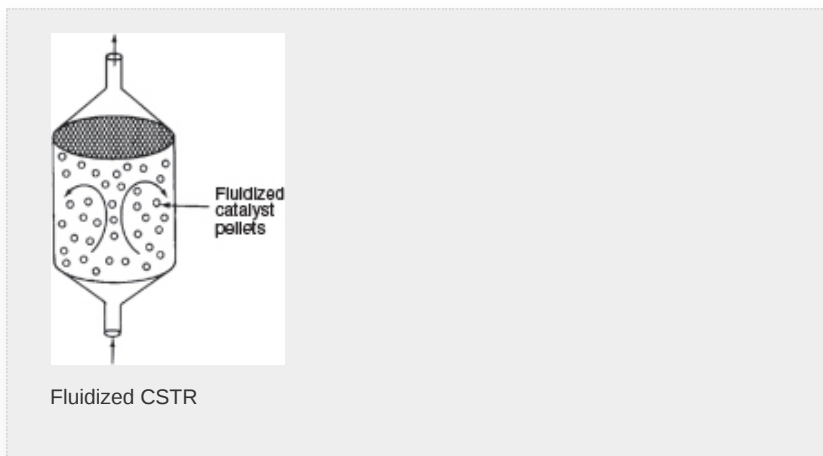


P5-20_B The irreversible first-order (wrt partial pressure of A) gas-phase reaction



is carried out isothermally in a “fluidized” catalytic CSTR containing 50 kg of catalyst.

Currently, 50% conversion is realized for pure A entering at a pressure of 20 atm. There is virtually no pressure drop in the CSTR. It is proposed to put a PBR containing the same catalyst weight in series with the CSTR. The pressure drop parameter for the PBR, α , given by Equation (5-29) is $\alpha = 0.018 \text{ kg}^{-1}$. The particle size is 0.2 mm, the bed porosity is 40%, and the viscosity is the same as that of air at 200°C.



1. Should the PBR be placed upstream or downstream of the CSTR in order to achieve the highest conversion? Explain qualitatively using concepts you learned in Chapter 2.
2. What is the conversion coming out of the first reactor?
3. What is the conversion exiting the last reactor? (**Ans:** $X = 0.76$)
4. What is the pressure at the exit of the packed bed? (**Ans:** $P = 6.32 \text{ atm}$)
5. How would your answers change if the catalyst diameter were decreased by a factor of 2 and the PBR diameter were increased by 50%, assuming turbulent flow?

P5-21_B A microreactor from the MIT group similar to the one shown in Figure P5-21_B was used to produce phosgene

in the gas phase. We continue our discussion on microreactors in [Chapter 6](#).

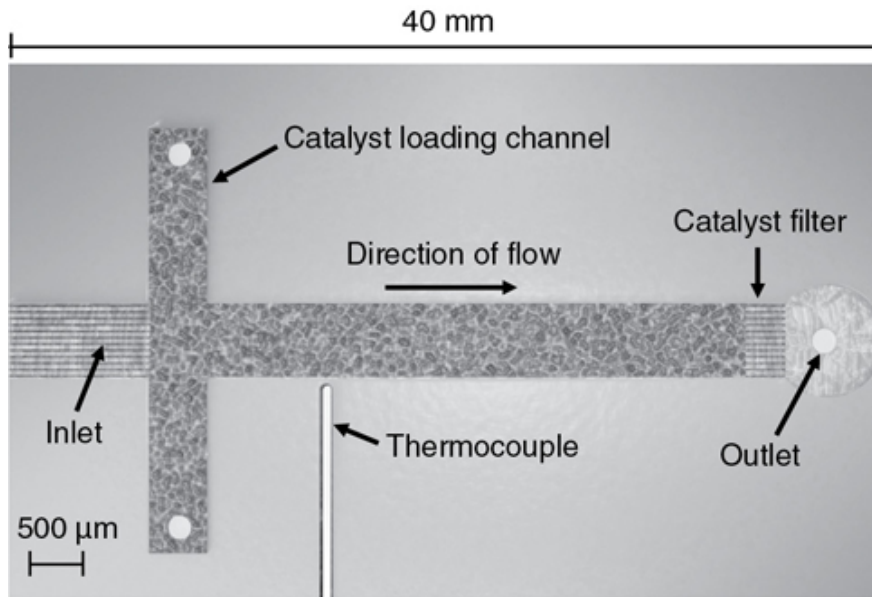
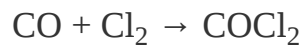


Figure P5-21_B Microreactor. (Image courtesy of Ryan Hartman, NYU.)



The microreactor is 20 mm long, 500 μm in diameter, and packed with catalyst particles 35 μm in diameter. The entering partial pressure of A is 231 kPa (2.29 atm), and the entering flow to each microreactor is equimolar. The molar flow rate of CO is 2×10^{-5} mol/s and the volumetric flow is 2.83×10^{-7} m³/s. The weight of catalyst in one microreactor: $W = 3.5 \times 10^{-6}$ kg. The reactor is kept iso-thermal at 120°C. Because the catalyst is also slightly different than the one in [Figure P5-21_B](#), the rate law is different as well:

$$-r'_A = k_A C_A C_B$$

Additional information:

$\alpha = 3.55 \times 10^5/\text{kg catalyst}$ (based on properties of air and $\phi = 0.4$)

$k = 0.004 \text{ m}^6/(\text{mol} \cdot \text{s} \cdot \text{kg catalyst})$ at 120°C

$u_0 = 2.83 \cdot 10^{-7} \text{ m}^3/\text{s}$, $\rho = 7 \text{ kg/m}^3$, $\mu = 1.94 \cdot 10^{-5} \text{ kg/m} \cdot \text{s}$

$A_c = 1.96 \cdot 10^{-7} \text{ m}^2$, $G = 10.1 \text{ kg/m}^2 \cdot \text{s}$

1. Plot the molar flow rates F_A , F_B , and F_C , the conversion X , and pressure ratio p along the length (i.e., catalyst weight, W) of the reactor.
2. Calculate the number of microreactors in parallel needed to produce 10000 kg/year phosgene.
3. Repeat part (a) for the case when the catalyst weight remains the same but the particle diameter is cut in half. If possible, compare your answer with part (a) and describe what you find, noting anything unusual.
4. How would your answers to part (a) change if the reaction were reversible with $K_C = 0.4 \text{ dm}^3/\text{mol}$? Describe what you find.
5. What are the advantages and disadvantages of using an array of microreactors over using one conventional packed-bed reactor that provides the same yield and conversion?
6. Write a question that involves critical thinking, and explain why it involves critical thinking. (See Preface, Tables P-3 and P-4.)
7. Apply to this problem one or more of the six ideas discussed in Table P-4 in the Complete Preface-Introduction on the Web Site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>).

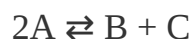
P5-22A A very proprietary industrial waste reaction, which we'll code as $A \rightarrow B + S$, is to be carried out in a 10-dm^3 CSTR followed by a 10-dm^3 PFR. The reaction is elementary, but A, which enters at a concentration of 0.001 mol/dm^3 and a molar flow rate of 20 mol/min , has trouble decomposing. The specific reaction rate at 42°C (i.e., room temperature in the Mojave desert) is 0.0001 s^{-1} . However, we don't know the activation energy; therefore, we cannot carry out this reaction in the winter in Michigan. Consequently, this reaction, while important, is not worth your time to study. Therefore, perhaps you want to take a break and go

watch a movie such as *Dances with Wolves* (all-time favorite of the author), *Bohemian Rhapsody*, *A Star is Born*, or *Despicable Me 3*. As a side note, the Jofostan Film Festival is held the last week in January in Riça, Jofostan. But don't try to attend the Jofostan Film Festival as it's only "A-List" celebrities such as Denzel Washington, Meryl Streep, and Sven Köttlov.

P5-23_B Walter White, Jesse Pinkman, and Mike Ehrmantraut stole 1000 gal of methylamine during an episode of the TV series *Breaking Bad* (See Season 4, Episode 10). Shortly thereafter, Jesse and Mike decided they would get out of the cooking business and sell their shares of the methylamine. Walter wanted to keep all of the methylamine for future meth cooks and not let Jesse and Mike have their shares. Suppose Jesse and Mike decided to sabotage Walter's cooking operation by ruining the methylamine using the following gas-phase reaction:



or, in short:



This reaction converts the methylamine to dimethylamine, using a silica-alumina catalyst. The molar flow rate into a packed-bed reactor is 23.6 mol/s and the entering pressure is 18 atm. Assume there is no pressure drop or temperature change in the reactor. The reaction rate follows an elementary rate law in terms of partial pressure.

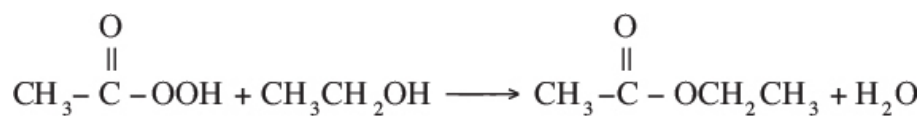
$$k_1 = 4.25 \times 10^{-6} \frac{\text{mol}}{\text{atm}^2 \cdot \text{gcatalyst} \cdot \text{s}} \quad \text{and} \quad K_e = 2.5$$

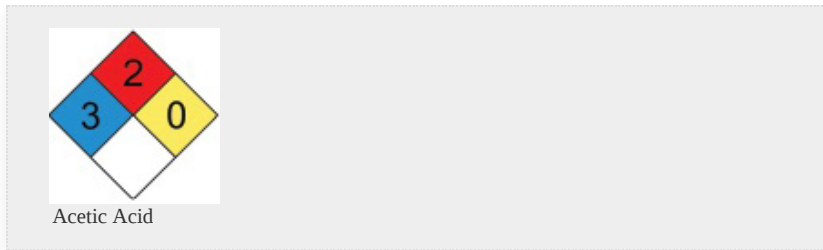
1. Write the mole balance.
2. Write the rate law in terms of partial pressures.
3. Set up a stoichiometric table for this reaction.
4. Write the partial pressures in terms of conversion.
5. Write the rate law solely in terms of conversion.
6. What is the equilibrium conversion, X_e ?
7. Write out your algorithm in terms of conversion.
8. How many kilograms of catalyst would Jesse need to load in a PBR to obtain a conversion of $0.9 X_e$? For $X = 0.75 X_e$?
9. How many kilograms of catalyst would be needed to obtain 90% of the equilibrium conversion in a fluidized bed reactor? If this weight is very, very large, what might you suggest to reduce the weight? (**Ans:** $W = 207.2 \text{ kg catalyst}$)
10. What conversion would be achieved in a 100 kg PBR with pressure drop and $\alpha = 0.0098 \text{ kg}^{-1}$? At what catalyst weight does the exit pressure fall below 1.0 atm?
11. Repeat (j) when pressure drop is accounted for with $\alpha = 6 \times 10^{-4} \text{ kg}^{-1}$.
While co-teaching CRE with me, PhD student Julia Faeth, created this problem using modified data from J. W. Mitchell, et al., *Ind. Eng. Chem. Res.* 33, 181–184 (1994).



Who done it?

P5-24_B OEQ (Old Exam Question). Ethyl acetate is an extensively used solvent and can be formed by the vapor-phase esterification of acetic acid and ethanol.

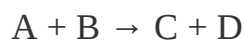




The reaction was studied using a microporous resin as a catalyst in a *packed-bed microreactor* (*Ind. Eng. Chem. Res.*, 26(2), 198(1987)). The reaction is first-order in ethanol and pseudo zero-order in acetic acid. The total volumetric feed rate is $25 \text{ dm}^3/\text{min}$, the initial pressure is 10 atm, the temperature is 223°C , and the pressure-drop parameter, α , equals 0.01 kg^{-1} . For an equal molar feed rate of acetic acid and ethanol, the specific reaction rate is about $1.3 \text{ dm}^3/\text{kg-cat-min}$.

1. Calculate the maximum weight of catalyst that one could use and maintain an exit pressure above 1 atm. (**Ans:** $W = 99 \text{ kg}$)
2. Write out the CRE algorithm and then solve these equations analytically to determine the catalyst weight necessary to achieve 90% conversion.
3. Write a Polymath program to plot and analyze X , p , and $f = v/v_0$ as a function of catalyst weight down the packed-bed reactor. You can either use your analytical equations for x , p , and f or you can plot these quantities using the Polymath program.
4. What is the ratio of catalyst needed to achieve the last 5% (85%–90%) conversion to the weight necessary to achieve the first 5% conversion (0%–5%) in the reactor? *Note:* You can use the results in part (c) to also answer this part.

P5-25_B The gas-phase reaction



takes place isothermally at 300 K in a packed-bed reactor in which the feed is equal molar in A and B with $C_{A0} = 0.1 \text{ mol/dm}^3$. The reaction is second order in A and zero order in B. Currently, 50% conversion is achieved in a reactor with 100 kg of catalysts for a volumetric flow rate

100 dm³/min. The pressure-drop parameter, α , is $\alpha = 0.0099 \text{ kg}^{-1}$. If the activation energy is 10000 cal/mol, what is the specific reaction-rate constant at 400 K?

P5-26_B Go to Professor Herz's Reactor Lab on the Web at www.reactorlab.net. Click on Download and then click on the English version link. Provide the information asked and then click Download. Select Division 2, Lab 2 of The Reactor Lab concerning a packed-bed reactor (labeled PFR) in which a gas with the physical properties of air flows over spherical catalyst pellets. Perform experiments here to get a feeling for how pressure drop varies with input parameters such as reactor diameter, pellet diameter, gas flow rate, and temperature. In order to get significant pressure drop, you may need to change some of the input values substantially from those shown when you enter the lab. If you get a notice that you can't get the desired flow, then you need to increase the inlet pressure. In [Chapter 10](#), you will learn how to analyze the conversion results in such a reactor.

SUPPLEMENTARY READING

- G. KEILLOR, *Pretty Good Joke Book, A Prairie Home Companion*. St. Paul, MN: Highbridge Co., 2000.
- J. B. BUTT, *Reaction Kinetics and Reactor Design*, 2nd ed. Revised and Expanded. New York: Marcel Dekker, Inc., 1999.
- H. S. FOGLER, *Current Fashions: What the Well-Dressed Chemical Reaction Engineer Will Be Wearing in Spring 2020*. Available Fall 2025.
- O. LEVENSPIEL, *Chemical Reaction Engineering*, 3rd ed. New York: Wiley, 1998, Chaps. 4 and 5.

Recent information on reactor design can usually be found in the following journals: *Chemical Engineering Science*, *Chemical Engineering Communications*, *Industrial and Engineering Chemistry Research*, *Canadian Journal of Chemical Engineering*, *AIChE Journal*, *Chemical Engineering Progress*.

6. Isothermal Reactor Design: Moles and Molar Flow Rates

Don't let your fears . . .

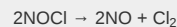
Get in the way of your dreams

—Anonymous

Overview. In [Chapter 5](#) we used conversion to design a number of isothermal reactors for single reactions. While in many situations writing the mole balances in terms of conversion is an extremely effective strategy, there are many instances where it is more convenient, and in some cases absolutely necessary, to write the mole balance in terms of moles (N_A , N_B) or molar flow rates (F_A , F_B), as shown in Table S1-1 in [Chapter 1](#). In this chapter, we show how to make small changes in our CRE algorithm to analyze these situations. Using our algorithm, we first write a mole balance *on each and every species*, and second, we need to relate the rates of reaction of each species to one another using the relative rates described in [Chapter 3](#), that is, Equation (3-1).

We will use molar flow rates in our mole balance to analyze

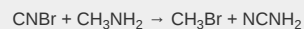
- A microreactor with the reaction



- A membrane reactor used for the dehydrogenation of ethylbenzene



- A semibatch reactor used for the reaction



We will again use mole balances in terms of these variables (N_i , F_i) for multiple reactions in [Chapter 8](#) and for heat effects in [Chapters 11–13](#).

6.1 THE MOLES AND MOLAR FLOW RATE BALANCE ALGORITHMS

Used for:

- Multiple rxns
- Membranes
- Unsteady state

There are many instances when it is much more convenient to work in terms of the number of moles (N_A , N_B) or molar flow rates (F_A , F_B , etc.) rather than conversion. Membrane reactors and multiple reactions taking place in the gas phase are two such cases where it is *absolutely* necessary to use molar flow rates rather than conversion. We now modify our CRE algorithm by using concentrations for liquids and molar flow rates for gases as our dependent variables. The main difference between the conversion algorithm and the molar flow rate/concentration algorithm is that, in the conversion algorithm, we needed to write a mole balance on only *one species*, whereas in the molar flow rate and concentration algorithm, we must write a mole balance on *each and every species*. This algorithm is shown in [Figure 6-1](#). First, we write the mole balances on all species present, as shown in Step ①. Next, we write the rate law, Step ②, and then we relate the mole balances to one another through the *relative rates of reaction*, as shown in Step ③. Steps ④ and ⑤ are used to relate the concentrations in the rate law to the molar flow rates. In Step ⑥, all the steps are combined by the ODE solver (e.g., Polymath, MATLAB, Wolfram, and Python).

6.2 MOLE BALANCES ON CSTRS, PFRS, PBRs, AND BATCH REACTORS

6.2.1 Liquid Phase

For liquid-phase reactions, the density remains constant and consequently there is no change in either the volume V or the volumetric flow rate, $v = v_0$, during the course of the reaction. Therefore, *concentration* is the preferred design variable. The mole balances derived in [Chapter 1](#) (Table S1-1) are now applied to each species for the generic reaction



The mole balances are then coupled to one another using the relative rates of reaction

Used to couple the mole balances

$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d} \quad (3-1)$$

to arrive at [Table 6-1](#), which gives the balance equations in terms of concentration for the four types of reactors we have been discussing. We see from [Table 6-1](#) that we have *only* to specify the parameter values for the system (C_{A0} , v_0 , etc.) and for the rate-law parameters (e.g., k_A , α , β) to solve the coupled ordinary differential equations for either BRs, PFRs, or PBRs, or to solve the coupled algebraic equations for a CSTR.

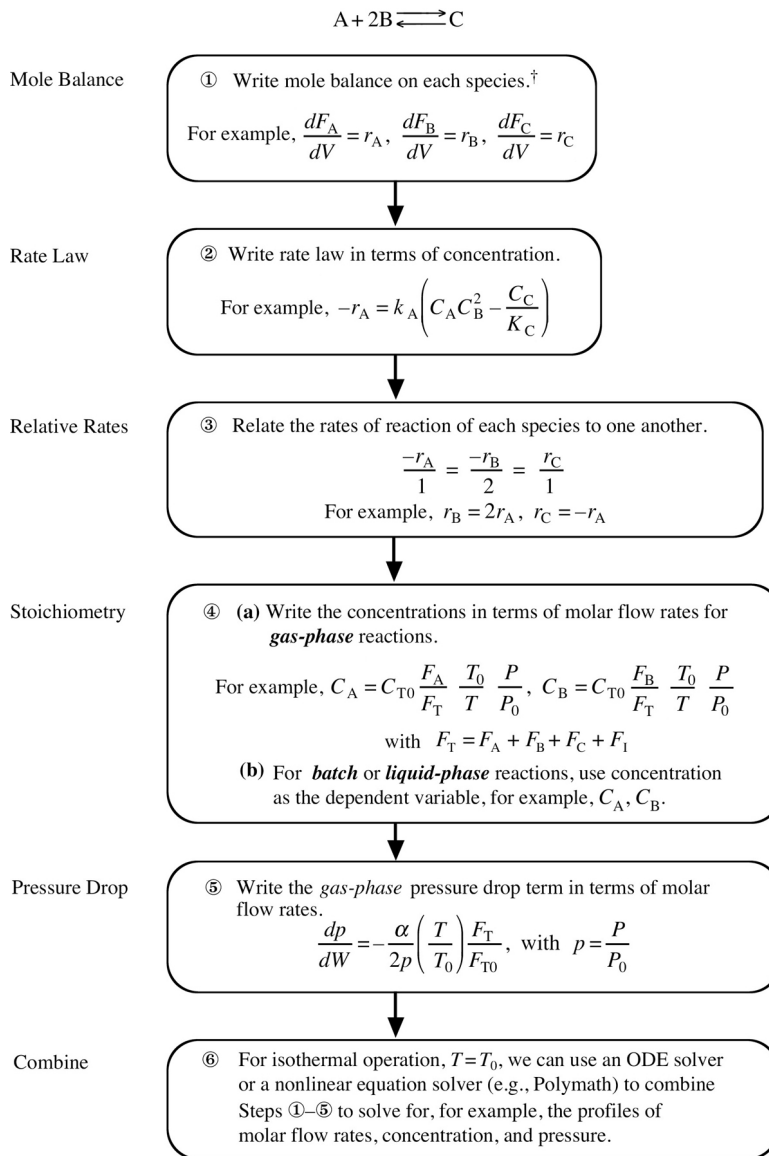


Figure 6-1 Isothermal reaction design algorithm for mole balances.

[†] For a PBR, use $\frac{dF_A}{dW} = r'_A$, $\frac{dF_B}{dW} = r'_B$, and $\frac{dF_C}{dW} = r'_C$.

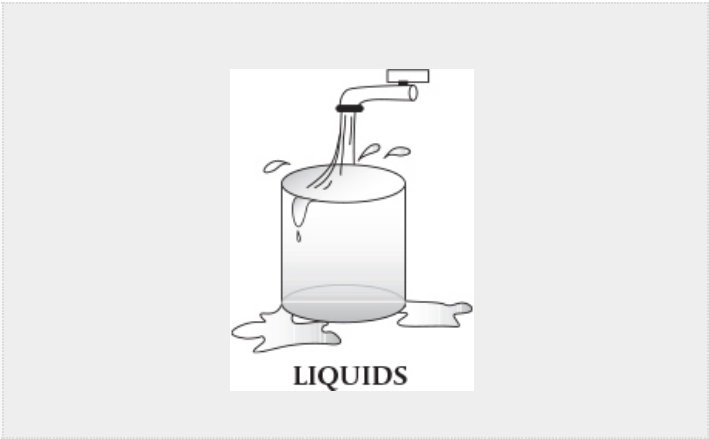


TABLE 6-1 MOLE BALANCES FOR LIQUID-PHASE REACTIONS

Batch	$\frac{dC_A}{dt} = r_A$	and	$\frac{dC_B}{dt} = \frac{b}{a} r_A$
CSTR	$V = \frac{v_0(C_{A0}-C_A)}{-r_A}$	and	$V = \frac{v_0(C_{B0}-C_B)}{-(b/a)r_A}$
PFR	$v_0 \frac{dC_A}{dV} = r_A$	and	$v_0 \frac{dC_B}{dV} = \frac{b}{a} r_A$
PBR	$v_0 \frac{dC_A}{dW} = r'_A$	and	$v_0 \frac{dC_B}{dW} = \frac{b}{a} r'_A$

6.2.2 Gas Phase

The mole balances for gas-phase reactions are given in [Table 6-2](#) in terms of the number of moles (batch) or molar flow rates for the generic rate law for the generic reaction, Equation (2-1). The molar flow rates for each species F_j are obtained from a mole balance on each species (i.e., A, B, C, and D), as given in [Table 6-2](#). For example, for a plug-flow reactor

$$\frac{dF_j}{dV} = r_j \quad (1-11)$$

Must write a mole balance on each and every species

The generic power-law rate law for species A is

Rate Law

$$-r_A = k_A C_A^\alpha C_B^\beta \quad (3-3)$$

The rate law wrt A is coupled with the equation for relative rates,

$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d} \quad (3-1)$$

Given the rate law, Equation (3-3), for species A, we use Equation (3-1) to substitute for species j , r_j , in Equation (1-11), the PFR mole balance.

To relate concentrations to molar flow rates, recall Equation (4-17), for gas-phase reactions with $p = P/P_0$

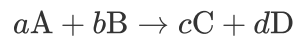
Stoichiometry

$$C_j = C_{T0} \frac{F_j}{F_T} \frac{T_0}{T} p \quad (4-17)$$

The pressure-drop equation, Equation (5-28), for isothermal operation ($T = T_0$) is

$$\frac{dp}{dW} = \frac{-\alpha}{2p} \frac{F_T}{F_{T0}} \quad (5-28)$$

TABLE 6-2 ALGORITHM FOR GAS-PHASE REACTIONS



1. Mole balances:

BRPFRPBRCTR

$$\frac{dN_A}{dt} = r_A V \quad \frac{dF_A}{dV} = r_A \quad \frac{dF_A}{dW} = r'_A \quad V = \frac{F_{A0} - F_A}{-r_A}$$

$$\frac{dN_B}{dt} = r_B V \quad \frac{dF_B}{dV} = r_B \quad \frac{dF_B}{dW} = r'_B \quad V = \frac{F_{B0} - F_B}{-r_B}$$

$$\frac{dN_C}{dt} = r_C V \quad \frac{dF_C}{dV} = r_C \quad \frac{dF_C}{dW} = r'_C \quad V = \frac{F_{C0} - F_C}{-r_C}$$

$$\frac{dN_D}{dt} = r_D V \quad \frac{dF_D}{dV} = r_D \quad \frac{dF_D}{dW} = r'_D \quad V = \frac{F_{D0} - F_D}{-r_D}$$

Also inerts, $\frac{dF_I}{dV} = 0 \quad \frac{dF_I}{dW} = 0 \quad F_I = F_{I0}$
 if any
 $\frac{dN_I}{dt} = 0$

We shall continue the algorithm using a **PBR** as an example.

2. Rates:

Rate Law

$$-r'_A = k_A C_A^\alpha C_B^\beta$$

Relative Rates

$$\frac{r'_A}{-a} = \frac{r'_B}{-b} = \frac{r'_C}{c} = \frac{r'_D}{d}$$

then

$$r'_B = \frac{b}{a} r'_A \quad r'_C = -\frac{c}{a} r'_A \quad r'_D = -\frac{d}{d} r'_A$$

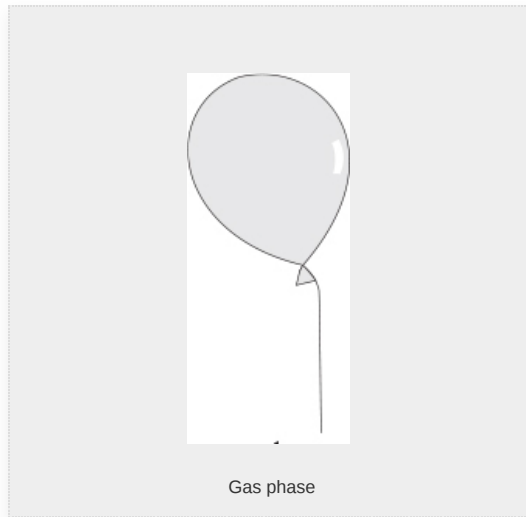
3. Stoichiometry:

Concentrations

$$C_A = C_{T0} \frac{F_A T_0}{F_T T} p \quad C_B = C_{T0} \frac{F_B T_0}{F_T T} p$$

$$C_C = C_{T0} \frac{F_C T_0}{F_T T} p \quad C_D = C_{T0} \frac{F_D T_0}{F_T T} p$$

$$\frac{dp}{dW} = \frac{-\alpha}{2p} \frac{F_T}{F_{T0}} \frac{T}{T_0}, p = \frac{P}{P_0}$$



$$\text{Total molar flow rate: } F_T = F_A + F_B + F_C + F_D + F_1$$

4. Combine:

1. Appropriate reactor mole balance on each species
2. Rate law
3. Concentration for each species
4. Pressure-drop equation

5. Evaluate:

1. Specify and enter parameter values: k_A , C_{T0} , $\alpha, \beta, T_0, a, b, c, d$
2. Specify and enter entering molar flow rates: F_{A0} , F_{B0} , F_{C0} , F_{D0} , and final volume, V_{final}

6. Use an ODE solver.

Many times we will let the ODE solver replace **Step 4, Combine.**

The total molar flow rate is given by the sum of the flow rates of the individual species

$$F_T = \sum_{j=1}^n F_j$$

When species A, B, C, D, and inert I are the only species present, then

$$F_T = F_A + F_B + F_C + F_D + F_I$$

We now combine all the preceding information, as shown in Table 6-2.¹

¹ View the YouTube video made by the chemical reaction engineering students at the University of Alabama, titled *Find Your Rhyme*. Videos can be accessed directly from the home page of the CRE Web site, www.umich.edu/~elements/6e/index.html.

6.3 APPLICATION OF THE PFR MOLAR FLOW RATE ALGORITHM TO A MICROREACTOR

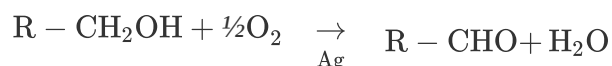
A photo of a micro reactor is shown in Figure P5-21_B on page 225.

Advantages of microreactors

Microreactors have emerged as a useful technology in CRE. They are characterized by their high surface-area-to-volume ratios in their microstructured regions that contain tubes or channels. A typical channel width might be 100 μm with a length of 20000 μm (2 cm). The resulting high surface-area-to-volume ratio (ca. 10000 m^2/m^3) reduces or even eliminates heat and mass transfer resistances often found in larger reactors. Consequently, surface-catalyzed reactions can be greatly facilitated, hot spots in highly exothermic reactions can

be minimized, and in many cases highly exothermic reactions can be carried out virtually isothermally. These features provide the opportunity for microreactors to be used to study the intrinsic kinetics of reactions. Another advantage of microreactors is their use in the production of toxic or explosive intermediates where a leak or microexplosion for a single unit will do minimal damage because of the small quantities of material involved. Other advantages include shorter residence times and narrower residence time distributions.

Figure 6-2 shows (a) a microreactor with a heat exchanger and (b) a microplant with reactor, valves, and mixers. Heat, \dot{Q} , can be added or taken away by the fluid flowing perpendicular to the reaction channels, as shown in Figure 6-2(a). Production in microreactor systems can be increased simply by adding more units in parallel. For example, the catalyzed reaction



required only 32 microreaction systems in parallel to produce 2000 tons/yr of acetate!

Microreactors are also used for the production of specialty chemicals, combinatorial chemical screening, lab-on-a-chip, and chemical sensors. In modeling microreactors, we will assume they are either in plug flow for which the mole balance is

$$\frac{dF_A}{dV} = r_A \quad (1-12)$$

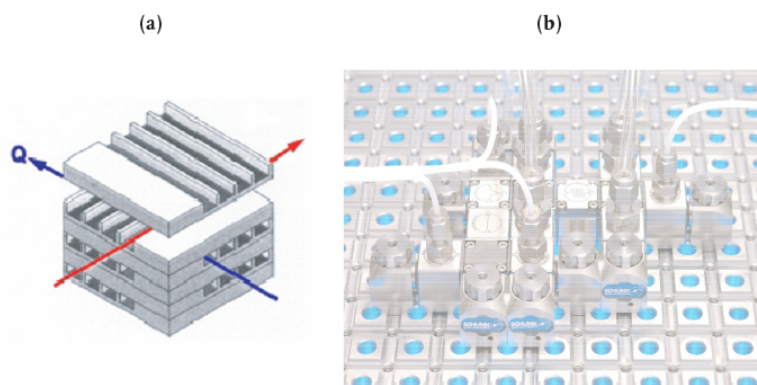
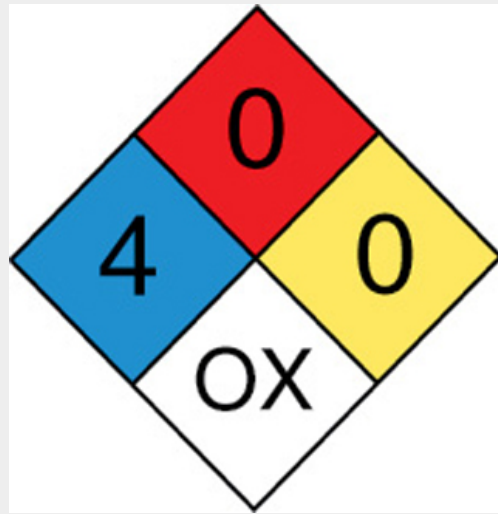


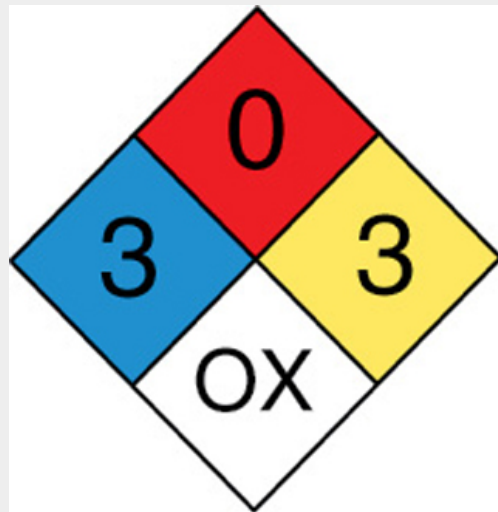
Figure 6-2 Microreactor (a) and microplant (b).
(Photo courtesy of Ehrfeld, Hessel, and Löwe,
*Microreactors: New Technology for Modern
Chemistry*, Weinheim, Germany: Wiley-VCH.)

or in laminar flow, in which case we will use the segregation model discussed in [Chapter 17](#). For the plug-flow case, the algorithm is described in [Figure 6-1](#).

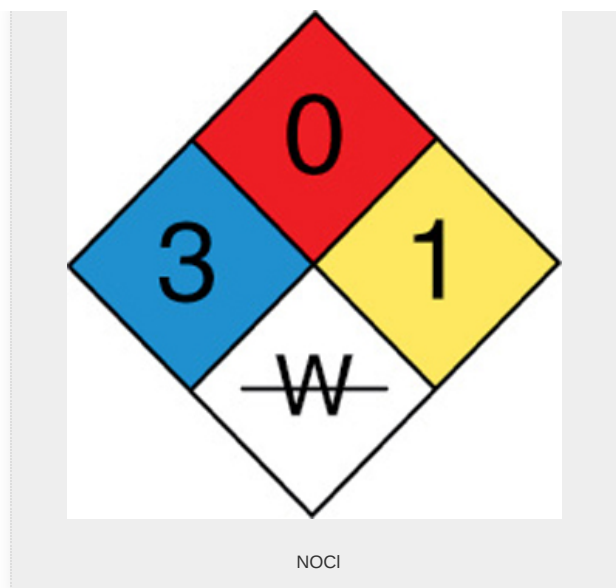
Example 6–1 Gas-Phase Reaction in a Microreactor
—Molar Flow Rates



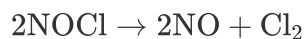
Cl



NO

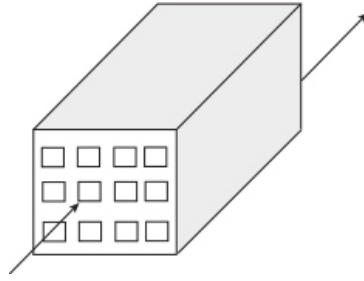


Nitrous oxide (NO) gas is used by a number of dentists on their patients (the author being one) to eliminate pain during drilling and tooth extraction. Nitrous oxide can be produced by the gas-phase second-order reaction.



is to be carried out at 425°C and 1641 kPa (16.2 atm). Pure NOCl is to be fed, and the reaction follows an elementary rate law.² It is desired to produce 20 tons of NO per year in a microreactor system using a bank of 10 microreactors in parallel. Each microreactor has 100 channels with each channel 0.2 mm square and 250 mm in length, giving a volume of a single channel to be 10⁻⁵ dm³.

² J. B. Butt, *Reaction Kinetics and Reactor Design*, 2nd ed. New York: Marcel Dekker, 2001, p. 153.



1. Plot and analyze the molar flow rates of NOCl, NO, and Cl₂ as a function of volume down the length of the reactor.
2. What is the reactor volume necessary to achieve 85% conversion of NOCl?

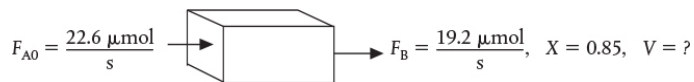
Additional Information

To produce 20 tons per year of NO at 85% conversion would require a feed rate of 0.0226 mol/s of NOCl, or 2.26×10^{-5} mol/s per channel. The reaction-rate constant is

$$k = 0.29 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \text{ at } 500 \text{ K with } E = 24 \frac{\text{kcal}}{\text{mol}}$$

Solution

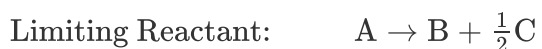
For one channel



Find V.

Although this particular problem could be solved using conversion, we shall illustrate how it can also be solved using molar flow rates as the variable in the mole balance. *Why do we do this?* We do this to give practice using molar flow rates as the variables in order to help prepare the reader for the more complex problems, such as multiple reactions, where conversion cannot be used as the design variable. However, at the end we can use molar flow rate F_A to calculate the conversion X .

We first write the reaction in symbolic form and then divide by the stoichio-metric coefficient of the limiting reactant, NOCl.

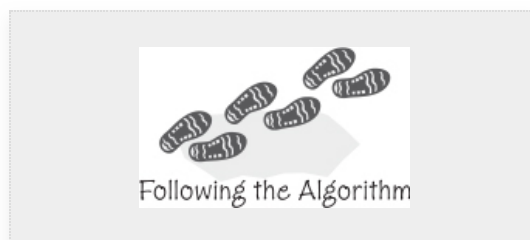


1. Mole balances on species A, B, and C:

$$\frac{dF_A}{dV} = r_A \quad (\text{E6-1.1})$$

$$\frac{dF_B}{dV} = r_B \quad (\text{E6-1.2})$$

$$\frac{dF_C}{dV} = r_C \quad (\text{E6-1.3})$$



2. Rates:

1. Rate Law

$$-r_A = kC_A^2, \text{ with } k = 0.29 \frac{\text{dm}^3}{\text{mol}\cdot\text{s}} \text{ at } 500 \text{ K} \quad (\text{E6-1.4})$$

2. Relative Rates

$$\frac{r_A}{-1} = \frac{r_B}{1} = \frac{r_C}{\frac{1}{2}}$$

$$r_B = -r_A$$

$$r_C = \frac{1}{2}r_A$$

3. Stoichiometry: Gas phase with $T = T_0$ and $P = P_0$, then

$$v = v_0 \frac{F_T}{F_{T0}} \quad \text{Concentration Gas Phase}$$

$$C_{Aj} = C_{T0} \frac{F_j}{F_T} p \frac{T_0}{T} \quad (4-17)$$

$$p = (1 - \alpha_p V)^{1/2} \quad (5-35)$$

Side Note: Calculations in the **Chapter 6** Expanded Material on the Web site

(<http://www.umich.edu/~elements/6e/06chap/alpha-P-calculation-Example-6-1.pdf>) using Equation (5-36) show that the pressure-drop parameter, α_p , for each channel is

be $\alpha_p = \frac{4f_F G^2}{A_{C,p} P_0 D} = 3.47 \text{ cm}^{-3}$. For a channel volume of $V = 0.01 \text{ cm}^3$ the pressure ratio p is

$$p = (1 - (3.47)(0.01))^{1/2} \approx 1$$

Therefore, we will neglect pressure drop, that is, $P = P_0$, $p = 1$.

Applying Equation (4-17) to species A, B, and C, for isothermal operation ($T = T_0$), and for no pressure drop, $P = P_0$, ($p = 1$), the concentrations are

$$C_A = C_{T0} \frac{F_A}{F_T}, C_B = C_{T0} \frac{F_B}{F_T}, C_C = C_{T0} \frac{F_C}{F_T} \quad (\text{E6-1.5})$$

with $F_T = F_A + F_B + F_C$

4. **Combine:** The rate law in terms of molar flow rates is

$$-r_A = k C_{T0}^2 \left(\frac{F_A}{F_T} \right)^2$$

combining all

$$\frac{dF_A}{dV} = -k C_{T0}^2 \left(\frac{F_A}{F_T} \right)^2 \quad (\text{E6-1.6})$$

$$\frac{dF_B}{dV} = k C_{T0}^2 \left(\frac{F_A}{F_T} \right)^2 \quad (\text{E6-1.7})$$

$$\frac{dF_C}{dV} = \frac{k}{2} C_{T0}^2 \left(\frac{F_A}{F_T} \right)^2 \quad (\text{E6-1.8})$$

We can also calculate the conversion X ,

$$X = \left(1 - \frac{F_A}{F_{A0}} \right)$$

5. **Evaluate:**

$$C_{T0} = \frac{P_0}{RT_0} = \frac{(1641 \text{ kPa})}{\left(8.314 \frac{\text{kPa} \cdot \text{dm}^3}{\text{mol} \cdot \text{K}} \right) 698 \text{ K}} = 0.286 \frac{\text{mol}}{\text{dm}^3} = \frac{0.286 \text{ mmol}}{\text{cm}^3}$$

When using Polymath or another ODE solver, one does not have to actually combine the mole balances, rate laws, and stoichiometry, as was done in the

Combine step previously in Chapter 5. The ODE solver will do that for you. Thanks, ODE solver!

The Polymath program and output are shown in Table E6-1.1 and Figure E6-1.1. Note that explicit Equation #6 in the Polymath program calculates the reaction-rate constant k at the specified temperature of 425°C (i.e., 698 K) for you.

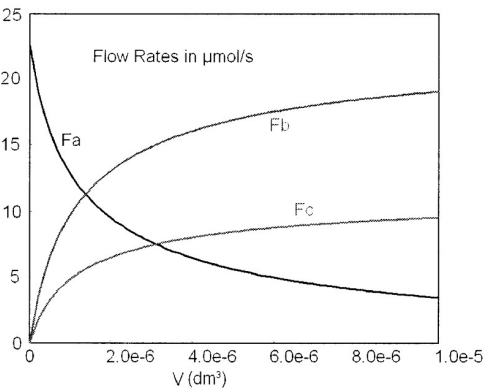


Figure E6-1.1 Profiles of microreactor molar flow rates.

Note that we see not much product is formed in the last part of the reactor, that is, beyond $V = 4 \times 10^{-6} \text{ dm}^3$.

TABLE E6-1.1 POLYMATH PROGRAM

Information on how to obtain and load the Polymath software can be found in Appendix D.

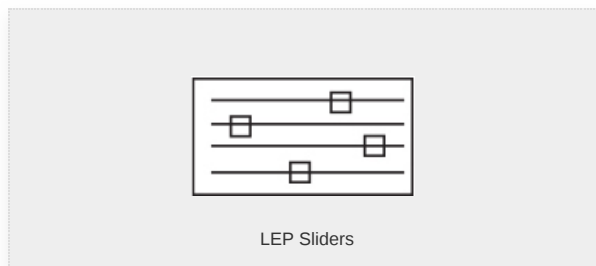
Differential equations 1 $d(F_a)/d(V) = r_b$ 2 $d(F_b)/d(V) = r_b$ 3 $d(F_c)/d(V) = r_c$	
Explicit equations 1 $T = 698$ 2 $C_{to} = 1641/8.314/T$	

3 $E = 24000$
 4 $F_t = F_a + F_b + F_c$
 5 $C_a = C_{to} * F_a / F_t$
 6 $k = 0.29 * \exp(E / (1.987 * (1/500 - 1/T)))$
 7 $F_{ao} = 0.0000226$
 8 $v_o = F_{ao} / C_{to}$
 9 $\tau = V / v_o$
 10 $r_a = -k * C_a^2$
 11 $X = 1 - F_a / F_{ao}$
 12 $r_b = -r_a$
 13 $r_c = -r_a / 2$

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	Ca	0.2827764	0.0307406
2	Cto	0.2827764	0.2827764
3	E	2.4E+04	2.4E+04
4	Fa	2.26E-05	3.495E-06
5	Fao	2.26E-05	2.26E-05
6	Fb	0	1.91E-05
7	Fc	0	9.552E-06
8	Ft	2.26E-05	3.215E-05
9	k	274.4284	274.4284
10	ra	-21.94397	-0.2593304
11	rateA	21.94397	0.2593304
12	rb	21.94397	0.2593304
13	rc	10.97199	0.1296652
14	T	698.	698.
15	Tau	0	0.1251223
16	V	0	1.0E-05
17	vo	7.992E-05	7.992E-05

18	X	0	0.8453416
----	---	---	-----------



Analysis: This gas-phase reaction in a PFR example could just as easily have been solved using conversion as a basis. However, membrane reactors and multiple reactions **cannot** be solved using conversion. You will note we just wrote out the equations in Steps 1–5 of our reaction algorithm (Table 6-2) and then typed them directly into our ODE solver, Polymath, to obtain the molar flow rate profiles shown in Figure E6-1.1. Notice the profiles change rapidly near the reactor entrance and then there is very little change after $4 \times 10^{-6} \text{ dm}^3$ down the reactor. Other interesting variables you will want to plot when you download this program from the *Living Example Problem* (i.e., **LEP**) file are the total molar flow rate, F_T ; the concentrations of the reacting species, C_A , C_B , and C_C (for C_B and C_C you will need to type in two additional equations); and the rates $-r_A$, r_B , and r_C . This task can be easily outsourced to the ChE students of Jofostan University in Riça for a small stipend.

6.4 MEMBRANE REACTORS

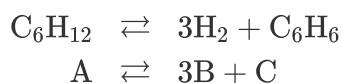
Membrane reactors can be used to increase conversion when the reaction is **thermodynamically limited**, as well as to increase the selectivity when multiple reactions are occurring. Thermodynamically limited reactions are reactions where the equilibrium lies far to the left (i.e., reactant side) and as a result there is little conversion. If the reaction is exothermic,

increasing the temperature will only drive the reaction further to the left, and decreasing the temperature will move the equilibrium to the right, but could result in a reaction rate so slow that there is very little conversion. If the reaction is endothermic, increasing the temperature will move the reaction to the right to favor a higher conversion; however, for many reactions these higher temperatures cause the catalyst to become deactivated.

By having one of the products pass through the membrane, we drive the reaction toward completion.

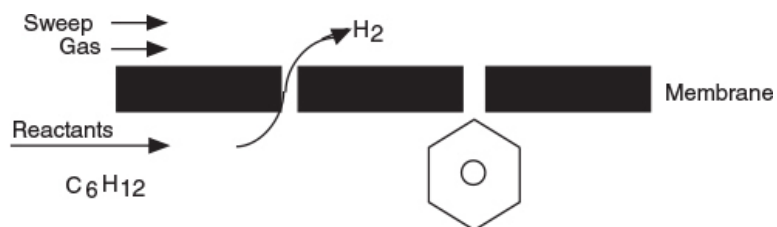
The term *membrane reactor* describes a number of different types of reactor configurations that contain a membrane. The membrane can either provide a barrier to certain components while being permeable to others, prevent certain components such as particulates from contacting the catalyst, or contain reactive sites and be a catalyst in itself. Like reactive distillation, the membrane reactor is another technique for driving reversible reactions to the right toward completion in order to achieve very high conversions. These high conversions can be achieved by having one of the reaction products diffuse out through a semipermeable membrane surrounding the reacting mixture. As a result, the reverse reaction will not be able to take place, and the reaction will continue to proceed to the right toward completion.

Two of the main types of catalytic membrane reactors are shown in Figure 6-3. The reactor in Figure 6-3(b) is called an *inert membrane reactor with catalyst pellets on the feed side* (IMRCF). Here, the membrane is inert and serves as a barrier to the reactants and some of the products. The reactor in Figure 6-3(c) is a *catalytic membrane reactor* (CMR). The catalyst is deposited directly on the membrane, and only specific reaction products are able to exit the permeate side. As an example, consider the reversible reaction where



H_2 diffuses through the membrane, while C_6H_6 does not.

the hydrogen molecule is small enough to diffuse through the small pores of the membrane, while C_6H_{12} and C_6H_6 cannot. Consequently, the reaction continues to proceed to the right even for a small value of the equilibrium constant.



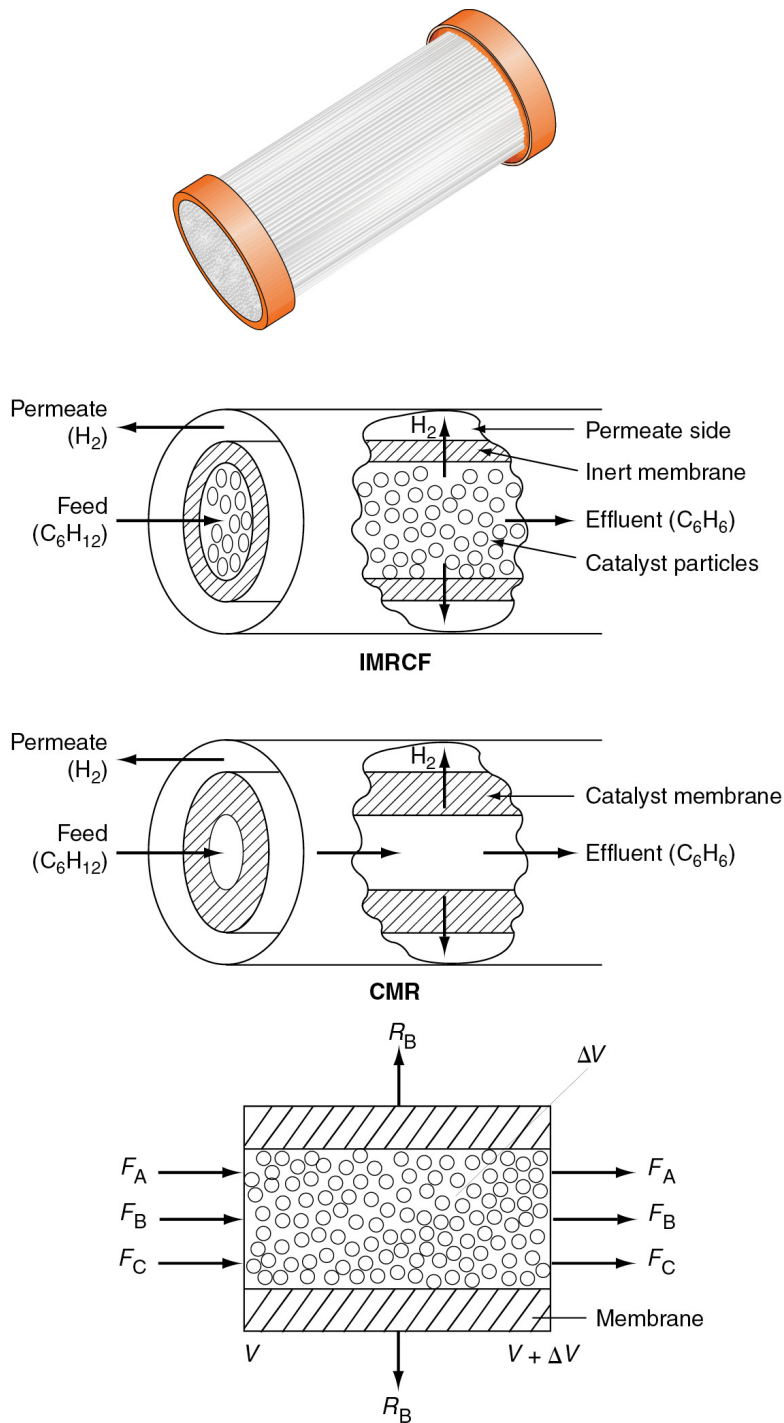


Figure 6-3 Membrane reactors. (a) Photo of ceramic reactors, (b) cross section of IMRCF, (c) cross section of CMR, (d) schematic of IMRCF for mole balance.

Hydrogen, species B, flows out through the sides of the reactor as it flows down the reactor while the other reactants and

products cannot leave until they exit the end of the reactor.

$$V = \frac{W}{\rho_b}$$

In analyzing membrane reactors, we only need to make a small change to the algorithm shown in [Figure 6-1](#). We shall choose the reactor volume rather than catalyst weight as our independent variable for this example. The catalyst weight, W , and reactor volume, V , are easily related through the bulk catalyst density, ρ_b (i.e., $W = \rho_b V$). We first consider the chemical species that stay within the reactor and do not diffuse out through the side, namely A and C, as shown in [Figure 6-3\(d\)](#). The steady state mole balances on A and C are derived in [Example 6-2](#) to give the usual differential form found in [Table S1-1](#) in [Chapter 1](#).

$$\frac{dF_A}{dV} = r_A \quad (1-11)$$

The mole balance on C is carried out in an identical manner to A, and the resulting equation is

$$\frac{dF_C}{dV} = r_C \quad (6-1)$$

However, the mole balance on B (H_2) must be modified because hydrogen leaves through both the sides of the reactor and at the end of the reactor.

First, we shall perform mole balances on the volume element ΔV shown in [Figure 6-3\(d\)](#). The mole balance on hydrogen (B) is over a differential volume ΔV shown in [Figure 6-3\(d\)](#) and it yields the following.

Balance on B in the catalytic bed:

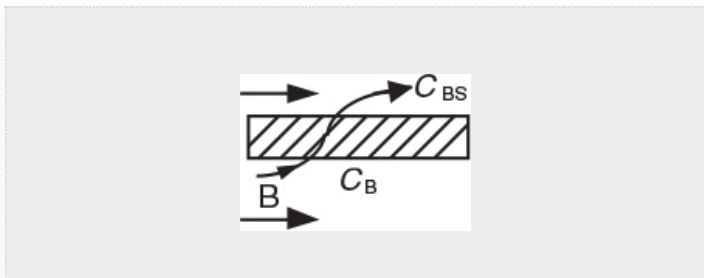
$$\underbrace{\left[\begin{array}{c} \text{In} \\ \text{by flow} \end{array} \right]}_{F_{B|_V}} - \underbrace{\left[\begin{array}{c} \text{Out} \\ \text{by flow} \end{array} \right]}_{F_{B|_{V+\Delta V}}} - \underbrace{\left[\begin{array}{c} \text{Out} \\ \text{by diffusion} \end{array} \right]}_{R_B \Delta V} + \underbrace{[\text{Generation}]}_{r_B \Delta V} = [\text{Accumulation}]$$

$$F_{B|_V} - F_{B|_{V+\Delta V}} - R_B \Delta V + r_B \Delta V = 0 \quad (6-2)$$

Now there are two "OUT" terms for species B.

where R_B is the molar rate of B leaving through the sides of the reactor per unit volume of reactor ($\text{mol/m}^3 \cdot \text{s}$). Dividing by ΔV and taking the limit as $\Delta V \rightarrow 0$ gives

$$\boxed{\frac{dF_B}{dV} = r_B - R_B} \quad (6-3)$$



The rate of transport of B out through the membrane R_B is the product of the molar flux of B normal to the membrane, W_B ($\text{mol/m}^2/\text{s}$), and the surface area per unit volume of reactor, a (m^2/m^3). The molar flux of B, W_B in ($\text{mol/m}^2/\text{s}$) out³ through the sides of the reactor is the product of the mass transfer coefficient, k'_C (m/s), and the concentration driving force across the membrane.

$$W_B = k'_C (C_B - C_{BS}) \quad (6-4)$$

³ See Chapter 14, section 14.4, for further elaboration on the mass transfer coefficient and its correlations in the literature.

Here, k'_C is the overall mass transfer coefficient in (m/s) and C_{BS} is the concentration of B in the sweep gas channel (mol/m^3). The overall mass transfer coefficient accounts for all resistances to transport: the tube-side resistance of the membrane, the membrane itself, and on the shell- (sweep gas) side resistance. Further elaboration of the mass transfer

coefficient and its correlations can be found in the literature and in Chapter 14. In general, this coefficient can be a function of the membrane and fluid properties, the fluid velocity, and the tube diameters.

To obtain the rate of removal of B per unit volume of reactor, R_B (mol/m³/s), we need to multiply the flux through the membrane, W_B (mol/m²·s), by the membrane surface area per volume of reactor, a (m²/m³); that is

$$R_B = W_B a = k'_C a (C_B - C_{BS}) \quad (6-5)$$

The membrane surface area per unit volume of reactor is

$$a = \frac{\text{Area}}{\text{Volume}} = \frac{\pi D L}{\frac{\pi D^2}{4} L} = \frac{4}{D}$$

Letting $k_C = k'_C a$ and assuming that the flow rate of the inert sweep gas is sufficiently high to keep the concentration in the sweep gas at essentially zero (i.e., $C_{BS} \approx 0$), we obtain

Rate of B out through the sides.

$$R_B = k_C C_B \quad (6-6)$$

where the units of k_C are s⁻¹.

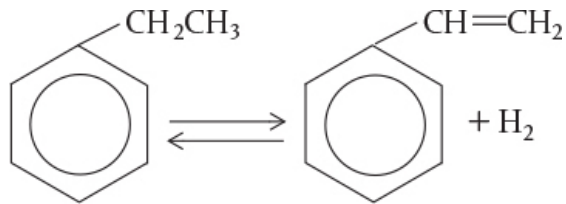
More detailed modeling of the transport and reaction steps in membrane reactors is beyond the scope of this text but can be found in *Membrane Reactor Technology*.⁴ The salient features, however, can be illustrated by the following example. When analyzing membrane reactors, we must use molar flow rates because expressing the molar flow rate of B in terms of conversion will not account for the amount of B that has left the reactor through the sides.

⁴ R. Govind and N. Itoh, eds., *Membrane Reactor Technology*, AIChE Symposium Series 85, no. 268; T. Sun and S. Khang, *Ind. Eng. Chem. Res.*, 27, 1136.

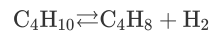
According to the DOE, 10 trillion Btu/yr could be saved by using membrane reactors.

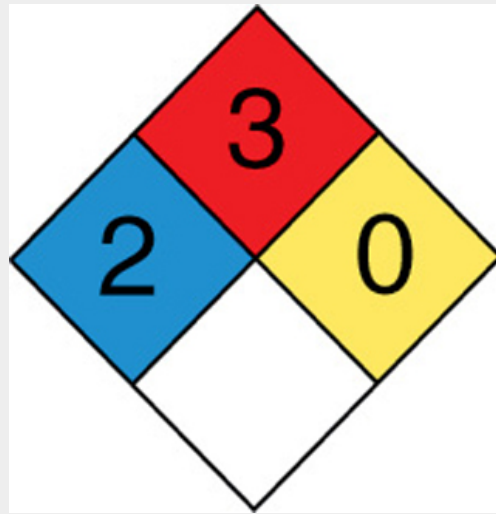
Example 6-2 Membrane Reactor

According to the Department of Energy (DOE), an energy saving of 10 trillion Btu per year could result from the use of catalytic membrane reactors as replacements for conventional reactors for dehydrogenation reactions such as the dehydrogenation of ethylbenzene to styrene

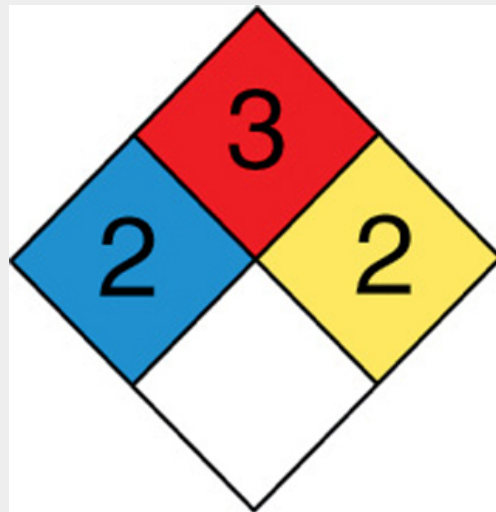


and of butane to butene:



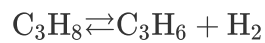


Ethyl Benzene



Styrene

The dehydrogenation of propane is another reaction that has proven successful with a membrane reactor.⁵



⁵ *J. Membrane Sci.*, 77, 221 (1993).

All the preceding elementary dehydrogenation reactions described above can be represented symbolically as



and will take place on the catalyst side of an IMRCF. The equilibrium constant for this reaction is quite small at 227°C (e.g., $K_C = 0.05 \text{ mol/dm}^3$). The membrane is permeable to B (e.g., H_2) but not to A and C. Pure gaseous A enters the reactor at 8.2 atm and 227°C ($C_{T0} = 0.2 \text{ mol/dm}^3$) at a molar flow rate of 10 mol/min.

The rate of diffusion of B out of the reactor per unit volume of reactor, R_B , is proportional to the concentration of B (i.e., $R_B = k_C C_B$).

1. Perform differential mole balances on A, B, and C to arrive at a set of coupled differential equations to solve.
2. Plot and analyze the molar flow rates of each species as a function of reactor volume.
3. Calculate the conversion of A at $V = 500 \text{ dm}^3$.

Additional information: Even though this reaction is a gas–solid catalytic reaction, we will use the bulk catalyst density in order to write our balances in terms of reactor volume rather than catalyst weight (recall $-r_A = -r'_A \rho_b$ and $W = \rho_b V$). For the bulk catalyst density of $\rho_b = 1.5 \text{ g/cm}^3$ and a 2-cm inside-diameter tube containing the catalyst pellets, the specific reaction rate, k , and the transport coefficient, k_C , are $k = 0.7 \text{ min}^{-1}$ and $k_C = 0.2 \text{ min}^{-1}$, respectively. As a first approximation, we will neglect pressure drop, that is, $p = 1$.

Solution

(a) As discussed earlier, we choose reactor volume rather than catalyst weight as our independent variable for this example. The catalyst weight, W , and reactor volume, V , are easily related through the bulk catalyst density, ρ_b , (i.e., $W = \rho_b V$). First, we shall perform mole balances on the volume element ΔV shown in Figure 6-3(d).

1. Mole balances:

Balance on A in the catalytic bed:

$$\left[\begin{array}{c} \text{In} \\ \text{by flow} \end{array} \right] - \left[\begin{array}{c} \text{Out} \\ \text{by flow} \end{array} \right] + [\text{Generation}] = [\text{Accumulation}]$$

$$\underbrace{F_A|_V} - \underbrace{F_A|_{V+\Delta V}} + \underbrace{r_A \Delta V} = 0$$

Mole balance on each and every species

Dividing by ΔV and taking the limit as $\Delta V \rightarrow 0$ gives

$$\boxed{\frac{dF_A}{dV} = r_A} \quad (\text{E6-2.1})$$

Balance on B in the catalytic bed:

The balance on B is given by Equation (6-3)

$$\boxed{\frac{dF_B}{dV} = r_B - R_B} \quad (\text{E6-2.2})$$

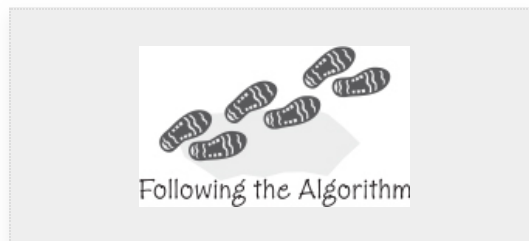
where R_B is the molar flow of B out through the membrane per unit volume of the reactor.

The mole balance on C is carried out in an identical manner to A, and the resulting equation is

$$\boxed{\frac{dF_C}{dV} = r_C} \quad (\text{E6-2.3})$$

2. Rates:

Rate Law



$$\boxed{-r_A = k \left(C_A - \frac{C_B C_C}{K_C} \right)} \quad (\text{E6-2.4})$$

Relative Rates

$$\frac{r_A}{-1} = \frac{r_B}{1} = \frac{r_C}{1} \quad (\text{E6-2.5})$$

$$\begin{aligned} r_B &= -r_A & (\text{E6-2.6}) \\ r_C &= -r_A & (\text{E6-2.7}) \end{aligned}$$

3. **Transport out of the reactor:** We apply Equation (6-5) for the case in which we assume the concentration of B on the sweep gas side of the membrane is essentially zero, $C_{BS} \approx 0$, to obtain

$$R_B = k_C C_B \quad (\text{E6-2.8})$$

where k_C is a transport coefficient. In this example, we shall assume that the resistance to species B out of the membrane is a constant and, consequently, k_C is a constant.

4. **Stoichiometry:** Recalling Equation (4-17) for the case of constant temperature and pressure, we have for isothermal operation, $T = T_0$, and no pressure drop, $P = P_0$, (i.e., $p = 1$).

Concentrations

$$C_A = C_{T0} \frac{F_A}{F_T} \quad (\text{E6-2.9})$$

$$C_B = C_{T0} \frac{F_B}{F_T} \quad (\text{E6-2.10})$$

$$C_C = C_{T0} \frac{F_C}{F_T} \quad (\text{E6-2.11})$$

$$F_T = F_A + F_B + F_C \quad (\text{E6-2.12})$$

$$X = \frac{F_{A0} - F_A}{F_{A0}} \quad (\text{E6-2.13})$$

5. **Combining and summarizing:**

$$\begin{aligned} \frac{dF_A}{dV} &= r_A \\ \frac{dF_B}{dV} &= -r_A - k_C C_{T0} \left(\frac{F_B}{F_T} \right) \\ \frac{dF_C}{dV} &= -r_A \\ -r_A &= k_C C_{T0} \left[\left(\frac{F_A}{F_T} \right) - \frac{C_{T0}}{K_C} \left(\frac{F_B}{F_T} \right) \left(\frac{F_C}{F_T} \right) \right] \\ F_T &= F_A + F_B + F_C \end{aligned}$$

Summary of equations describing flow and reaction in a membrane reactor

6. **Parameter evaluation:**

$$C_{T0} = \frac{P_0}{RT_0} = \frac{830.6 \text{ kPa}}{[8.314 \text{ k Pa} \cdot \text{dm}^3 / (\text{mol} \cdot \text{K})] (500 \text{ K})} = 0.2 \frac{\text{mol}}{\text{dm}^3}$$

$$\begin{aligned}
 k &= 0.7 \text{ min}^{-1}, K_C = 0.05 \text{ mol/dm}^3, k_C = 0.2 \text{ min}^{-1} \\
 F_{A0} &= 10 \text{ mol/min} \\
 F_{B0} &= F_{C0} = 0
 \end{aligned}$$

7. **Numerical solution:** Equations (E6-2.1)–(E6-2.13) were solved using Poly-math, MATLAB, Wolfram, and Python. The profiles of the molar flow rates are shown below. Table E6-2.1 shows the Polymath programs, and Figure E6-2.1 shows the results of the numerical solution for the entering conditions.

$$V = 0 : F_A = F_{A0}, \quad F_B = 0, \quad F_C = 0$$

Information on how to obtain and download the Polymath, Wolfram, and Python software can be found on the Web site as well as in Appendix D.

TABLE E6-2.1 POLYMATH PROGRAM

Differential equations 1 $d(F_A)/d(V) = r_a$ 2 $d(F_B)/d(V) = r_a - k_C \cdot C_{T0} \cdot (F_B/F_T)$ 3 $d(F_C)/d(V) = -r_a$			
Explicit equations 1 $K_C = 0.05$ 2 $F_T = F_A + F_B + F_C$ 3 $k = 0.7$ 4 $C_{T0} = 0.2$ 5 $r_a = -k \cdot C_{T0} \cdot ((F_A/F_T) - C_{T0}/K_C \cdot (F_B/F_T) \cdot (F_C/F_T))$ 6 $k_C = 0.2$ 7 $\text{Rate} = -r_a$ 8 $R_B = k_C \cdot C_{T0} \cdot (F_B/F_T)$ 9 $F_{A0} = 10$ 10 $X = (F_{A0} - F_A)/F_{A0}$			
Calculated values of DEQ variables			
	Variable	Initial value	Final value
1	Cto	0.2	0.2
2	Fa	10	3.995179
3	Fao	10.	10.
4	Fb	0	1.832577

5	Fc	0	6.004821
6	Ft	10.	11.83258
7	k	0.7	0.7
8	kc	0.2	0.2
9	kc	0.05	0.05
10	ra	-0.14	-0.0032558
11	Rate	0.14	0.0032558
12	Rb	0	0.006195
13	V	0	500.
14	X	0	0.6004821

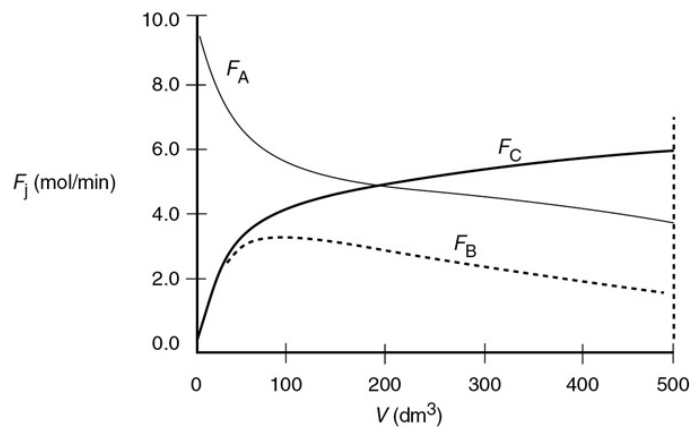
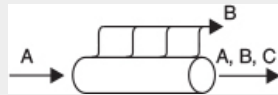


Figure E6-2.1 Polymath solutions.

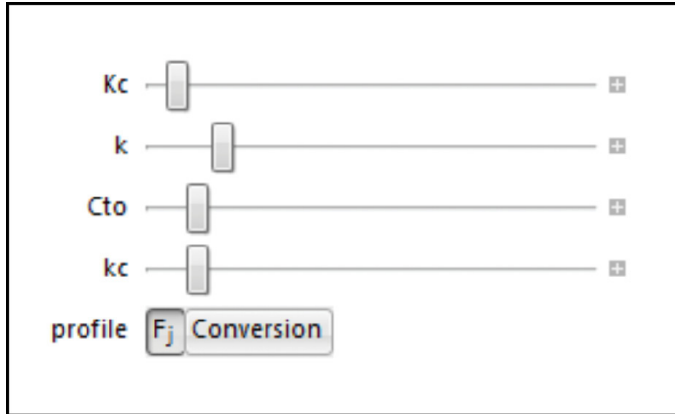


Figure E6-2.2 Wolfram sliders.

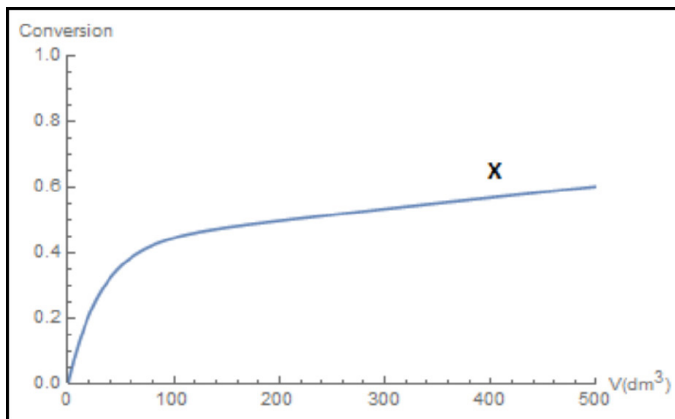


Figure E6-2.3 Wolfram profiles.

(b) Figures E6-2.2 and E6-2.3 show the Wolfram variables and the conversion profiles respectively. We note that F_B goes through a maximum as a result of the competition between the rate of B being formed from A and the rate of B being removed through the sides of the reactor.

(c) From Figure E6-2.1, we see that the exit molar flow rate of A at 500 dm^3 is 4 mol/min , for which the corresponding conversion is

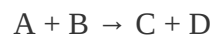
$$X = \frac{F_{A0} - F_A}{F_{A0}} = \frac{10 - 4}{10} = 0.60$$

We note and emphasize that the conversion profile X was calculated *after the fact* and not used to obtain the

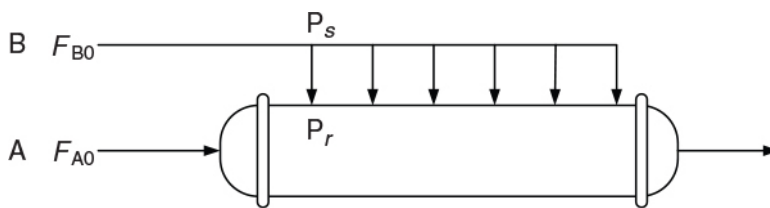
molar flow rates.

Analysis: The molar flow rate of A drops rapidly until about 100 dm^3 , where the reaction approaches equilibrium. At this point, the reaction will only proceed to the right at the rate at which B is removed through the sides of the membrane, as noted by the similar slopes of F_A and F_B in this plot. You will want to use the Wolfram or Python sliders in Living Example Problem, LEP 6-1A(b) to show that if B is removed rapidly, F_B will become close to zero and the reaction behaves as if it is irreversible, and that if B is removed slowly, F_B and C_B will be large throughout the reactor and the rate of reaction, $-r_A$, will be small as we approach equilibrium.

Use of Membrane Reactors to Enhance Selectivity. In addition to species leaving through the sides of the membrane reactor, species can also be fed to the reactor through the sides of the membrane. For example, for the reaction



species A will be fed only to the entrance, and species B will be fed only through the membrane as shown here.



As we will see in Chapter 8, this arrangement is often used to improve selectivity when multiple reactions take place. Here, B is usually fed uniformly through the membrane along the length of the reactor. The balance on B is

$$\frac{dF_B}{dV} = r_B + R_B \quad (6-7)$$

where $R_B = F_{B0}/V_t$ with F_{B0} , representing the total molar feed rate of B through the sides and V_t the total reactor volume. The feed rate of B can be controlled by controlling the pressure drop across the reactor membrane.⁶ This arrangement will keep the concentration of A high and the concentration of B low to maximize the selectivity given by Equation (E8-2.2) for the reactions given in Section 8.6, for example, Example 8-8.

⁶ The velocity of B through the membrane, U_B , is given by Darcy's law

$$U_B = K(P_s - P_r)$$

where K is the membrane permeability, P_s is the shell-side pressure, and P_r the reactor-side pressure

$$F_{B0} = \overbrace{C_{B0} a U_B V_t}^{R_B} = R_B V_t$$

where, as before, a is the membrane surface area per unit volume, C_{B0} is the entering concentration of B, and V_t is the total reactor volume.

6.5 UNSTEADY-STATE OPERATION OF STIRRED REACTORS

In Chapter 5 we discussed the unsteady operation of one type of reactor, the batch reactor. In this section, we discuss two other aspects of unsteady operation: startup of a CSTR and of semibatch reactors. First, the startup of a CSTR is examined to determine the time necessary to reach steady-state operation (see Figure 6-4(a)), and then semibatch reactors are discussed. In each of these cases, we are interested in predicting the concentration and conversion as a function of time. Closed-form analytical solutions to the differential equations arising from the mole balance of these reaction types can be obtained only for zero-and first-order reactions. ODE solvers must be used for other reaction orders.

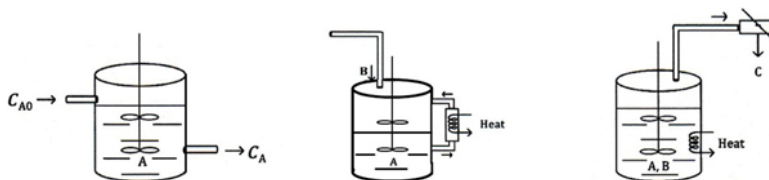


Figure 6-4 Semibatch reactors: **(a)** CSTR startup, **(b)** semibatch with cooling, and **(c)** reactive distillation.

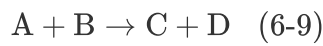
An unsteady-state analysis can be used to determine the startup time for a CSTR (Figure 6-4(a)) and this analysis is given in the *Expanded Material* for Chapter 6 on the CRE Web site

(http://www.umich.edu/~elements/6e/06chap/expanded_ch06_cstr.pdf). Here, we show the time to steady state for a first-order reaction is approximately

$$t_s = \frac{4.6 \tau}{1 + \tau k} \quad (6-8)$$

For most first-order systems, the time to reach steady state is three to four space times.

There are two basic types of semibatch operations. In one type, one of the reactants in the reaction



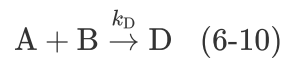
(e.g., B) is slowly fed to a reactor containing the other reactant (e.g., A), which has already been charged to a reactor such as that shown in Figure 6-4(b). This type of reactor is generally used when unwanted side reactions occur at high concentrations of B (see Section 8.1) or when the reaction is highly exothermic (Chapter 11). In some reactions, the reactant B is a gas and is bubbled continuously through liquid reactant A. Examples of reactions used in this type of **semibatch reactor** operation include *ammonolysis*, *chlorination*, and *hydrolysis*. The other type of semibatch reactor is reactive distillation and is shown schematically in Figure 6-4(c). Here, reactants A and B are charged simultaneously and one of the products vaporizes and is withdrawn continuously. Removal of one of the products in this manner (e.g., C) shifts the equilibrium toward the right, increasing the final conversion well above that which would be achieved had C not been removed. In addition, removal of one of the products further concentrates the reactant, thereby

producing an increased rate of reaction and decreased processing time. This type of reaction operation is called *reactive distillation*. Examples of reactions carried out in this type of reactor include *acetylation reactions* and *esterification reactions* in which water is removed.

6.6 SEMIBATCH REACTORS

6.6.1 Motivation for Using a Semibatch Reactor

One of the best reasons to use semibatch reactors is to enhance selectivity in liquid-phase reactions. For example, consider the following two simultaneous reactions. One reaction produces the desired product D



with the rate law

$$r_D = k_D C_A^2 C_B \quad (6-11)$$

and the other reaction produces an undesired product U



with the rate law

$$r_U = k_U C_A C_B^2 \quad (6-13)$$

The instantaneous selectivity of D to U, $S_{D/U}$, is the ratio of the rate of formation of the desired product D to the rate of formation of the undesired product U and is given in Equation (6-14), and in Chapter 8 Equation (8-1).

We want $S_{D/U}$ as large as possible.

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_D C_A^2 C_B}{k_U C_A C_B^2} = \frac{k_D}{k_U} \frac{C_A}{C_B} \quad (6-14)$$

and guides us in how to produce the most amount of our desired product and the least amount of our undesired product (see Section 8.1). We see from Equation (6-14) that the selectivity, $S_{D/U}$ can be increased by keeping the concentration of A high and the concentration of B low. This result can be achieved through the use of the semibatch reactor, which is charged with pure A and to which B is fed slowly to A in the vat.

6.6.2 Semibatch Reactor Mole Balances

We will focus our attention primarily on a semibatch reactor with a constant molar feed. A schematic diagram of this semibatch reactor is shown in Figure 6-5. We shall consider the elementary liquid-phase reaction

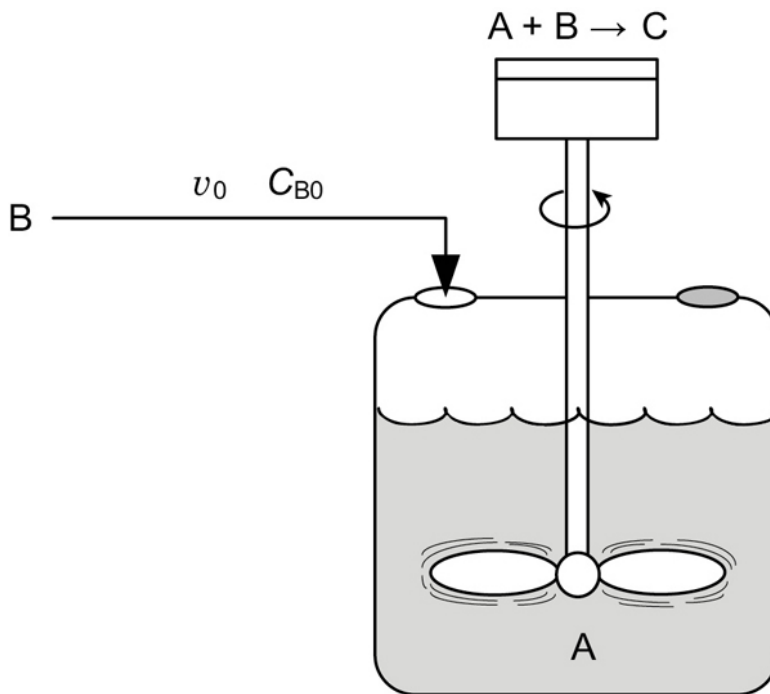
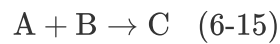


Figure 6-5 Semibatch reactor.

in which reactant B is slowly added to a well-mixed vat containing reactant A. A **mole balance on species A yields**

Mole balance on species A

$$\underbrace{\left[\text{Rate} \right]_{\text{in}}}_0 - \underbrace{\left[\text{Rate} \right]_{\text{out}}}_0 + \underbrace{\left[\text{Rate of generation} \right]}_{r_A V(t)} = \underbrace{\left[\text{Rate of accumulation} \right]}_{\frac{dN_A}{dt}} \quad (6-16)$$

Three variables can be used to formulate and solve semibatch reactor problems: the concentrations, C_j , the number of moles, N_j , of species j respectively and the conversion, X . We will use the subscript “0” to represent feed concentrations, for example, C_{B0} , and the subscript “i” to represent initial conditions, for example, C_{Ai} .

We shall use concentration as our preferred variable, leaving the analysis of semibatch reactors using the number of moles, N_j , and conversion X to the CRE Web site *Summary Notes* (<http://www.umich.edu/~elements/6e/06chap/summary.html>) and *Professional Reference Shelf* (http://www.umich.edu/~elements/6e/06chap/prof-prs_cstr.html) for Chapter 6.

Recalling that the number of moles of A, N_A , is just the product of the concentration of A, C_A , and the volume, V , (i.e., $(N_A = C_A V)$), we can rewrite Equation (6-16) as

$$r_A V = \frac{dN_A}{dt} = \frac{d(C_A V)}{dt} = \frac{V dC_A}{dt} + C_A \frac{dV}{dt} \quad (6-17)$$

We note that since the reactor is being filled, the volume, V , varies with time. The reactor volume at any time t can be found from an **overall mass balance** of all species. The mass flow rate into the reactor, \dot{m}_0 , is just the product of the liquid density, ρ_0 , and volumetric flow rate v_0 . The mass of liquid inside the reactor, m , is just the product of the liquid density ρ and the volume of liquid V in the reactor, that is $m = \rho V$. There is no mass flow out and no generation of mass.

Overall mass balance

$$\begin{array}{ccccccccc}
 \left[\begin{array}{c} \text{Mass} \\ \text{rate} \\ \text{in} \end{array} \right] & - & \left[\begin{array}{c} \text{Mass} \\ \text{rate} \\ \text{out} \end{array} \right] & + & \left[\begin{array}{c} \text{Rate of} \\ \text{mass} \\ \text{generation} \end{array} \right] & = & \left[\begin{array}{c} \text{Rate of} \\ \text{mass} \\ \text{accumulation} \end{array} \right] \\
 \dot{m}_0 & - & 0 & + & 0 & = & \frac{dm}{dt} \\
 \underbrace{\rho_0 v_0} & - & \underbrace{0} & + & \underbrace{0} & = & \underbrace{\frac{d(\rho V)}{dt}} & (6-18)
 \end{array}$$

For a constant-density system, $\rho_0 = \rho$, and

$$\frac{dV}{dt} = v_0 \quad (6-19)$$

with the initial condition $V = V_0$ at $t = 0$, integrating for the case of constant volumetric flow rate v_0 yields

Semibatch reactor volume as a function of time

$$V = V_0 + v_0 t \quad (6-20)$$

Substituting Equation (6-19) into the right-hand side of Equation (6-17) and rearranging gives us

$$-v_0 C_A + V r_A = \frac{V dC_A}{dt}$$

The **balance on A**, seen in Equation (6-17), can be rewritten as

Mole balance on A

$$\frac{dC_A}{dt} = r_A - \frac{v_0}{V} C_A \quad (6-21)$$

A **mole balance on B** that is fed to the reactor at a rate F_{B0} is

$$\begin{array}{ccccccc}
 \text{In} & - & \text{Out} & + & \text{Generation} & = & \text{Accumulation} \\
 \underbrace{F_{B0}} & - & \underbrace{0} & + & \underbrace{r_B V} & = & \underbrace{\frac{dN_B}{dt}}
 \end{array}$$

Rearranging gives

$$\frac{dN_B}{dt} = r_B V + F_{B0} \quad (6-22)$$

Substituting for N_B in terms of concentration and reactor volume ($N_B = C_B V$), differentiating, and then using Equation (6-19) to substitute for (dV/dt) , and recalling $F_{B0} = C_{B0} v_0$ the mole balance on B given in Equation (6-22) becomes

$$\frac{dN_B}{dt} = \frac{d(V C_B)}{dt} = \frac{dV}{dt} C_B + \frac{V dC_B}{dt} = r_B V + F_{B0} = r_B V + v_0 C_{B0}$$

Rearranging gives

Mole balance on B

$$\boxed{\frac{dC_B}{dt} = r_B + \frac{v_0(C_{B0} - C_B)}{V}} \quad (6-23)$$

Similarly, for species C we have

$$\frac{dN_C}{dt} = r_C V = -r_A V \quad (6-24)$$

$$\frac{dN_C}{dt} = \frac{d(C_C V)}{dt} = V \frac{dC_C}{dt} + C_C \frac{dV}{dt} = V \frac{dC_C}{dt} + v_0 C_C \quad (6-25)$$

Combining Equations (6-24) and (6-25) and rearranging we obtain

Mole balance on C

$$\boxed{\frac{dC_C}{dt} = r_C - \frac{v_0 C_C}{V}} \quad (6-26)$$

Following the same procedure for species D

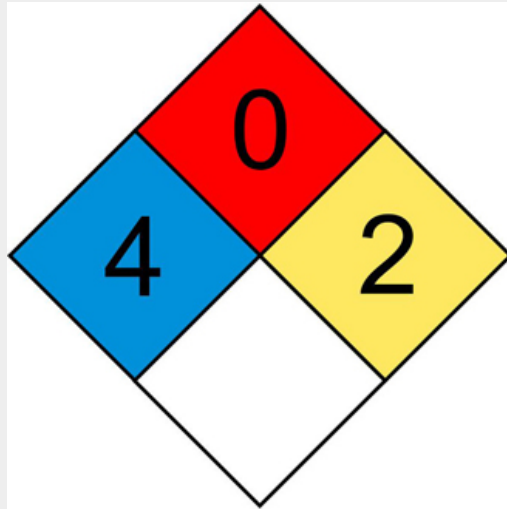
Mole balance on D

$$\boxed{\frac{dC_D}{dt} = r_D - \frac{v_0 C_D}{V}} \quad (6-27)$$

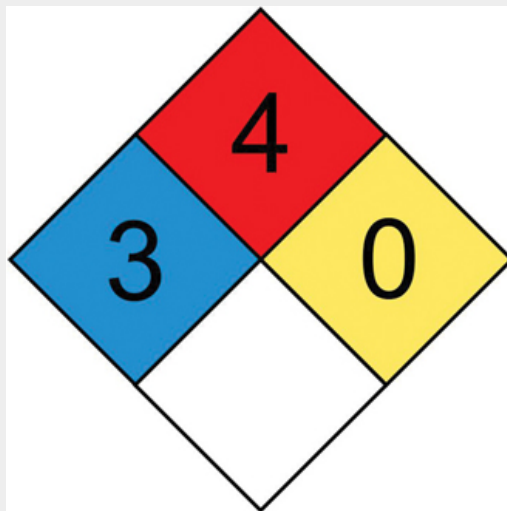
At time $t = 0$, the initial concentrations of B, C, and D in the vat are zero, $C_{Bi} = C_{Ci} = C_{Di} = 0$. The concentration of B in the feed is C_{B0} . If the reaction order is other than zero- or first-order, or if the reaction is nonisothermal, we *must* use

numerical techniques to determine the concentrations and conversion as a function of time. Equations (6-21), (6-23), (6-26), and (6-27) are easily solved with an ODE solver.

**Example 6–3 Isothermal Semibatch Reactor with
Second-Order Reaction**

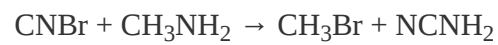


Cyanogen Bromide

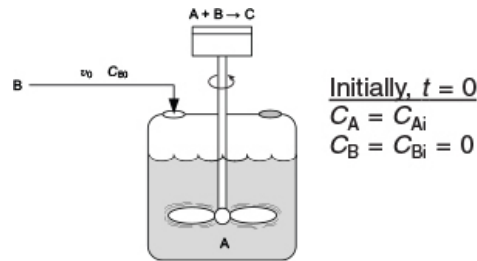


Methylamine

The production of methyl bromide is an irreversible liquid-phase reaction that follows an elementary rate law. The reaction



is carried out isothermally in a semibatch reactor. An aqueous solution of methyl amine (B) at a concentration of $C_{B0} = 0.025 \text{ mol/dm}^3$ is to be fed at a volumetric rate of $0.05 \text{ dm}^3/\text{s}$ to an aqueous solution of bromine cyanide (A) contained in a glass-lined reactor.



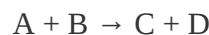
The initial volume of liquid in the vat is to be 5 dm^3 with a bromine-cyanide concentration of $C_A = C_{Ai} = 0.05 \text{ mol/dm}^3$. The specific reaction-rate constant is

$$k = 2.2 \text{ dm}^3/\text{s} \cdot \text{mol}$$

Solve for the concentrations of bromine cyanide (A), methyl amine (B), methyl bromide (C), and cyanamide (D), and the rate of reaction as a function of time, and then analyze your results.

Solution

Symbolically, we write the reaction as



1. Mole Balances:

Mole Balance on every species

$$\frac{dC_A}{dt} = r_A - \frac{v_0 C_A}{V} \quad [\text{At } t = 0, C_A = C_{Ai}] \quad (6-21)$$

$$\frac{dC_B}{dt} = \frac{v_0 (C_{B0} - C_B)}{V} + r_B \quad [\text{At } t = 0, C_B = C_{Bi} = 0] \quad (6-23)$$

$$\frac{dC_C}{dt} = r_C - \frac{v_0 C_C}{V} \quad [\text{At } t = 0, C_C = 0] \quad (6-26)$$

$$\frac{dC_D}{dt} = r_D - \frac{v_0 C_D}{V} \quad [\text{At } t = 0, C_D = 0] \quad (6-27)$$

2. Rates:

Rates: Law Relative

1. Rate Law (Elementary)

$$-r_A = k C_A C_B \quad (\text{E6-3.1})$$

2. Relative Rates

$$-r_A = -r_B = r_C = r_D \quad (\text{E6-3.2})$$

3. Combine:

Before going to the stoichiometry step, normally Step 3, let's combine the mole balances from Equations (6-21), (6-23), (6-26), and (6-27), the rate law Equation (E6-3.1), and the relative rates Equation (E6-3.2), to arrive at the following forms of the mole balances on A, B, C, and D solely in terms of concentrations

Combined mole balances and rate laws on A, B, C, and D

$$\frac{dC_A}{dt} = -k C_A C_B - \frac{v_0 C_A}{V} \quad (\text{E6-3.3})$$

$$\frac{dC_B}{dt} = -k C_A C_B + \frac{v_0 (C_{B0} - C_B)}{V} \quad (\text{E6-3.4})$$

$$\frac{dC_C}{dt} = k C_A C_B = \frac{v_0 C_C}{V} \quad (\text{E6-3.5})$$

$$\frac{dC_D}{dt} = k C_A C_B = \frac{v_0 C_D}{V} \quad (\text{E6-3.6})$$

4. Stoichiometry:

The volume of liquid in the reactor at any time t is

$$V = V_0 + v_0 t \quad (\text{E6-3.7})$$

These coupled equations are easily solved with an ODE solver such as Polymath.

After the fact, we could also calculate the conversion of A from the concentration of A:

$$X = \frac{N_{Ai} - N_A}{N_{Ai}} \quad (\text{E6-3.8})$$

Substituting for N_{Ai} and N_A

$$X = \frac{C_{Ai}V_0 - C_A V}{C_{Ai}V_0}$$

(E6-3.9)

5. Evaluate:

The initial conditions are $t = 0$, $C_{Ai} = 0.05 \text{ mol/dm}^3$, $C_B = C_C = C_D = 0$, and $V_0 = 5 \text{ dm}^3$.

Equations (E6-3.2)–(E6-3.9) are easily solved with the aid of an ODE solver such as Polymath, Wolfram, Python, or MATLAB (Table E6-3.1).

The concentrations of bromine cyanide (A), methyl amine (B), and methyl bromide (C) are shown as a function of time in Figure E6-3.1, and the rate is shown in Figure E6-3.2.

We note that the concentration of methyl bromide (C), which is identical to the concentration of cyanamide (D) goes through a maximum. The maximum occurs because once all of A has been consumed, then no more C will be formed and the continual flow of B into the reactor will thus dilute the moles of C produced and hence the concentration of C.

TABLE E6-3.1 POLYMATH PROGRAM

Differential equations 1 $d(Ca)/d(t) = ra - vo*Ca/V$ 2 $d(Cb)/d(t) = ra + (Cbo - Cb)*vo/V$ 3 $d(Cc)/d(t) = -ra - vo*Cc/V$ $d(Cd)/d(t) = -ra - vo*Cd/V$			
Explicit equations 1 $vo = 0.05$ 2 $Vo = 5$ 3 $V = Vo + vo*t$ 4 $k = 2.2$ 5 $Cbo = 0.025$ 6 $ra = -k*Ca*Cb$ 7 $Cao = 0.05$ 8 $rate = -ra$ 9 $X = (Cao*Vo - Ca*V)/(Cao*Vo)$			
Calculated values of DEQ variables			
	Variable	Initial value	Final value
1	Ca	0.05	7.731E-06

2	Cao	0.05	0.05
3	Cb	0	0.0125077
4	Cbo	0.025	0.025
5	Cc	0	0.0083256
6	Cd	0	0.0083256
7	k	2.2	2.2
8	ra	0	-2.127E-07
9	rate	0	2.127E-07
10	t	0	500.
11	V	5.	30.
12	vo	0.05	0.05
13	Vo	5.	5.
14	X	0	0.9990722

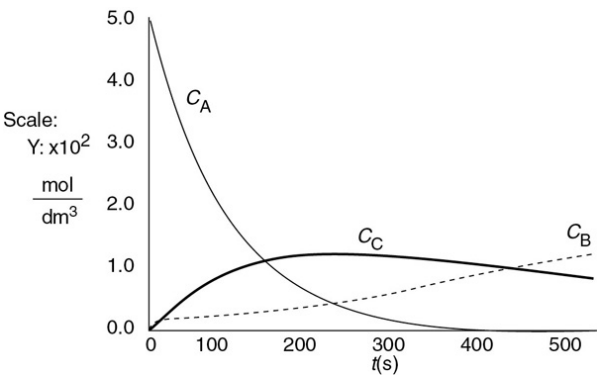


Figure E6-3.1 Polymath output: concentration–time trajectories.

Why does the concentration of CH_3Br (C) go through a maximum wrt time?

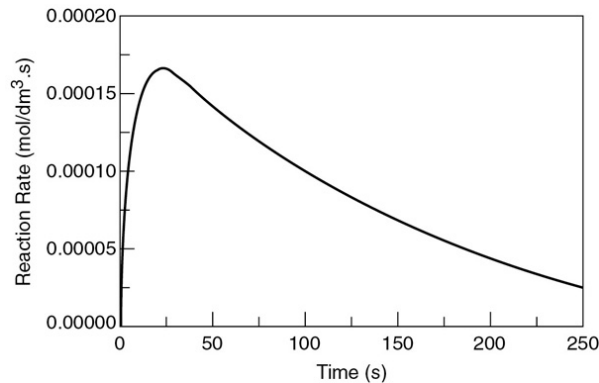
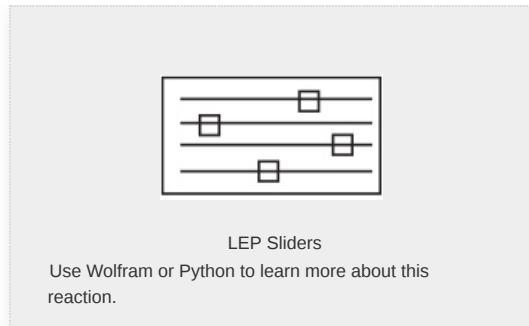


Figure E6-3.2 Reaction rate–time trajectory.

Takeaway Lesson: Wrong choice of type of reactor.

Analysis: Let's look at the trends. The concentration of A falls close to zero at about 250 seconds, as does the reaction rate. Consequently, very little C and D are formed after this time, and what has been formed begins to be diluted as B continues to be added to the reactor and stops just before it overflows. Now what do you think of the time to carry out this reaction? It's about 5 minutes, hardly enough time to turn the valves on and off. *Takeaway lesson:* While this example showed how to analyze a semibatch reactor, you would not use a semibatch reactor to carry out this reaction at this temperature because the times are too short. Instead, you would use a tubular reactor with B fed through the sides or a number of CSTRs in series with A fed to the first reactor and small amounts of B fed to each of the following reactors. We will discuss this situation further in [Chapter 8](#).

6.6.3 Equilibrium Conversion

For reversible reactions carried out in a semibatch reactor, the maximum attainable conversion (i.e., the *equilibrium conversion*) will change as the reaction proceeds because more

reactant is continuously added to the reactor. This addition shifts the equilibrium continually to the right to form more product.

An outline of what is given in the *Summary Notes* is on the CRE Web site follows:

At equilibrium

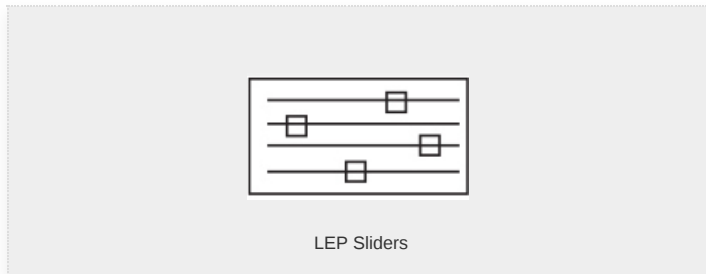
$$K_C = \frac{N_{Ce}N_{De}}{N_{Ae}N_{Be}} \quad (6-28)$$

Using the number of moles in terms of conversion

$$\begin{aligned} N_{Ae} &= N_{A0}(1 - X_e) & N_{Ce} &= N_{A0}X_e \\ N_{De} &= N_{A0}X_e & N_{Be} &= F_{B0}t - N_{A0}X_e \end{aligned} \quad (6-29)$$

Substituting

$$K_C = \frac{N_{A0}X_e^2}{(1-X_e)(F_{B0}t - N_{A0}X_e)} \quad (6-30)$$



Solving for X_e

$$X_e = \frac{K_C \left(1 + \frac{F_{B0}t}{N_{A0}}\right) - \sqrt{\left[K_C \left(1 + \frac{F_{B0}t}{N_{A0}}\right)\right]^2 - 4(K_C - 1)K_C \frac{tF_{B0}}{N_{A0}}}}{2(K_C - 1)} \quad (6-31)$$

Go to the [Chapter 6 LEPs](#) and click on Equation (6-31) to learn how the various parameters affect the X_e versus t curve. One notes the equilibrium conversion, X_e , changes with time. Further discussion on this point and calculation of the equilibrium conversion can be found in *Professional Reference Shelf R6.1*, in the example problem on the CRE Web site.

6.7 AND NOW... A WORD FROM OUR SPONSOR—SAFETY 6 (AWFOS—S6 THE

BOWTIE DIAGRAM)

The BowTie diagram is applied to a hazard to help us identify and address both the preventative actions (safeguards) and the contingency actions (mitigating actions). The left-hand side of the Initiating Event shows the potential problems and safeguards, while the right side shows actions that should be taken if the incident were to occur.

The safety analysis of the incident worksheet discussed in AWFOS–S5 can be used to help construct our BowTie diagram. We first brainstorm to pro-actively identify the potential problems and then brainstorm all the things that could cause each potential problem to occur. For each cause we identify an action, (safeguard) we could take to prevent the initiating event from occurring. Next, we brainstorm all the mitigating actions we could take to limit the severity of the incident, should the initiating event occur. There are three outstanding videos that discuss the BowTie Diagram: (1) a 2-minute quick overview (<https://www.youtube.com/watch?v=vB0O4TPm2q0>), (2) a 5-minute video (<https://www.youtube.com/watch?v=P7Z6L7fjsi0>) that has all the components, and (3) an in-depth video (<https://www.youtube.com/watch?v=VsKgSDbHP3A>).

Examples of the BowTie diagram for CSB accidents can be found on the safety Web site (<http://umich.edu/~safeche/bowtie.html>). Figure 6-7 applies the BowTie Diagram in Figure 6-6 to the incident discussed in Chapter 5, the Acetone Drum Explosion.

An excellent representation of the BowTie method applied to prevent/mitigate an elderly person falling is demonstrated in the link (<http://www.patientsafetybowties.com/knowledge-base/6-the-bowtie-method-Topevent>). *Further Reading on the BowTie Diagram:*

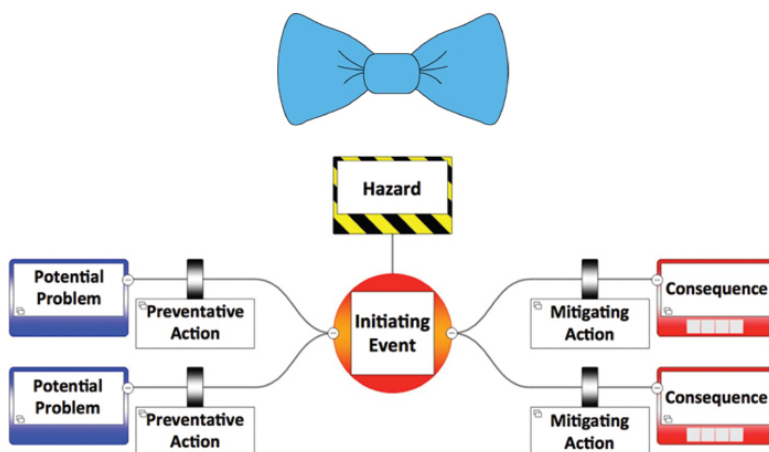


Figure 6-6 BowTie diagram.

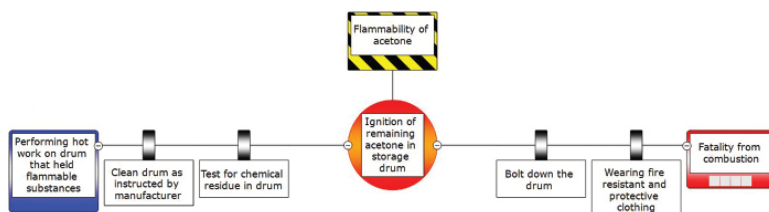


Figure 6-7 BowTie diagram of acetone accident.

The Bowtie Method. (2018). Retrieved from Patient Safety BowTies:

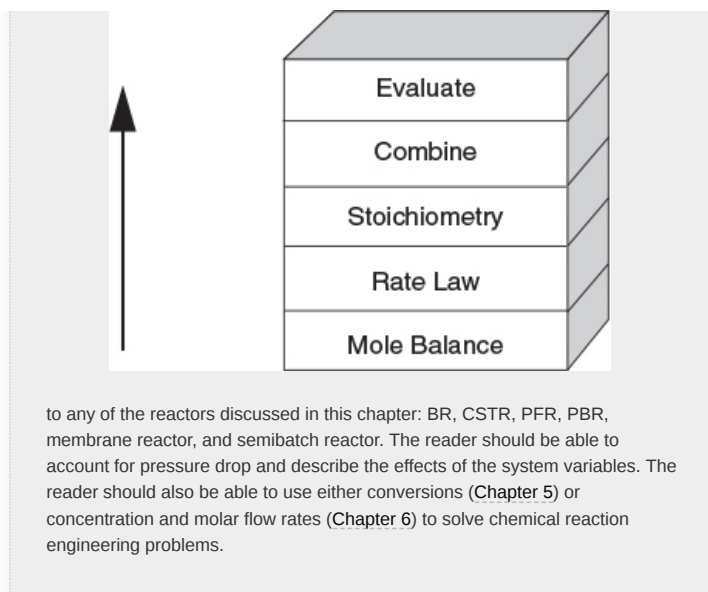
<http://www.patientsafetybowties.com/knowledge-base/6-the-bowtie-method#Top%20event>.

D. Hatch, P. McCulloch, and I. Travers, "Visual HAZOP," *The Chemical Engineer*, (917), 27–32 (2017, November).

B. K. Vaughn, and K. Bloch, "Use the bow tie diagram to help reduce process safety risks," *Chemical Engineering Progress*, 30–36 (2016, December).

The CRE Algorithm

Closure. Chapters 5 and 6 present the heart of chemical reaction engineering for isothermal reactors. After completing these chapters, the reader should be able to apply the algorithm building blocks



SUMMARY

Solution Algorithm—Measures Other Than Conversion

1. **Gas-Phase PFR:** When using measures other than conversion for reactor design, the mole balances are written for each species in the reacting mixture:

Mole balances on each and every species

$$\frac{dF_A}{dV} = r_A, \frac{dF_B}{dV} = r_B, \frac{dF_C}{dV} = r_C, \frac{dF_D}{dV} = r_D \quad (\text{S6-1})$$

The mole balances are then coupled through their relative rates of reaction. If

Rate Law

$$-r_A = kC_A^\alpha C_B^\beta \quad (\text{S6-2})$$

for $aA + bB \rightarrow cC + dD$, then

Relative Rates

$$r_B = \frac{b}{a}r_A, r_C = -\frac{c}{a}r_A, r_D = -\frac{d}{a}r_A \quad (\text{S6-3})$$

Concentration can also be expressed in terms of the number of moles (batch) and in terms of molar flow rates (PFR, CSTR, PBR).

$$Gas: C_A = C_{T0} \frac{F_A}{F_T} \frac{P}{P_0} \frac{T_0}{T} = C_{T0} \frac{F_A}{F_T} \frac{T_0}{T} p \quad (S6-4)$$

$$C_B = C_{T0} \frac{F_B}{F_T} \frac{T_0}{T} p \quad (S6-5)$$

Stoichiometry

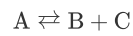
$$p = \frac{P}{P_0}$$

$$F_T = F_A + F_B + F_C + F_D + F_1 \quad (S6-6)$$

$$\frac{dp}{dW} = \frac{-\alpha}{2p} \left(\frac{F_T}{F_{T0}} \right) \left(\frac{T}{T_0} \right) \quad (S6-7)$$

$$Liquid: C_A = \frac{F_A}{v_0} \quad (S6-8)$$

2. **Membrane Reactors:** The mole balances for the reaction



when reactant A and product C do not diffuse out the membrane

Mole Balance

$$\frac{dF_A}{dV} = r_A, \frac{dF_B}{dV} = r_B - R_B, \text{ and } \frac{dF_C}{dV} = r_C \quad (S6-9)$$

with

$$R_B = k_C C_B \quad (S6-10)$$

Transport Law

and k_C is the overall mass transfer coefficient.

3. **Semibatch Reactors:** Reactant B is fed continuously to a vat initially containing only A



Mole Balances

$$\boxed{\frac{dC_A}{dt} = r_A - \frac{v_0}{V} C_A} \quad (S6-11)$$

$$\boxed{\frac{dC_B}{dt} = r_B + \frac{v_0(C_{B0} - C_B)}{V}} \quad (S6-12)$$

$$\frac{dC_C}{dt} = r_C - \frac{v_0 C_C}{V} \quad (\text{S6-13})$$

$$\frac{dC_D}{dt} = r_D - \frac{v_0 C_D}{V} \quad (\text{S6-14})$$

$$\text{Volume : } V = V_0 + v_0 t \quad (\text{S6-15})$$

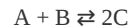
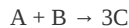
Rate Law

$$-r_A = k \left[C_A C_B - \frac{C_C C_D}{K_e} \right] \quad (\text{S6-16})$$

ODE SOLVER ALGORITHM

When using an ordinary differential equation (ODE) solver such as Polymath, MATLAB, Wolfram, or Python it is usually easier to leave the mole balances, rate laws, and concentrations as separate equations, rather than combining them into a single equation as we did to obtain an analytical solution. Writing the equations separately leaves it to the computer to combine them and produce a solution. The formulations for a gas-phase packed-bed reactor with pressure drop and a liquid-phase semibatch reactor are given below for two elementary reactions carried out isothermally.

LEP 6-4 Algorithm for a Gas-Phase Reaction LEP 6-5 Algorithm for a Liquid-Phase Reaction



Packed-Bed Reactor

Semibatch Reactor

$$\begin{aligned} \frac{dF_A}{dW} &= r'_A \\ \frac{dF_B}{dW} &= r'_B \\ \frac{dF_C}{dW} &= r'_C \\ r'_A &= -k C_A C_B \end{aligned}$$

$$\begin{aligned} \frac{dC_A}{dt} &= r_A - \frac{v_0 C_A}{V} \\ \frac{dC_B}{dt} &= r_B + \frac{v_0 (C_{B0} - C_B)}{V} \\ \frac{dC_C}{dt} &= -2r_A - \frac{v_0 C_C}{V} \end{aligned}$$

$$r'_B = r'_A$$

$$r'_C = 3(r'_A)$$

$$C_A = C_{T0} \frac{F_A}{F_T} p$$

$$C_B = C_{T0} \frac{F_B}{F_T} p$$

$$C_C = C_{T0} \frac{F_C}{F_T} p$$

$$\frac{dp}{dW} = -\frac{\alpha}{2p} \frac{F_T}{F_{T0}}$$

$$r_A = -k \left[C_A C_B - \frac{C_C^2}{K_C} \right]$$

$$V = V_0 + v_0 t$$

$$X = \frac{V_0 C_{Ai} - V C_A}{V_0 C_{Ai}}$$

$$k = 0.15, K_C = 16.0, V_0 = 10.0$$

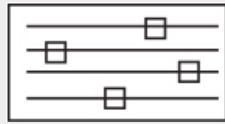
$$\nu_0 = 0.1, C_{B0} = 0.1, C_{Ai} = 0.04$$

$$t_{\text{final}} = 200$$

$$F_{T0} = 30, F_{A0} = 15, C_{T0} = 0.02, C_{A0} = 0.01,$$

$$C_{B0} = 0.01, k = 5000, \alpha = 0.009$$

$$W_{\text{final}} = 80$$



Use Wolfram to learn more about this reactor and reaction.

The Polymath, MATLAB, Wolfram, and Python solutions to the above equations are given on the CRE Web site in

Chapter 6

(<http://www.umich.edu/~elements/6e/06chap/live.html>).

CRE WEB SITE MATERIALS

(<http://umich.edu/~elements/6e/06chap/obj.html#/>)

Useful Links

Living
Example
Problems

Extra
Help

Additional
Materials

Professional
Reference
Shelf

Computer
Simulation
Problem
Statements

YouTube
Videos

Evaluation

Self Tests

Clicker
Questions

Interactive Computer Games

(<http://umich.edu/~elements/6e/icm/index.html>)



Tic-Tac Interactive Game

(<http://umich.edu/~elements/6e/icm/tictac.html>)



Wetlands

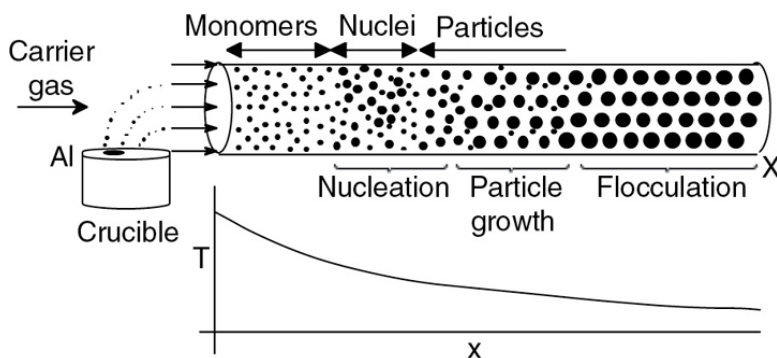
(http://umich.edu/~elements/6e/web_mod/wetlands/index.htm)

Aerosol Reactors

(http://www.umich.edu/~elements/6e/web_mod/aerosol/index.htm)

Aerosol reactors are used to synthesize nano-size particles. Owing to their size, shape, and high specific surface area, nanoparticles can be used in a number of applications such as pigments in cosmetics, membranes, photocatalytic reactors, catalysts and ceramics, and catalytic reactors.

We use the production of aluminum particles as an example of an aerosol plug-flow reactor (APFR) operation. A stream of argon gas saturated with Al vapor is cooled.



Aerosol reactor and temperature profile.

As the gas is cooled, it becomes supersaturated, leading to the nucleation of particles. This nucleation is a result of molecules colliding and agglomerating until a critical nucleus size is reached and a particle is formed. As these particles move down the reactor, the supersaturated gas molecules condense on the particles, causing them to grow in size and then to flocculate. In the development on the CRE Web site in the Web modules category, we will model the formation and growth of aluminum nanoparticles in an AFPR.

QUESTIONS, SIMULATIONS, AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$A = \bullet \quad B = \blacksquare \quad C = \blacklozenge \quad D = \blacklozenge\blacklozenge$$



Homework Problems

In each of the following questions and problems, rather than just drawing a box around your answer, write a sentence or two describing how you solved the problem, the assumptions you made, the reasonableness of your answer, what you learned, and any other facts that you want to include. You may wish to refer to W. Strunk and E. B. White, *The Elements of Style*, 4th ed. New York: Macmillan, 2000 and Joseph M. Williams, *Style: Ten Lessons in Clarity & Grace*, 6th ed. Glenview, IL: Scott, Foresman, 1999, to enhance the quality of your sentences. See the preface for additional generic parts (x), (y), and (z) to the home problems.

Before solving the problems, state or sketch qualitatively the expected results or trends.

Questions

Q6-1_A QBR (*Question Before Reading*). What are the steps in the CRE algorithm that must be added when conversion is not used as a variable and which step is usually the most difficult to implement?

Q6-2_A i>clicker. Go to the Web site (http://www.umich.edu/~elements/6e/06chap/iclicker_ch6_q1.html) and view at least five i>clicker questions. Choose one that could be used as is, or a variation thereof, to be included on the next exam. You also could consider the opposite case: explain why the question should *not* be on the next exam. In either case, explain your reasoning.

Q6-3_A Read through all the problems at the end of this chapter. Make up and solve an *original* problem based on the material in this chapter. **(a)** Use real data and reactions for further instructions. **(b)** Make up a reaction and data. **(c)** Use an example from everyday life (e.g., cooking spaghetti; see Question Q5-4_A).

Q6-4_A How would you modify Table 6-2 for

1. A constant-volume gas-phase reaction, and
2. A variable-volume gas-phase reaction?

Q6-5_B What are the similarities and differences between the *BowTie Diagram*, the *Safety Analysis of the Incident*, and the *Swiss Cheese Model*?

Q6-6_A Robert the Worrier: What if... you were asked to explore the example problems in this chapter to learn the effects of varying the different parameters? This sensitivity analysis can be carried out by downloading the examples from the CRE Web site. For each of the example problems you investigate, write a paragraph describing your findings.

Q6-7_A Go to the LearnChemE screencasts link for Chapter 6 (<http://www.learncheme.com/screencasts/kinetics-reactor-design>).

1. View one or more of the screencast 5- to 6-minute videos and write a two sentence evaluation.
2. In the membrane reactor, what are the benefits of removing hydrogen?
3. View two other LearnChemE videos for this chapter and list two things that should be improved upon and two things that were well done.

Computer Simulations and Experiments

P6-1_B AWFOS–S6 List two similarities and two differences between the Safety Analysis of the Incident Algorithm and the BowTie Diagram.

1. Example 6-1: Gas-Phase Reaction in a Microreactor

Wolfram and Python

1. Use Wolfram and/or Python to Compare what happens when T and E_A are each set at their maximum and minimum values (e.g., E_{Amax} , T_{min} , E_{Amax} , T_{max}), and then move the other slider and write a set of conclusions.

Polymath

2. Compare Figure E6-1.1 profiles with those for a reversible reaction with $K_C = 0.02 \text{ mol/dm}^3$ and describe the differences in the profiles.
3. How would your profiles change for the case of an irreversible reaction with pressure drop when $\alpha_p = 99 \times 10^3 \text{ dm}^{-3}$ for each tube?

2. Example 6-2: Membrane Reactor

Wolfram and Python

A Stop and Smell the Roses Simulation. Vary the sliders to develop an intuitive feel of membrane reactors.



1. Starting with the default settings (all in proper default units) on the LEP simulation (i.e., $K_C = 0.05$, $k = 0.7$, $C_{T0} = 0.2$, and $k_C = 0.2$), vary each parameter individually and describe what you find. Note and explain any maximum or minimum values of your plots down the length (i.e., volume = 500 dm³) of your reactor. *Hint*: Go to the extremes of the range of variables.
2. Repeat (i) but set K_C at its maximum value and then vary k and k_C , and describe what you find.
3. Write a set of conclusions from your experiments in (i) and (ii).

Polymath

4. Vary ratios of parameters such as (k/k_C) and $(k\tau C_{A0}/K_C)$ (note: $\tau = 400$ min) and write a paragraph describing what you find. What ratio of parameters has the greatest effect on the conversion $X = (F_{A0} - F_A)/F_{A0}$? (Trial and Error Solution)
 5. Include pressure drop with $\alpha = 0.002$ dm⁻³ and compare the conversion profiles for the two cases.
 6. Write a summary paragraph of all the trends and your results.
 7. Make up a question/problem on membrane reactors with a solution in which Wolfram must be used to obtain the answer. *Hint*: Apply to this problem one or more of the six ideas discussed in Table P-4 in the Complete Preface-Introduction on the Web site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>). Also comment on what types of questions you would ask when using Wolfram.
3. **Example 6-2: Membrane Reactor Again**

Polymath

Rework part (b) for the case when the reaction produces 3 mole of hydrogen



You will need to make minor modifications to the LEP Polymath code on the Web site. All the parameters remain the same except the equilibrium constant, which is $K_C = 0.001 \left(\frac{\text{mol}}{\text{dm}^3} \right)^3$.

4. **Example 6-3: Isothermal Semibatch Reactor with a Second-Order Reaction**

Wolfram and Python

1. Describe what happens as C_{B0} , u_0 , and V_0 are varied one at a time between their maximum and minimum values. Explain *why* the variations from the base case look the way they do.
2. After using the slider to vary the parameter, write a set of conclusions.

Polymath

3. Redo this example problem assuming the reaction is reversible with $K_C = 0.1$. Modify the Polymath code and compare with the irreversible case. (Only a couple of changes in the Polymath program are necessary.)
5. **Example 6-4: Algorithm for a Gas-Phase Reactor with Pressure Drop**
- Wolfram and Python**

1. Determine which slider has the greatest effect on conversion.
2. The entering pressure in reactor was set at 10 atm. Which parameter(s) cause(s) the exit pressure drop to atmospheric pressure, i.e., $p = 0.1$? Give the values of those parameters.
3. After using the sliders to vary the parameters, write a set of conclusions.

6. Example 6-5: Algorithm for a Semibatch Liquid-Phase Reactor

Wolfram and Python

1. Why is the conversion almost negligible below 20 minutes for the values of the initial settings?
2. Describe what happens when you decrease K_C and increase k at the same time. How does this change affect the maximum concentration of B?
3. What slider variables have the greatest effect on conversion?

Web Modules

7. **Web Module on Wetlands** on the CRE Web site. Download the Polymath program and vary a number of parameters such as rainfall, evaporation rate, atrazine concentration, and liquid flow rate, and write a paragraph describing what you find. This topic is a hot Ch.E. research area.
8. **Web Module on Aerosol Reactors** on the CRE Web site. Download the Polymath program and (1) vary the parameters, such as cooling rate and flow rate, and describe their effect on each of the regimes: nucleation, growth, and flocculation. Write a paragraph describing what you find. (2) It is proposed to replace the carrier gas by helium.
 1. Compare your plots (He vs. Ar) of the number of Al particles as a function of time. Explain the shape of the plots.
 2. How does the final value of d_p compare with that when the carrier gas was argon? Explain.
 3. Compare the time at which the rate of nucleation reaches a peak in the two cases (carrier gas = Ar and He). Discuss the comparison.

Data for a He molecule: mass = 6.64×10^{-27} kg, volume = 1.33×10^{-29} m³, surface area = 2.72×10^{-19} m², bulk density = 0.164 kg/m³, at a temperature of 25°C and pressure of 1 atm.

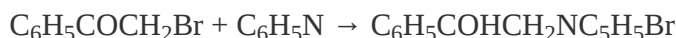
Interactive Computer Games

P6-2_B Download the Interactive Computer Games (ICG) from the CRE Web site

(<http://www.umich.edu/~elements/6e/icm/tictac.html>).

Play the game and then record your performance number, which indicates your mastery of the material. Your instructor has the key to decode your performance number. Knowledge of all sections is necessary to pit your wit against the computer adversary in playing a game of Tic-Tac-Toe.

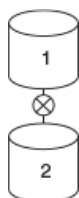
Performance number: _____

Problems**P6-3_C OEQ** (*Old Exam Question*). The second-order liquid-phase reaction

is carried out in a batch reactor at 35°C. The specific reaction-rate constant is 0.0445 dm³/mol/min. Reactor 1 is charged with 1000 dm³, where the concentration of each reactant after mixing is 2M.

1. What is the conversion after 10, 50, and 100 minutes?

Now, consider the case when, after filling reactor 1, the drain at the bottom of reactor 1 is left open and it drains into reactor 2, mounted below it, at a volumetric rate of 10 dm³/min.



2. What will be the conversion and concentration of each species in reactor 1 after 10, 50, and 80 minutes in the reactor that is being drained? (**Ans:** At $t = 10$ min then $X = 0.47$)
3. What is the conversion and concentration of each species in reactor 2 that is filling up with the liquid from reactor 1 after 10 and after 50 minutes? (**Ans:** At $t = 50$ min then $X = 0.82$)
4. At the end of 50 minutes, the contents of the two reactors are added together. What is the overall conversion after mixing?
5. Apply one or more of the six ideas in Preface Table P-4, page xxvii, to this problem.

P6-4_B The elementary gas-phase reaction

is carried out isothermally at 400 K in a flow reactor with no pressure drop. The specific reaction rate at 50°C is 10⁻⁴ min⁻¹ (from pericosity data) and the activation energy is 85 kJ/mol. Pure di-*tert*-butyl peroxide enters the reactor at

10 atm and 127°C and a molar flow rate of 2.5 mol/min, that is, $F_A = 2.5$ mol/min.

1. Use the algorithm for molar flow rates to formulate and solve the problem. Plot F_A , F_B , F_C , and then X as a function of plug-flow reactor volume and space time to achieve 90% conversion.
2. Calculate the plug-flow volume and space time for a CSTR for 90% conversion.

P6-5_B For the reaction and data in Problem P6-4_B, we now consider the case when the reaction is reversible with $K_C = 0.025$ dm⁶/mol² and the reaction is carried out at 300 K in a membrane reactor where C₂H₆ is diffusing out. The membrane transport coefficient is $k_C = 0.08$ s⁻¹.

1. What is the equilibrium conversion and what is the exit conversion in a conventional PFR? (**Ans:** $X_{eq} = 0.52$, $X = 0.47$)
2. Plot and analyze the conversion and molar flow rates in the membrane reactor as a function of reactor volume up to the point where 80% conversion of di-tert-butyl peroxide is achieved. Note any maxima in the flow rates.
3. Apply the ideas in Tables P-2 and P-4 in the Complete Preface-Introduction on the Web site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>) to generate new questions to be added to this problem—three each for both critical and creative thinking.

P6-6_C **OEQ (Old Exam Question).** (*Membrane reactor*) The first-order, gas-phase, reversible reaction



is taking place in a membrane reactor. Pure A enters the reactor, and B diffuses out through the membrane.

Unfortunately, a small amount of the reactant A also diffuses through the membrane.

1. Plot and analyze the flow rates of A, B, and C and the conversion X down the reactor, as well as the flow rates of A and B through the membrane.
2. Next, compare the conversion profiles in a conventional PFR with those of a membrane reactor from part (a). What generalizations can you make?
3. Would the conversion of A be greater or smaller if C were diffusing out instead of B?
4. Discuss qualitatively how your curves would change if the temperature were increased significantly or decreased significantly for an exothermic reaction. Repeat the discussion for an endothermic reaction.

Additional information:

$$k = 10 \text{ min}^{-1}$$

$$K_C = 0.01 \text{ mol}^2/\text{dm}^6$$

$$k_{CA} = 1 \text{ min}^{-1}$$

$$k_{CB} = 40 \text{ min}^{-1}$$

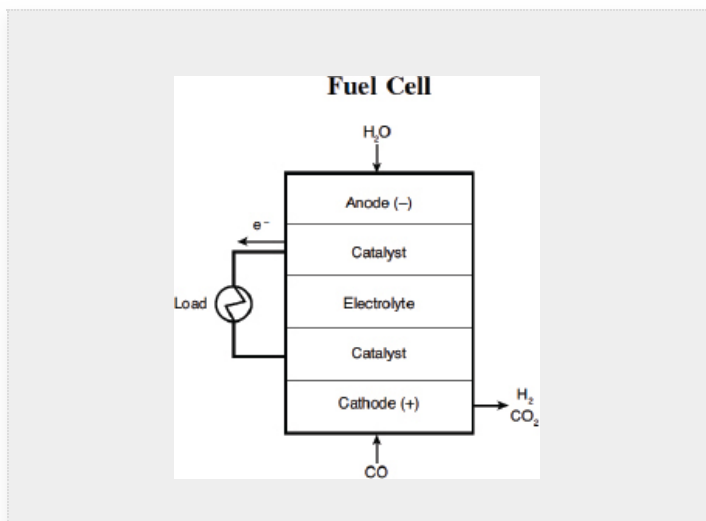
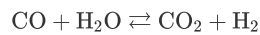
$$F_{A0} = 100 \text{ mol/min}$$

$$v_0 = 100 \text{ dm}^3/\text{min}$$

$$V_{\text{reactor}} = 20 \text{ dm}^3$$

P6-7_B Fuel Cells Rationale. With the focus on alternative clean-energy sources, we are moving toward an increased use of fuel cells to operate appliances ranging from computers to automobiles. For example, the hydrogen/oxygen fuel cell produces *clean energy* as the products are water and electricity, which may lead to a hydrogen-based economy instead of a petroleum-based economy.

A large component in the processing train for fuel cells is the water-gas shift membrane reactor. (M. Gummala, N. Gupta, B. Olsomer, and Z. Dardas, *Paper 103c*, 2003, AIChE National Meeting, New Orleans, LA.)



Here, CO and water are fed to the membrane reactor containing the catalyst. Hydrogen can diffuse out the sides of the membrane, while CO, H₂O, and CO₂ cannot. Based on the following information, plot the concentrations and molar flow rates of each of the reacting species down the length of the membrane reactor. Assume the following: The volumetric feed is 10 dm³/min at 10 atm, and the equimolar feed of CO and water vapor with $C_{T0} = 0.4$ mol/dm³. The equilibrium constant is $K_e = 1.44$, with $k = 1.37$ dm⁶/mol kg-cat · min, bulk density, $\rho = 1000$ kg/m³, and the mass transfer coefficient $k_{H_2} = 0.1$ dm³/kg-cat · min. *Hint:* First calculate the entering molar flow rate of CO and then relate F_A and X .

1. What is the membrane reactor catalyst weight necessary to achieve 85% conversion of CO?
2. Sophia wants you to compare the MR with a conventional PFR. What will you tell her?
3. For that same membrane reactor catalyst weight, Nicolas wants to know what would be the conversion of CO if the feed rate were doubled?

P6-8C OEQ (Old Exam Question). The production of ethylene glycol from ethylene chlorohydrin and sodium bicarbonate



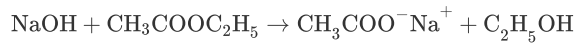
is carried out in a semibatch reactor. A 1.5-molar solution of ethylene chlorohydrin is fed at a rate of 0.1 mol/min to 1500 dm³ of a 0.75-molar solution of sodium bicarbonate. The reaction is elementary and carried out isothermally at 30°C where the specific reaction rate is 5.1 dm³/mol/h. Higher temperatures produce unwanted side reactions. The reactor can hold a maximum of 2500 dm³ of liquid. Assume constant density.

1. Plot and analyze the conversion, reaction rate, concentration of reactants and products, and number of moles of glycol formed as a function of time.
2. Suppose you could vary the flow rate between 0.01 and 200 mol/min. What flow rate and holding time would you choose to make the greatest number of moles of ethylene glycol in 24 hours, keeping in mind the downtimes for cleaning, filling, and so on, shown in Table 5-3?
3. Suppose the ethylene chlorohydrin is fed at a rate of 0.15 mol/min until the reactor is full and then shut in. Plot the conversion as a function of

time.

4. Discuss what you learned from this problem and what you believe to be the point of this problem.

P6-9_C The following elementary reaction is to be carried out in the liquid phase

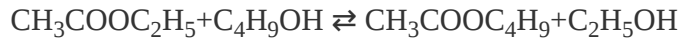


The initial concentrations are 0.2 M in NaOH and 0.25 M in $\text{CH}_3\text{COOC}_2\text{H}_5$ with $k = 5.2 \times 10^{-5} \text{ dm}^3/\text{mol}\cdot\text{s}$ at 20°C with $E = 42,810 \text{ J/mol}$. Design a set of operating conditions (e.g., v_0 , T , . . .) to produce 200 mol/day of ethanol in a semibatch reactor and not operate above 37°C and below a concentration of NaOH of 0.02 molar.⁷ The semibatch reactor you have available is 1.5 m in diameter and 2.5 m tall. The reactor down time is $(t_c + t_e + t_f) = 3 \text{ h}$.

⁷ Manual of Chemical Engineering Laboratory, University of Nancy, Nancy, France, 1994 (eric@ist.uni-stuttgart.de).

P6-10_B Go to Professor Herz's Reactor Lab Web site at www.reactorlab.net. From the menu at the top of the page, select Download and then click on the English version link. Provide the required information and then download, install, and open the software. Select Division D2, Lab L2 and there the labeled PFR of The Reactor Lab concerning a packed-bed reactor (labeled PFR) in which a gas with the physical properties of air flows over spherical catalyst pellets. Perform experiments here to get a feeling for how pressure drop varies with input parameters such as reactor diameter, pellet diameter, gas-flow rate, and temperature. In order to get significant pressure drop, you may need to change some of the input values substantially from those shown when you enter the lab. If you get a notice that you can't get the desired flow, then you need to increase the inlet pressure.

P6-11_B **OEQ (Old Exam Question).** Pure butanol is to be fed into a *semibatch reactor* containing pure ethyl acetate to produce butyl acetate and ethanol. The reaction



is elementary and reversible. The reaction is carried out isothermally at 300 K. At this temperature, the equilibrium constant is 1.08 and the specific reaction rate is $9 \times 10^{-5} \text{ dm}^3/\text{mol}\cdot\text{s}$. Initially, there is 200 dm^3 of ethyl acetate in the vat, and butanol is fed at a volumetric rate of $0.05 \text{ dm}^3/\text{s}$. The feed and initial concentrations of butanol and ethyl acetate are 10.93 and 7.72 mol/dm^3 , respectively.

1. Plot and analyze the equilibrium conversion of ethyl acetate as a function of time.
2. Plot and analyze the conversion of ethyl acetate, the rate of reaction, and the concentration of butanol as a function of time.
3. Rework part (b), assuming that ethanol evaporates (reactive distillation) as soon as it forms. (This is a graduate level question.)
4. Use Polymath or some other ODE solver to learn the sensitivity of conversion to various combinations of parameters (e.g., vary F_{B0} , N_{A0} , v_0).
5. Apply one or more of the six ideas in Preface Table P-4, page xxvii, to this problem.
6. Write a question that requires critical thinking and then explain why your question requires critical thinking. *Hint:* See Preface Section G.

P6-12C Use the reaction data in Problem P6-11B and the molar flow rate algorithm to carry out the following problems:

1. Calculate the CSTR volume to achieve 80% of the equilibrium conversion for an equal molar feed and for a volumetric feed of $0.05 \text{ dm}^3/\text{s}$.
2. Safety. Now consider the case where we want to shut down the reactor by feeding water at a volumetric rate of $0.05 \text{ dm}^3/\text{s}$. How long will it take to reduce the rate to 1% of the rate in the CSTR under the conditions of part (a)?

P6-13C *OEQ (Old Exam Question)*. An isothermal reversible reaction $A \rightleftharpoons B$ is carried out in an aqueous solution. The reaction is first-order in both directions. The forward rate constant is 0.4 h^{-1} and the equilibrium constant is 4.0. The feed to the plant contains 100 kg/m^3 of A and enters at the rate of $12 \text{ m}^3/\text{h}$. Reactor effluents pass to a separator, where B is completely recovered. The reactor is a *stirred tank* of volume 60 m^3 . A fraction, f_1 , of the unreacted effluent is recycled

as a solution containing 100 kg/m^3 of A and the remainder is discarded. Product B is worth \$2 per kilogram and operating costs are \$50 per cubic meter of solution entering the separator. What value of f maximizes the operational profit of the plant? What fraction A fed to the plant is converted at the optimum?
Source: H. . Shankar, IIT Mumbai.

SUPPLEMENTARY READING

MAXWELL ANTHONY, presidential inauguration address,
“*The economic future of Jofostan and the chemical reaction industry and one’s ability to deal with multiple reactions.*” Riça, Jofostan, January 1, 2022.

GARRISON KEILLOR and TIM RUSSELL, *Dusty and Lefty: The Lives of the Cowboys* (Audio CD). St. Paul, MN: High-bridge Audio, 2006.

G. F. FROMENT and K. B. BISCHOFF, *Chemical Reactor Analysis and Design*, 2nd ed. New York: Wiley, 1990.

Recent information on reactor design can usually be found in the following journals: *Chemical Engineering Science*, *Chemical Engineering Communications*, *Industrial and Engineering Chemistry Research*, *Canadian Journal of Chemical Engineering*, *Jofostan Journal of Chemical Engineering*, *AIChE Journal*, and *Chemical Engineering Progress*.

7. Collection and Analysis of Rate Data

You can observe a lot just by watching.

—Yogi Berra, New York Yankees

Overview. In Chapters 5 and 6, we showed that once the rate law is known, it can be substituted into the appropriate mole balance, and then through the use of the appropriate stoichiometric relationships, we can apply the CRE algorithm to analyze any isothermal reaction system. In this chapter, we focus on ways of obtaining and analyzing reaction-rate data to obtain the rate law for a specific reaction.

We discuss two common types of reactors used for obtaining rate data: the batch reactor, which is used primarily for homogeneous reactions, and the differential reactor, which is used for solid–fluid heterogeneous reactions. In batch reactor experiments, concentration, pressure, and/or volume are usually measured and recorded at different times during the course of the reaction. Data are collected from the batch reactor during transient operation, whereas measurements on the differential reactor are made during steady-state operation. In experiments with a differential reactor, the product concentration is usually monitored for different sets of feed conditions.

Three different methods of analyzing the data collected are used:

- The integral method
- The differential method
- Nonlinear regression

The integral and differential methods are used primarily in analyzing batch reactor data. Because a number of software packages (e.g., Poly-math, MATLAB) are now available to analyze data, a rather extensive discussion of nonlinear regression is included.

7.1 THE ALGORITHM FOR DATA ANALYSIS

For batch systems, the usual procedure is to collect concentration–time data, which we then use to determine the rate law. Table 7-1 gives a seven-step procedure we will emphasize in analyzing reaction engineering data.

Data for homogeneous reactions is most often obtained in a batch reactor. After postulating a rate law in Step 1 and

combining it with a mole balance in Step 2, we next use any or all of the methods in Step 5 to process the data and arrive at the reaction orders and specific reaction-rate constants.

Analysis of heterogeneous reactions is shown in Step 6. For gas–solid heterogeneous reactions, we need to have an understanding of the reaction and possible mechanisms in order to postulate the rate law in Step 6B. After studying Chapter 10 on heterogeneous reactions, one will be able to postulate different rate laws and then use Polymath nonlinear regression to choose the “best” rate-law and reaction-rate-law parameters (see Example 10-3 on pages 494–496).

The procedure we will use to delineate the rate law and rate-law parameters is given in Table 7-1.

TABLE 7-1 STEPS IN ANALYZING RATE DATA

1.	Postulate a rate law.
A.	Power-law models for <i>homogeneous reactions</i>
	$-r_A = kC_A^\alpha, \quad -r_A = kC_A^\alpha C_B^\beta$
B.	Langmuir-Hinshelwood models for <i>heterogeneous reactions</i>
	$-r'_A = \frac{kP_A}{1+K_AP_A}, \quad -r'_A = \frac{kP_AP_B}{(1+K_AP_A+P_B)^2}$
2.	Select reactor type and corresponding mole balance.

A. If batch reactor (Section 7.2), use mole balance on Reactant A

$$-r_A = -\frac{dC_A}{dt} \quad (\text{T7-1.1})$$

B. If differential PBR (Section 7.6), use mole balance on Product P (A → P)

$$-r'_A = \frac{F_P}{\Delta W} = C_P v_0 / \Delta W \quad (\text{T7-1.2})$$

3. **Process your data in terms of the measured variable** (e.g., N_A , C_A , or P_A). If necessary, rewrite your mole balance in terms of the measured variable (e.g., P_A).

4. **Look for simplifications.** For example, if one of the reactants is in excess, assume its concentration is constant. If the gas-phase mole fraction of reactant A is small, set. $\varepsilon \approx 0$

5. **For a batch reactor, calculate $-r_A$ as a function of concentration C_A to determine the reaction order.**

A. *Differential analysis* (Section 7.4)

Combine the mole balance (T7-1.1) and power-law model (T7-1.3)

$$-r_A = k C_A^\alpha \quad (\text{T7-1.3})$$

$$-\frac{dC_A}{dt} = k C_A^\alpha \quad (\text{T7-1.4})$$

and then take the natural log

$$\ln \left(-\frac{dC_A}{dt} \right) = \ln (-r_A) = \ln k + \alpha \ln C_A \quad (\text{T7-1.5})$$

(1) Find $-\frac{dC_A}{dt}$ from C_A versus t data by either the

(a) Graphical differentiation (not often used)

(b) Finite difference method or

(c) Polynomial fit

(2) Either plot $\left[\ln \left(-\frac{dC_A}{dt} \right) \right]$ versus $\ln C_A$ to find reaction order α , which is the slope of the line fit to the data

or

(3) Use nonlinear regression to find α and k simultaneously.

(4) The *method of initial rates*

(<http://www.umich.edu/~elements/6e/07chap/prof-7-1.html>).

This method is used for highly reversible reactions and requires multiple experiments at different initial

concentrations. Here we need to find $\left(\frac{dC_A}{dt}\right)_{t=0}$ as a function of C_{A0}

$$\ln\left(-\frac{dC_A}{dt}\right)_{t=0} = \ln k + \alpha \ln C_{A0} \quad (\text{T7-1.6})$$

One can use Equation (T7-1.6) to plot the data as described in (2) above or as in (3) above use regression.

B. *Integral method (Section 7.3)*

For $-r_A = kC_A^\alpha$, the combined mole balance and rate law is

$$-\frac{dC_A}{dt} = kC_A^\alpha \quad (\text{T7-1.4})$$

Guess α and integrate Equation (T7-1.4). Rearrange your equation to obtain the appropriate function of C_A , which when plotted as a function of time should be linear. If it is linear, then the guessed value of α is correct and the slope is the specific reaction rate, k . If it is not linear, guess again for α . If you guess $\alpha = 0, 1$, and 2 , and none of these orders fit the data, proceed to nonlinear regression.

C. *Nonlinear regression (Polymath; Section 7.5):*

Integrate Equation (T7-1.4) to obtain

$$t = \frac{1}{k} \left[\frac{C_{A0}^{(1-\alpha)} - C_A^{(1-\alpha)}}{(1-\alpha)} \right] \text{ for } \alpha \neq 1 \quad (\text{T7-1.7})$$

Whenever possible, I would encourage the use of nonlinear regression.

Use Polymath regression to find α and k . A Polymath tutorial on regression with screen shots can be found on the CRE Web site at http://umich.edu/~elements/6e/07chap/Example_7-3_Polymath_nonlinear_regression_tutorial.pdf and at http://www.umich.edu/~elements/6e/software/nonlinear_regression_tutorial.pdf.

6. For differential PBR, calculate $-r'_A$ as a function of C_A or P_A (Section 7.6).

- A. Calculate $-r'_A = \frac{v_0 C_p}{\Delta W}$ as a function of reactant concentration, C_A or partial pressure P_A .
- B. Choose a model (see Chapter 10), for example,

$$-r'_A = \frac{k P_A}{1 + K_A P_A}$$

- C. Use nonlinear regression to find the best model and model parameters. See example on the CRE Web site *Summary Notes for Chapter 10*, using data from heterogeneous catalysis.

7. Analyze your rate law model for “goodness of fit.” Calculate a correlation coefficient.

7.2 DETERMINING THE REACTION ORDER FOR EACH OF TWO REACTANTS USING THE METHOD OF EXCESS

Batch reactors are used primarily to determine rate-law parameters for homogeneous reactions. This determination is usually achieved by measuring concentration as a function of time and then using either the integral, differential, or nonlinear regression method of data analysis to determine the reaction order, α , and specific reaction-rate constant, k . If some reaction parameter other than concentration is monitored, such as pressure, the mole balance must be rewritten in terms of the measured variable (e.g., pressure, as shown in the example in *Solved Problems* on the CRE Web site at

<http://www.umich.edu/~elements/6e/07chap/pdf/excd5-1.pdf>).

Process data in terms of the measured variable.

When a reaction is *irreversible*, it is possible in many cases to determine the reaction order α and the specific rate constant by either nonlinear regression or by numerically differentiating *concentration versus time data*. This latter method is most applicable when reaction conditions are such that the rate is essentially a function of the concentration of only one reactant; for example, if, for the decomposition reaction

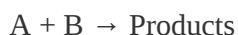


$$-r_A = k_A C_A^\alpha \quad (7-1)$$

then the differential method may be used.

Assume that the rate law is of the form $-r_A = k_A C_A^\alpha$.

However, by utilizing the method of excess, it is also possible to determine the relationship between $-r_A$ and the concentration of other reactants. That is, for the irreversible reaction



with the rate law

$$-r_A = k_A C_A^\alpha C_B^\beta \quad (7-2)$$

where α and β are both unknown, the reaction could first be run in an excess of B so that C_B remains essentially unchanged during the course of the reaction (i.e., $C_B \approx C_{B0}$) and

$$-r_A = k' C_A^\alpha \quad (7-3)$$

where

$$k' = k_A C_B^\beta \approx k_A C_{B0}^\beta$$

Method of excess

After determining α , the reaction is carried out in an excess of A, for which the rate law is approximated as

$$-r_A = k'' C_B^\beta \quad (7-4)$$

where $k'' = k_A C_A^\alpha \approx k_A C_{A0}^\alpha$

Once α and β are determined, k_A can be calculated from the measurement of $-r_A$ at known concentrations of A and B

$$k_A = \frac{-r_A}{C_A^\alpha C_B^\beta} = \frac{(\text{dm}^3/\text{mol})^{\alpha+\beta-1}}{\text{s}} \quad (7-5)$$

Both α and β can be determined by using the method of excess, coupled with a differential analysis of data for batch systems.

One could also carry out many experiments using the *methods of initial rates*

(<http://www.umich.edu/~elements/6e/07chap/prof-7-1.html>) to find $-r_{A0}$ as a function of C_{A0} and C_{B0} and then use regression to find k , α , and β as shown on the CRE Web site in

Professional Reference Shelf R3

(http://www.umich.edu/~elements/6e/07chap/pdf/least_squares.pdf).

7.3 INTEGRAL METHOD

The integral method is the quickest method to use to determine the rate law if the order turns out to zero, first, or second order. In the integral method, we guess the reaction order, α , in the combined batch reactor mole balance and rate law equation

$$\frac{dC_A}{dt} = -kC_A^\alpha \quad (7-6)$$

The integral method uses a trial-and-error procedure to find the reaction order.

and integrate the differential equation to obtain the concentration as a function of time. If the order α we assumed is correct, then the appropriate plot (determined from this integration) of the concentration–time data should be linear. The integral method is used most often when the reaction order is known and it is desired to evaluate the specific reaction-rate constant at different temperatures to determine the activation energy.

In the integral method of analysis of rate data, we are looking for the appropriate function of concentration corresponding to a particular rate law that is linear with time. We need to be familiar with the methods of obtaining these linear plots for reactions of *zero, first, and second order*.

It is important to know how to generate *linear* plots of functions of C_A versus t for zero-, first-, and second-order reactions.

For the reaction



carried out in a constant-volume batch reactor, the mole balance is

$$\frac{dC_A}{dt} = r_A$$

For a zero-order reaction, $r_A = -k$, and the combined rate law and mole balance is

$$\frac{dC_A}{dt} = -k \quad (7-7)$$

Integrating $C_A = C_{A0}$ with at $t = 0$, we have

$$C_A = C_{A0} - kt \quad (7-8)$$

Zero order

A plot of the concentration of A as a function of time will be linear (Figure 7-1) with slope $(-k)$ for a zero-order reaction carried out in a constant-volume batch reactor.

If the reaction is first order (Figure 7-2), integration of the combined *mole balance and the rate law*

$$-\frac{dC_A}{dt} = kC_A$$

with the limits $C_A = C_{A0}$ at $t = 0$ gives

$$\ln \frac{C_{A0}}{C_A} = kt \quad (7-9)$$

First order

Consequently, we see that the slope of a plot of $[\ln (C_{A0}/C_A)]$ as a function of time is indeed linear with slope k .

If the reaction is second order (Figure 7-3), then

$$-\frac{dC_A}{dt} = kC_A^2$$

#important

We need to know these plots for zero-, first- and second-order reactions.

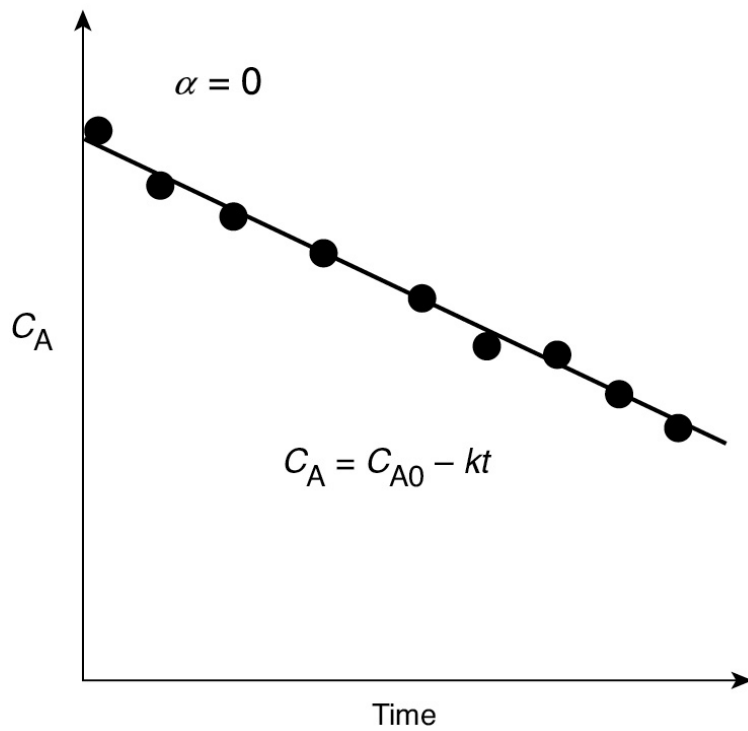


Figure 7-1 Zero-order reaction.

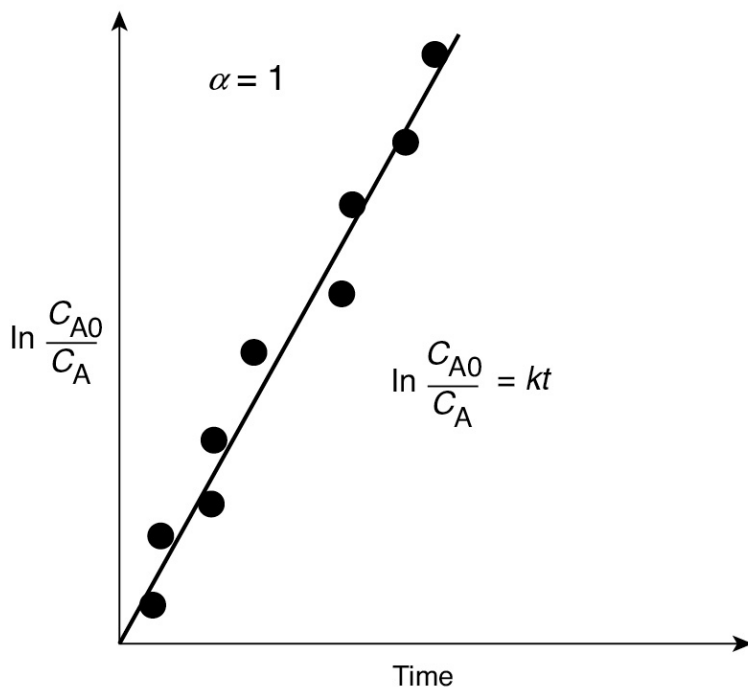


Figure 7-2 First-order reaction.

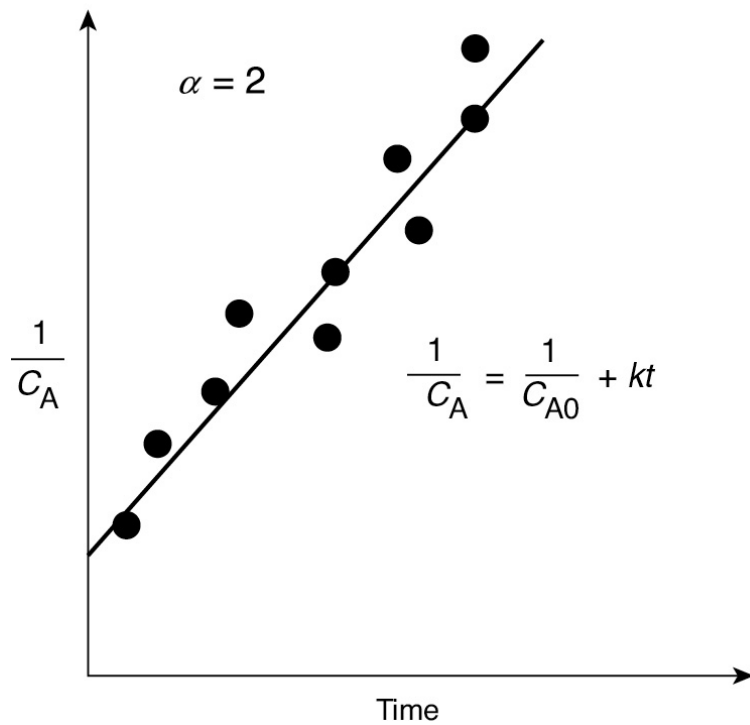


Figure 7-3 Second-order reaction.

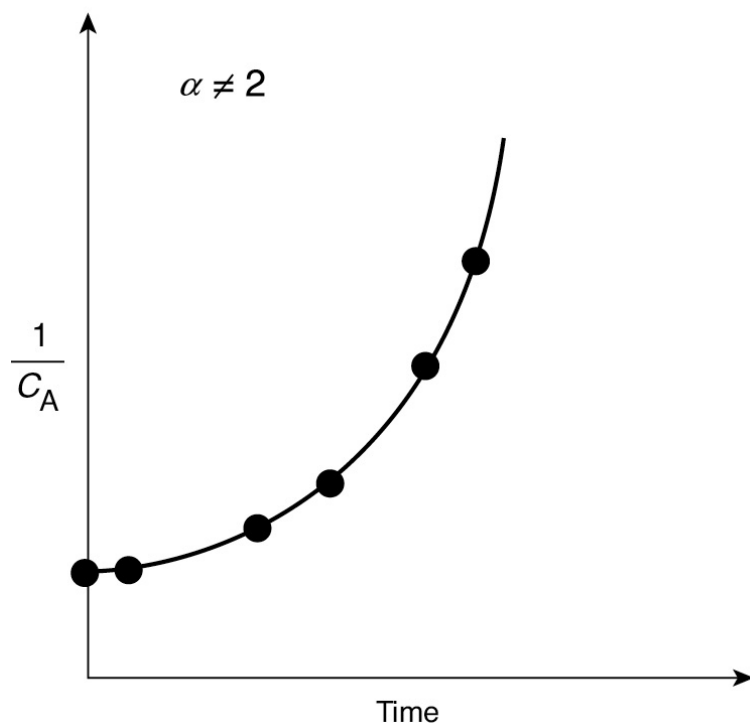


Figure 7-4 Plot of reciprocal reactant concentration as a function of time for a reaction of unknown order.

Integrating, with $C_A = C_{A0}$ initially (i.e., $t = 0$), yields

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt \quad (7-10)$$

Second order

We see that for a second-order reaction a plot of $(1/C_A)$ as a function of time should be linear with slope k .

In [Figures 7-1, 7-2, and 7-3](#), we saw that when we plotted the appropriate function of concentration (i.e., C_A , $\ln C_A$, or $1/C_A$) versus time, the plots were linear, and we concluded that the reactions were zero, first, or second order, respectively.

However, if the plots of concentration data versus time had turned out **not to be linear**, such as shown in [Figure 7-4](#), we would say that the proposed reaction order did not fit the data. In the case of [Figure 7-4](#), we would conclude that the reaction is not second order. After finding that the integral method for zero, first, and second orders also do not fit the data, one should use one of the other methods discussed in [Table 7-1](#), such as the *differential method* of analysis or *nonlinear regression*.

The idea is to arrange the data so that a linear relationship is obtained.

It is important to restate that, given a reaction-rate law, you should be able to quickly choose the appropriate function of concentration or conversion that yields a straight line when plotted against time or space time. The goodness-of-fit of such a line may be assessed statistically by calculating the linear correlation coefficient, r^2 , which should be as close to 1 as possible. The value of r^2 is given in the output of Polymath's nonlinear regression analysis.

Example 7–1 Integral Method of CRE Data Analysis

The liquid-phase reaction



was carried out in a batch reactor at 25°C in a solution of benzene and pyridine in an excess of methanol ($C_{B0} = 0.5 \frac{\text{mol}}{\text{dm}^3}$). (We need to point out that this batch reactor was purchased at the Sunday markets in Riça, Jofostan.) Pyridine reacts with HCl, which then precipitates as pyridine hydro-chloride thereby making the reaction irreversible. The reaction is first order in methanol. The concentration of triphenyl methyl chloride (A) was measured as a function of time and is shown Table E7-1.1.

#BeCareful Watch for leaks!

TABLE E7-1.1 RAW DATA

$t \text{ (min)}$	0	5	10	15	20	25	30
		0	0	0	0	0	0
C_A	0	0.	0.	0.	0.	0.	0.
(mol/dm^3)	.	0	03	02	02	01	01
	0	3	06	56	22	95	74
	5	8					

1. Use the integral method to confirm that the reaction is second order with regard to triphenyl methyl chloride.
2. Determine the pseudo rate constant $k' = kC_{B0}$.
3. Assume the reaction is first order in methanol and determine the true specific reaction rate constant, k , for this over all third-order reaction.

Solution

We use the power-law model, Equation (7-2), along with information from the problem statement that the

reaction is first order in methanol, (B), that is, $\beta = 1$ to obtain

$$-r_A = kC_A^\alpha C_B \quad (\text{E7-1.1})$$

1. *Excess methanol:* The initial concentration of methanol (B) is 10 times that of trityl (A), so even if all A were consumed, 90% of B remains. Consequently, we will take the concentration of B as a constant and combine it with k to form

$$-r_A = kC_A^\alpha C_{B0} = k'C_A^\alpha \quad (\text{E7-1.2})$$

where k' is the pseudo rate constant $k' = kC_{B0}$ and k is the true rate constant. Substituting $\alpha = 2$ and combining with the mole balance on a batch reactor, we obtain

$$-\frac{dC_A}{dt} = k'C_A^2 \quad (\text{E7-1.3})$$

Integrating with $C_A = C_{A0}$ at $t = 0$

$$t = \frac{1}{k'} \left[\frac{1}{C_A} - \frac{1}{C_{A0}} \right] \quad (\text{E7-1.4})$$

Rearranging

$$\boxed{\frac{1}{C_A} = \frac{1}{C_{A0}} + k't} \quad (\text{E7-1.5})$$

from Equation (E7-1.5), we see that if the reaction is indeed second order then a plot of $(1/C_A)$ versus t should be linear. Using the data in Table E7-1.1, we calculate $(1/C_A)$ to construct Table E7-1.2.

TABLE E7-1.2 PROCESSED DATA

t	0	5	1	1	2	2	3
(min)		0	0	5	0	5	0
n)			0	0	0	0	0
C_A	0	0	0	0	0	0	0
(m
ol/	0	0	0	0	0	0	0
dm	5	3	3	2	2	1	1
³)		8	0	5	2	9	7
			6	6	2	5	4
$1/C_A$	2	2	3	3	4	5	5
(d	0	6	2	9	5	1	7
m ³ /	
mo		3	7	1		3	5
l)							

2. In a graphical solution, the data in Table E7-1.2 is used to construct a plot of $(1/C_A)$ as a function of t , which will yield the pseudo-specific reaction rate k' . This plot is shown in Figure E7-1.1. Again, Excel or Polymath could be used to find k' from the data in Table E7-1.2.

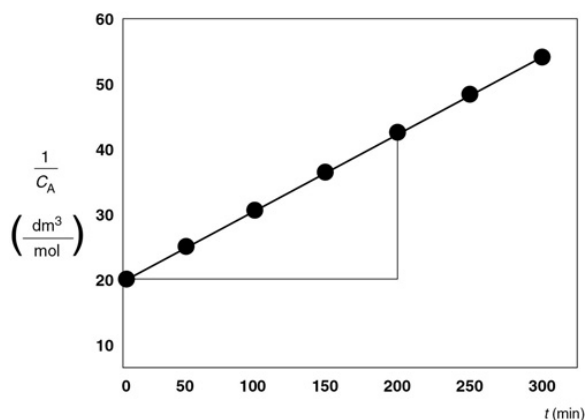


Figure E7-1.1 Plot of the reciprocal of C_A versus t for a second-order reaction.

We note in passing that if you used Excel or similar analysis, then the slope would most likely be part of your computer output.

The slope of the line is the specific reaction rate k' , which using the points at $t = 0$ and $t = 200$, k is calculated to be

$$k' = \frac{\Delta(\frac{1}{C_A})}{\Delta t} = \frac{(44-20)(\frac{\text{dm}^3}{\text{mol}})}{(200-0)\text{min}} = 0.12 \frac{\text{dm}^3}{\text{mol} \cdot \text{min}} \quad (\text{E7-1.6})$$

We see from the Excel analysis and plot that the slope of the line is $0.12 \text{ dm}^3/\text{mol} \cdot \text{min}$.

3. We now use Equation (E7-1.6), along with the initial concentration of methanol, to find the true rate constant, k .

$$k = \frac{k'}{C_{B0}} = \frac{0.12 \frac{\text{dm}^3/\text{mol}/\text{min}}{\text{mol}/\text{dm}^3}}{0.5} = 0.24 \left(\frac{\text{dm}^3}{\text{mol}} \right)^2 / \text{min}$$

The rate law is

$$-r_A = \left[0.24 \left(\frac{\text{dm}^3}{\text{mol}} \right)^2 / \text{min} \right] C_A^2 C_B \quad (\text{E7-1.7})$$

We note that the integral method tends to smooth the data.

Analysis: In this example, the reaction orders are known so that the integral method can be used to (1) verify the reaction is second order in trityl and (2) to find the specific pseudo reaction rate $k' = kC_{B0}$ for the

case of excess methanol (B). Knowing k' and C_{B0} , we then found the true rate constant k .

7.4 DIFFERENTIAL METHOD OF ANALYSIS

The differential method is an excellent technique to use when you want to look for inconsistencies in one's experimental data. To outline the procedure used in the differential method of analysis, we consider a reaction carried out isothermally in a constant-volume batch reactor and the concentration of A, recorded as a function of time. By combining the mole balance with the rate law given by Equation (7-1), we obtain

$$-\frac{dC_A}{dt} = k_A C_A^\alpha$$

Constant-volume batch reactor

After taking the natural logarithm of both sides of the above equation,

$$\ln \left(-\frac{dC_A}{dt} \right) = \ln k_A + \alpha \ln C_A \quad (7-11)$$

observe that the slope of a plot of $[\ln (-dC_A/dt)]$ as a function of $(\ln C_A)$ is the reaction order, α (see Figure 7-5).

Figure 7-5(a) shows a plot of $[-(dC_A/dt)]$ versus $[C_A]$ on log-log paper (or use Excel to make the plot) where the slope is equal to the reaction order α . The specific reaction rate, k_A , can be found by first choosing a concentration at a point on the plot, say C_{Ap} , and then finding the corresponding value of $[-(dC_A/dt)_p]$ on the line, as shown in Figure 7-5(b). The concentration point chosen, C_{Ap} , to find the *derivative* at C_{Ap} , need not be a data point; it just needs to be on the line. After raising C_{Ap} to the power α , we divide it into $[-(dC_A/dt)_p]$ to determine k_A

Plot $\ln \left(-\frac{dC_A}{dt} \right)$ versus $\ln C_A$ to find α and k_A .

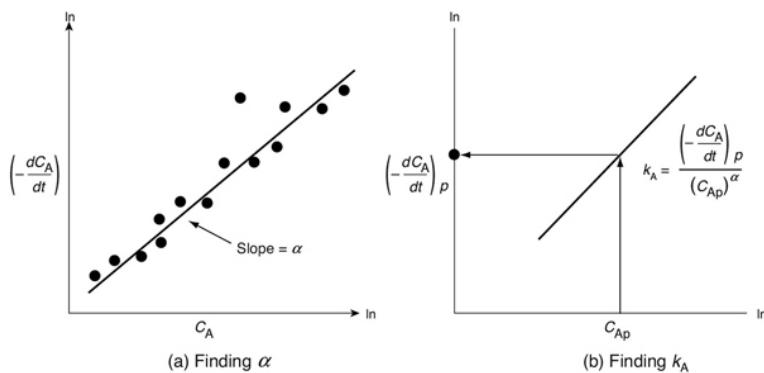


Figure 7-5 Differential method to determine reaction order.

$$k_A = \frac{-(dC_A/dt)_P}{(C_{Ap})^\alpha} \quad (7-12)$$

To obtain the derivative $(-dC_A/dt)$ used in this plot, we must differentiate the concentration–time data either numerically or graphically. Three methods to determine the derivative from data giving the concentration as a function of time are

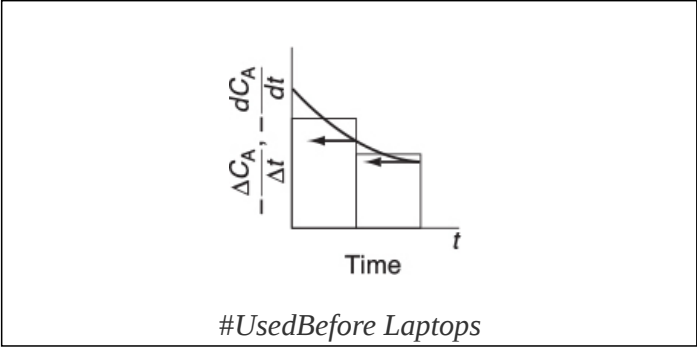
- Graphical differentiation
- Numerical differentiation formulas
- Differentiation of a polynomial fit to the data

Methods for finding $-\frac{dC_A}{dt}$ from concentration–time data

We shall only discuss the graphical and numerical methods.

7.4.1 Graphical Differentiation Method

This method is very old (from slide rule days—“What’s a slide rule, Grandfather?”), when compared with the numerous software packages. So why do we use it? Because with this method, disparities in the data are easily seen. Consequently, it is advantageous to use this technique to analyze the data before planning the next set of experiments. As explained in [Appendix A.2](#), the graphical method involves plotting $(-\Delta C_A/\Delta t)$ as a function of t and then using equal-area differentiation to obtain $(-dC_A/dt)$. An illustrative example is also given in [Appendix A.2](#).



In addition to the graphical technique used to differentiate the data, two other methods are commonly used: differentiation formulas and polynomial fitting.

See Appendix

7.4.2 Numerical Method

Numerical differentiation formulas can be used when the data points in the independent variable are *equally spaced*, such as $t_1 - t_0 = t_2 - t_1 = \Delta t$. (See Table 7-2.)

TABLE 7-2 RAW DATA

Time (min)	t_0	t_1	t_2	t_3	t_4	t_5
Concentration (mol/dm ³)	C A0	C A1	C A2	C A3	C A4	C A5

Raw Data

The three-point differentiation formulas¹ shown in Table 7-3 can be used to calculate dC_A/dt .

¹ B. Carnahan, H. A. Luther, and J. O. Wilkes, *Applied Numerical Methods*, New York: Wiley, 1969, p. 129.

TABLE 7-3 DIFFERENTIATION FORMULAS

Initial point:	$\left(\frac{dC_A}{dt}\right)_{t_0} = \frac{-3C_{A0} + 4C_{A1} - C_{A2}}{2\Delta t}$	(7-13)
Interior points:	$\left(\frac{dC_A}{dt}\right)_{t_i} = \frac{1}{2\Delta t} [C_{A(i+1)} - C_{A(i-1)}]$ $\left[e.g., \left(\frac{dC_A}{dt}\right)_{t_3} = \frac{1}{2\Delta t} [C_{A4} - C_{A2}] \right]$	(7-14)
Last point:	$\left(\frac{dC_A}{dt}\right)_{t_5} = \frac{1}{2\Delta t} [C_{A3} - 4C_{A4} + 3C_{A5}]$	(7-15)

Equations (7-13) and (7-15) are used for the first and last data points, respectively, while Equation (7-14) is used for all intermediate data points (see Step 5B in [Example 7-2](#)).

7.4.3 Finding the Rate-Law Parameters

Now, using either the graphical method, differentiation formulas, or the polynomial derivative, [Table 7-4](#) can be set up.

TABLE 7-4 PROCESSED DATA

Time	t_0	t_1	t_2	t_3
Concentration	C_{A0}	C_{A1}	C_{A2}	C_{A3}
Derivative	$(-\frac{dC_A}{dt})_0$	$(-\frac{dC_A}{dt})_1$	$(-\frac{dC_A}{dt})_2$	$(-\frac{dC_A}{dt})_3$

Processed data

The reaction order can now be found from a plot of $\ln(-dC_A/dt)$ as a function of $\ln C_A$, as shown in [Figure 7-5\(a\)](#),

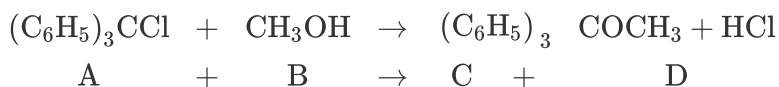
since

$$\ln \left(- \frac{dC_A}{dt} \right) = \ln k_A + \alpha \ln C_A \quad (7-16)$$

Before solving the following example problems, review the steps to determine the reaction-rate law from a set of data points (Table 7-1).

Example 7-2 Determining the Rate Law

The reaction of triphenyl methyl chloride (trityl) (A) and methanol (B) discussed in [Example 7-1](#) is now analyzed using the differential method.



The concentration–time data in [Table E7-2.1](#) was obtained in a batch reactor.

TABLE E7-2.1 RAW DATA

Time (min)	0	5	1	1	2	2	3
		0	0	5	0	5	0
			0	0	0	0	0
Concentration of A (mol/dm ³) × 10 ³ (At t = 0, C _A = 0.05 M)	5	3	3	2	2	1	1
	0	8	0	5	2	9	7
		
			6	6	2	5	4

The initial concentration of methanol was 0.5 mol/dm³.

Part (1) Determine the reaction order with respect to triphenyl methyl chloride.

Part (2) In a separate set of experiments, the reaction order wrt methanol was found to be first order. Determine the specific reaction-rate constant.

Solution

Part (1) Find the reaction order with respect to trityl.

Step 1 Postulate a rate law.

$$-r_A = kC_A^\alpha C_B^\beta \quad (\text{E7-2.1})$$

Step 2 Process your data in terms of the measured variable, which in this case is C_A .

Step 3 Look for simplifications. Because the concentration of methanol is 10 times the initial concentration of triphenyl methyl chloride, its concentration is essentially constant

$$C_B \cong C_{B0} \quad (\text{E7-2.2})$$

Substituting for C_B in Equation (E7-2.1)

$$-r_A = \underbrace{k C_{B0}^\beta}_{k'} C_A^\alpha$$

$$-r_A = k' C_A^\alpha \quad (\text{E7-2.3})$$

Step 4 Apply the CRE algorithm.

Mole Balance:

$$\frac{dN_A}{dt} = r_A V \quad (\text{E7-2.4})$$

Rate Law:

$$-r_A = k' C_A^\alpha \quad (\text{E7-2.3})$$

Stoichiometry: Liquid $V = V_0$

$$C_A = \frac{N_A}{V_0}$$



Combine: Mole balance, rate law, and stoichiometry

$$-\frac{dC_A}{dt} = k' C_A^\alpha \quad (\text{E7-2.5})$$

Evaluate: Taking the natural log of both sides of Equation (E7-2.5)

$$\ln \left[-\frac{dC_A}{dt} \right] = \ln k' + \alpha \ln C_A \quad (\text{E7-2.6})$$

The slope of a plot of $\ln \left[-\frac{dC_A}{dt} \right]$ versus $\ln C_A$ will yield the reaction order α with respect to triphenyl methyl chloride (A).

Step 5 Find $\left[-\frac{dC_A}{dt} \right]$ as a function of C_A from concentration–time data.

Step 5A Graphical Method. *#ForOldTimesSake.*

To see how this problem was solved in the 1960s, go to the [Chapter 7 Expanded Material](#) on the Web site.

Step 5B Finite Difference Method. As mentioned this technique helps identify disparities in the data, especially between successive measurements. We now show how to calculate (dC_A/dt) using the finite difference formulas (i.e., Equations (7-13)–(7-15)).

$$\begin{aligned}
t = 0 \left(\frac{dC_A}{dt} \right)_{t=0} &= \frac{-3C_{A0} + 4C_{A1} - C_{A2}}{2\Delta t} \\
&= \frac{[-3(50) + 4(38) - 30.6] \times 10^{-3}}{100} \\
&= -2.86 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min} \\
&- \frac{dC_A}{dt} \times 10^4 = 2.86 \text{ mol/dm}^3 \cdot \text{min} \\
t = 50 \left(\frac{dC_A}{dt} \right)_1 &= \frac{C_{A2} - C_{A0}}{2\Delta t} = \frac{(30.6 - 50) \times 10^{-3}}{100} \\
&= -1.94 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min} \\
t = 100 \left(\frac{dC_A}{dt} \right)_2 &= \frac{C_{A3} - C_{A1}}{2\Delta t} = \frac{(25.6 - 38) \times 10^{-3}}{100} \\
&= -1.24 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min} \\
t = 150 \left(\frac{dC_A}{dt} \right)_3 &= \frac{C_{A4} - C_{A2}}{2\Delta t} = \frac{(22.2 - 30.6) \times 10^{-3}}{100} \\
&= -0.84 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min} \\
t = 200 \left(\frac{dC_A}{dt} \right)_4 &= \frac{C_{A5} - C_{A3}}{2\Delta t} = \frac{(19.5 - 25.6) \times 10^{-3}}{100} \\
&= -0.61 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min} \\
t = 250 \left(\frac{dC_A}{dt} \right)_5 &= \left(\frac{C_{A6} - C_{A4}}{2\Delta t} = \frac{(17.4 - 22.2) \times 10^{-3}}{100} \right) \\
&= -0.48 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min} \\
t = 300 \left(\frac{dC_A}{dt} \right)_6 &= \frac{C_{A4} - 4C_{A5} + 3C_{A6}}{2\Delta t} = \frac{[22.2 - 4(19.5) + 3(17.4)] \times 10^{-3}}{100} \\
&= -0.36 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min}
\end{aligned}$$

1000) on log-log paper, as shown in Figure E7-2.1. We could also substitute the parameter values in Table E7-2.2 into Excel to find α and k' . Note that most of the points for both methods fall virtually on top of one another. This table is, in a way, redundant because it is not necessary to always find $(-dC_A/dt)$ by both techniques, graphical and finite difference.

TABLE E7-2.2 SUMMARY OF PROCESSED DATA

t (min)	<u>Graphical</u> $-\frac{dC_A}{dt} \times 10000$ (mol/dm ³ · min)	<u>Finite Difference</u> $-\frac{dC_A}{dt} \times 10000$ (mol/dm ³ · min)	$C_A \times 1000$ (mol/dm ³)
0	3.0	2.86	50
50	1.86	1.94	38
100	1.20	1.24	30.6
150	0.80	0.84	25.6
200	0.68	0.61	22.2
250	0.54	0.48	19.5
300	0.42	0.36	17.4

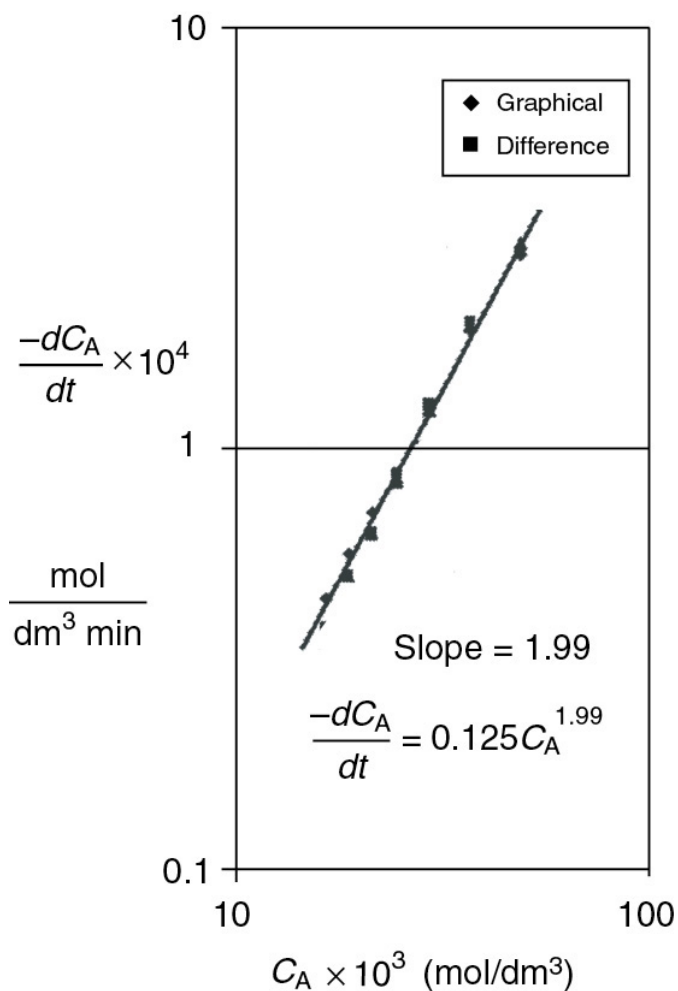


Figure E7-2.1 Excel plot to determine α and k .

#HowToImpress YourEmployer

From Figure E7-2.1, we found the slope to be 1.99, so that the reaction is said to be second order ($\alpha = 2.0$) with respect to triphenyl methyl chloride. Recall when the cycle lengths on the x-axis and the y-axis are the same on log-log paper, then we simply measure the slope with a ruler. However, with all the software on your computer it would be *more impressive to your professor or employer* if you typed the data into Excel or Polymath, or some other spreadsheet software, and then printed the results.

To evaluate k' , we can evaluate the derivative in Figure E7-2.1 at $C_{Ap} = 20 \times 10^{-3} \text{ mol/dm}^3$, which is

$$\left(-\frac{dC_A}{dt}\right)_p = 0.5 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min} \quad (\text{E7-2.7})$$

then

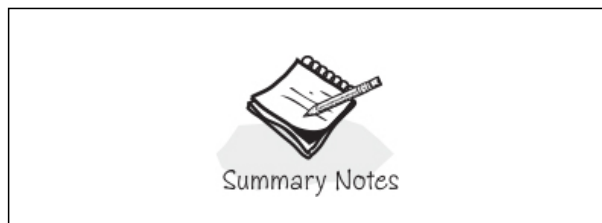
$$k' = \frac{\left(-\frac{dC_A}{dt}\right)_p}{C_{Ap}^2} \quad (\text{E7-2.8})$$

$$= \frac{0.5 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min}}{(20 \times 10^{-3} \text{ mol/dm}^3)^2} = 0.125 \text{ dm}^3/\text{mol} \cdot \text{min}$$

As will be shown in Section 7-5, we could also use nonlinear regression on Equation (E7-1.5) to find k'

$$k' = 0.122 \text{ dm}^3/\text{mol} \cdot \text{min} \quad (\text{E7-2.9})$$

The Excel graph shown in Figure E7-2.1 gives $\alpha = 1.99$ and $k' = 0.13 \text{ dm}^3/\text{mol} \cdot \text{min}$. We now set $\alpha = 2$ and regress again to find $k' = 0.122 \text{ dm}^3/\text{mol} \cdot \text{min}$.



ODE Regression. There are techniques and software becoming available whereby an ODE solver can be combined with a regression program to solve differential equations, such as

$$-\frac{dC_A}{dt} = k'_A C_A^\alpha \quad (\text{E7-2.5})$$

to find k'_A and α from concentration–time data.

Part (2) The reaction was said to be first order with respect to methanol, $\beta = 1$.

$$k' = C_{B0}^\beta k = C_{B0} k \quad (\text{E7-2.10})$$

Assuming C_{B0} is constant at 0.5 mol/dm^3 and solving for k yields²

$$k = \frac{k'}{C_{B0}} = \frac{0.122 \frac{\text{dm}^3}{\text{mol} \cdot \text{min}}}{0.5 \frac{\text{mol}}{\text{dm}^3}}$$

$$k = 0.244 (\text{dm}^3/\text{mol})^2/\text{min}$$

² M. Hoepfner and D. K. Roper, "Describing temperature increases in plasmon-resonant nanoparticle systems," *J. Therm. Anal. Calorim.*, 98(1), 197–202 (2009).

The rate law is

$$-r_A = \left[0.244 (\text{dm}^3/\text{mol})^2/\text{min} \right] C_A^2 C_B \quad (\text{E7-2.11})$$

Analysis: In this example, the differential method of data analysis was used to find the reaction order with respect to trityl ($\alpha = 1.99$) and the pseudo rate constant ($k' = 0.125 (\text{dm}^3/\text{mol})/\text{min}$). However, as we mentioned earlier it would probably be more impressive to your employer or professor if you typed the data into your computer and used a software package to find k . We discuss one such software package in [Section 7.5](#). The reaction order was rounded up to $\alpha = 2$ and the data was regressed again to obtain $k' = 0.122 (\text{dm}^3/\text{mol})/\text{min}$, again knowing k' and C_{B0} , and the true rate constant is $k = 0.244 (\text{dm}^3/\text{mol})^2/\text{min}$. We used two techniques to differentiate the concentration–time data to find $\left(\frac{dC_A}{dt}\right)$: the graphical technique and the finite difference technique.

By comparing the methods of analysis of the rate data presented in [Examples 7-1](#) and [7-2](#), we note that the differential method tends to accentuate the uncertainties in the data, while the integral method tends to smooth the data, thereby disguising the uncertainties in it. In most analyses, *it is imperative that the engineer know the limits and uncertainties in the data!!* This prior knowledge is necessary to provide for a safety factor when scaling up a process from laboratory experiments to design either a pilot plant or full-scale industrial plant.

Integral method normally used to find k when order is known

7.5 NONLINEAR REGRESSION

In nonlinear regression analysis, we search for those parameter values that minimize the sum of the squares of the differences between the measured values and the calculated values for *all* the data points. Not only can nonlinear regression find the best estimates of parameter values, it can also be used to discriminate between different rate-law models, such as the Langmuir-Hinshelwood models discussed in [Chapter 10](#).

Many software programs are available to find these parameter values so that all one has to do is enter the data. The Polymath software will be used to illustrate this technique. In order to carry out the search efficiently, in some cases one has to enter initial estimates of the parameter values close to the actual values. These estimates can be obtained using the linear-least-squares technique discussed on the CRE Web site *Professional Reference Shelf R7.3*

(<http://www.umich.edu/~elements/6e/07chap/pdf/leastsquares.pdf>).

Compare the calculated parameter value with the measured value.

We will now apply nonlinear regression to reaction-rate data to determine the rate-law parameters. Here, we make initial estimates of the parameter values (e.g., reaction order, specific rate constant) in order to *calculate* the concentration for each data point, C_{ic} , obtained by solving an integrated form of the combined mole balance and rate law. We then compare the *measured* concentration at that point, C_{im} , with the calculated value, C_{ic} , for the parameter values chosen. We make this comparison by calculating the sum of the squares of the differences at each point $\Sigma(C_{im} - C_{ic})^2$. We then continue to choose new parameter values and search for those values of the rate-law parameters that will minimize the sum of the squared differences of the measured concentrations, C_{im} , and the calculated concentrations values, C_{ic} . That is, we want to

find the rate-law parameters for which the sum of the squares of the difference at all data points, that is, $\sum (C_{im} - C_{ic})^2$ is a minimum. If we carried out N experiments, we would want to find the parameter values (e.g., E , activation energy, reaction orders) that minimize the quantity

$$\sigma^2 = \frac{s^2}{N-K} = \sum_{i=1}^N \frac{(C_{im} - C_{ic})^2}{N-K} \quad (7-17)$$

where

$$s^2 = \sum_{i=1}^{i=N} (C_{im} - C_{ic})^2$$

N = number of runs

K = number of parameters to be determined

C_{im} = measured concentration rate for run i

C_{ic} = calculated concentration rate for run i

One notes that if we minimize S^2 in Equation (7-17), we minimize σ^2 .

To illustrate this technique, let's consider the reaction



for which we want to learn the reaction order, α , and the specific reaction rate, k ,

$$-r_A = kC_A^\alpha$$

The reaction rate will be measured at a number of different concentrations. We now choose (guess) values of α and k , and calculate the concentration (C_{ic}) at each point, i , that the concentration was measured experimentally. We then subtract the calculated value (C_{ic}) from the measured value (C_{im}), square the result, and find the sum the squares for all the runs for the values of k and α that we have chosen.

This procedure is continued by further varying α and k until we find those values of k and α that minimize the sum of the squares. Many well-known searching techniques are available to obtain the minimum value σ_{\min}^2 .³ Figure 7-6 shows a hypothetical plot of the sum of the squares as a function of the parameters α and k :

$$\sigma^2 = f(k, \alpha) \quad (7-18)$$

³ (a) University of Michigan colleagues B. Carnahan and J. O. Wilkes, *Digital Computing and Numerical Methods*, New York: Wiley, 1973, p. 405. (b) D. J. Wilde and C. S. Beightler, *Foundations of Optimization*, 2nd ed. Upper Saddle River, NJ: Pearson, 1979. (c) D. Miller and M. Frenklach, *Int. J. Chem. Kinet.*, 15, 677 (1983).

Look at the top circle. We see that there are many combinations of α and k (e.g., $\alpha = 2.2$, $k = 4.8$ or $\alpha = 1.8$, $k = 5.3$) that will give a value of $\sigma^2 = 57$. The same is true for $\sigma^2 = 1.85$. We need to find the combination of α and k that gives the lowest value of σ^2 .

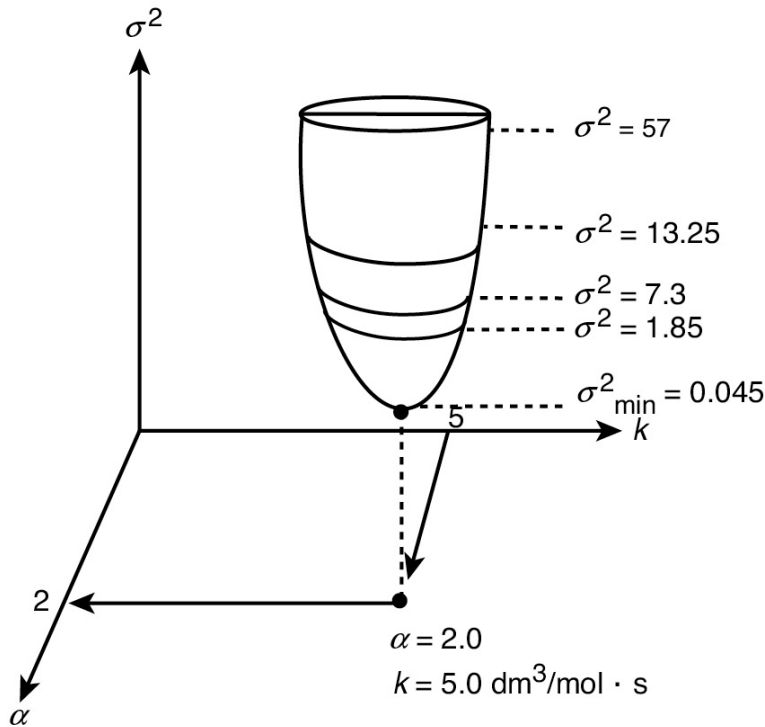


Figure 7-6 Minimum sum of squares.

In searching to find the parameter values that give the minimum of the sum of squares σ^2 , one can use a number of optimization techniques or software packages. The computerized searching procedure begins by guessing parameter values and then calculating $(C_{im} - C_{ic})$ and then σ^2 for these values. Next, a few sets of parameters are chosen around the initial guess, and σ^2 is calculated for these sets as well. The search technique looks for the smallest value of σ^2 in the vicinity of the initial guess and then proceeds along a trajectory in the direction of decreasing σ^2 to choose the next set of different parameter values and determine the corresponding σ^2 as shown as a contour plot in Figure 7-7. Starting at $\alpha = 1$ and $k = 1$, the trajectory, shown by the arrows, is continually adjusted by choosing α and k . We see in Figure 7-7 that the trajectory leads us to a minimum value of $\sigma^2 = 0.045 \text{ (mol/dm}^3\text{)}^2$ at which point $\alpha = 2$ and $k = 5 \text{ (dm}^3\text{/mol)}$.

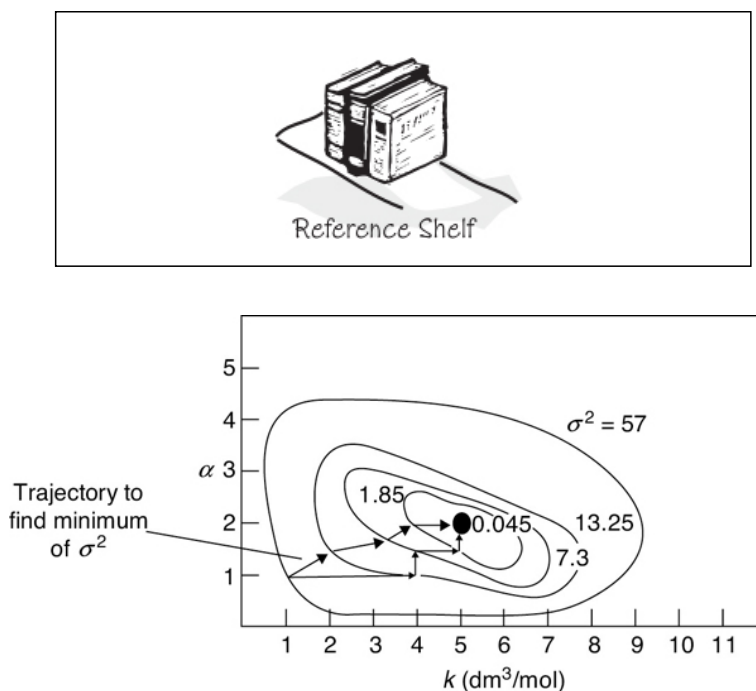


Figure 7-7 Trajectory to find the best values of k and α .

If the equations are highly nonlinear, your initial guesses of α and k are very important. A number of software packages are available to carry out the procedure to determine the best estimates of the parameter values and the corresponding confidence limits. All we have to do is to (1) enter the experimental values into the computer, (2) specify the model, (3) enter the initial guesses of the parameters, then (4) push the “compute” button, and (5) view the best estimates of the parameter values along with 95% confidence limits. If the confidence limits for a given parameter are larger than the parameter itself, the parameter is probably not significant and should be dropped from the model as demonstrated in [Chapter 10, Example 10-3](#). If all the model parameters are smaller than the confidence limits, that model should be eliminated and a new model equation chosen. The software is run again to analyze the new model.

7.5.1 Concentration–Time Data

We will now use nonlinear regression to determine the rate-law parameters from concentration–time data obtained in batch experiments. We recall that the combined rate-law

stoichiometry mole balance for a constant-volume batch reactor is

$$\frac{dC_A}{dt} = -kC_A^\alpha \quad (7-19)$$

We now integrate Equation (7-6) for the case $\alpha \neq 1$ to give

$$C_{A0}^{1-\alpha} - C_A^{1-\alpha} = (1-\alpha)kt$$

Rearranging to obtain the concentration as a function of time, we obtain

$$C_A = \left[C_{A0}^{1-\alpha} - (1-\alpha)kt \right]^{1/(1-\alpha)} \quad (7-20)$$

Now we could use either Polymath or MATLAB to find the values of α and k that would minimize the sum of squares of the differences between the measured concentrations, C_{Aim} , and calculated concentrations, C_{Aic} . That is, for N data points,

$$s^2 = \sum_{i=1}^N (C_{Aim} - C_{Aic})^2 = \sum_{i=1}^N \left[C_{Aim} - \left[C_{A0}^{1-\alpha} - (1-\alpha)kt_i \right]^{1/(1-\alpha)} \right]^2 \quad (7-21)$$

we want the values of α and k that will make s^2 a minimum.

If Polymath is used, one should use the absolute value, *abs*, for the term in brackets in Equation (7-21), that is,

$$s^2 = \sum_{i=1}^n \left[C_{Aim} - \left\{ \text{abs} \left[C_{A0}^{1-\alpha} - (1-\alpha)kt_i \right] \right\}^{1/(1-\alpha)} \right]^2 \quad (7-22)$$

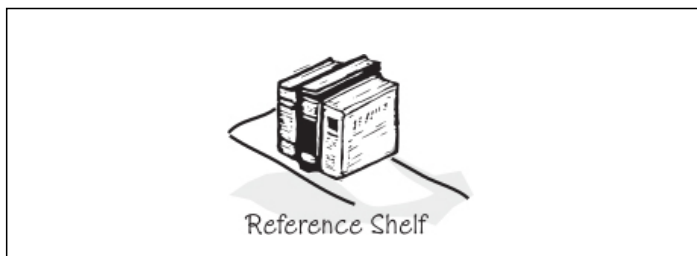
Another, and perhaps easier, way to solve for the parameter values is to use time rather than concentrations, rearranging Equation (7-20) to get

$$t_c = \frac{C_{A0}^{1-\alpha} - C_A^{1-\alpha}}{k(1-\alpha)} \quad (7-23)$$

That is, we find the values of k and α that minimize

$$s^2 = \sum_{i=1}^N (t_{im} - t_{ic})^2 = \sum_{i=1}^N \left[t_{im} - \frac{C_{A0}^{1-\alpha} - C_{Ai}^{1-\alpha}}{k(1-\alpha)} \right]^2 \quad (7-24)$$

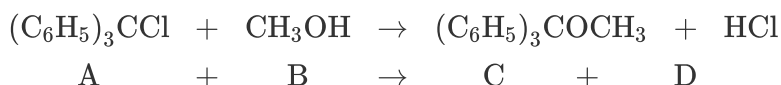
Finally, a discussion of *weighted least squares* as applied to a first-order reaction is provided in the *Professional Reference Shelf R7.4* on the CRE Web site.



Example 7-3 Use of Regression to Find the Rate-Law Parameters[†]

[†] See tutorial at <http://www.umich.edu/~elements/6e/07chap/live.html> and http://www.umich.edu/~elements/6e/07chap/Example_7-3_Polymath_nonlinear_regression_tutorial.pdf.

We shall use the reaction and data in Examples E7-1 and E7-2 to illustrate how to use regression to find α and k' .



The Polymath regression program is included on the CRE Web site. Recalling Equation (E7-2.5)

$$-\frac{dC_A}{dt} = k' C_A^\alpha \quad (\text{E7-2.3})$$

and integrating with the initial condition when $t = 0$ and $C_A = C_{A0}$ for $\alpha \neq 1.0$

$$t = \frac{1}{k'} \frac{C_{A0}^{(1-\alpha)} - C_A^{(1-\alpha)}}{(1-\alpha)} \quad (\text{E7-3.1})$$

Given or assuming k' and α , Equation (E7-2.5) can be solved (cf. Equation E7-3.1) to calculate the time t to reach a concentration C_A , or, alternatively we could calculate the concentration C_A at time t . We can proceed two ways from this point, both of which will give the same result. We can search for the combination α and k that minimizes $[\sigma^2 = \Sigma(t_{im} - t_{ic})^2]$, or we could solve Equation (E7-3.1) for C_A and find α and k that minimize $[\sigma^2 = \Sigma(C_{Aim} - C_{Aic})^2]$.

We shall choose the former. So, substituting for the initial concentration $C_{A0} = 0.05 \text{ mol/dm}^3$ into Equation (E7-3.1)

$$t = \frac{1}{k'} \frac{(0.05)^{(1-\alpha)} - C_A^{(1-\alpha)}}{(1-\alpha)} \quad (\text{E7-3.2})$$

For $C_{A0} = 0.05 \text{ mol/dm}^3$, that is, Equation (E7-3.1) becomes

$$t_c = \frac{1}{k'} \frac{(0.05)^{(1-\alpha)} - C_A^{(1-\alpha)}}{(1-\alpha)} \quad (\text{E7-3.3})$$

We want to minimize s^2 to give α and k' .

$$s^2 = \sum_{i=1}^N (t_{im} - t_{ic})^2 = \sum_{i=1}^N \left[t_{im} - \frac{0.05^{(1-\alpha)} - C_{Aic}^{(1-\alpha)}}{k'(1-\alpha)} \right]^2 \quad (7-25)$$

We shall carry out a first regression to find approximate values of α and k . Next, we use a common procedure, which is to round α off to an integer and then carry out a second regression to find the best value of k after α has been set equal to an integer.

TABLE E7-3.1 RESULTS OF 1ST REGRESSION

POLYMATH Results

Example 7-3.1 Use of Regression to Find Rate Law Parameters 08-05-2004

Nonlinear regression (L-M)**Model:** $t = (.05^{(1-a)} - Ca^{(1-a)}) / (k^{(1-a)})$

Variable	Ini guess	Value	95% confidence
a	3	2.04472	0.0317031
k	0.1	0.1467193	0.0164118

Nonlinear regression settings
Max # iterations = 64

Precision
 R^2 = 0.9999717
 R^2_{adj} = 0.999966
Rmsd = 0.2011604
Variance = 0.3965618

TABLE E7-3.2 RESULTS OF 2ND REGRESSION WITH $\alpha =$
2

POLYMATH Results

Example 7-3.2 Use of Regression to Find Rate Law Parameters 08-05-2004

Nonlinear regression (L-M)**Model:** $t = (.05^{(1-2)} - Ca^{(1-2)}) / (k^{(1-2)})$

Variable	Ini guess	Value	95% confidence
k	0.1	0.1253404	7.022E-04

Nonlinear regression settings
Max # iterations = 64

Precision
 R^2 = 0.9998978
 R^2_{adj} = 0.9998978
Rmsd = 0.3821581
Variance = 1.1926993

The results shown are

$\alpha = 2.04$:	$\alpha = 2.0$
$k' = 0.147 \text{ dm}^3/\text{mol} \cdot \text{min}$:	$k' = 0.125 \text{ dm}^3/\text{mol} \cdot \text{min}$

The first regression gives $\alpha = 2.04$, as shown in Table E7-3.1. We shall round off α to make the reaction

second order, (i.e., $\alpha = 2.00$). Now having fixed α at 2.0, we must do *another* regression (cf. [Table E7-3.2](#)) on k' because the k' given in [Table E.7-3.1](#) is for $\alpha = 2.04$. We now regress the equation

$$t = \frac{1}{k'} \left[\frac{1}{C_A} - \frac{1}{C_{A0}} \right]$$

The second regression gives $k' = 0.125 \text{ dm}^3/\text{mol} \cdot \text{min}$. We now calculate k

$$k = \frac{k'}{C_{A0}} = \frac{0.125 (\text{dm}^3/\text{mol})}{0.5 (\text{dm}^3/\text{mol})_{\min}} = 0.25 \left(\frac{\text{dm}^3}{\text{mol}} \right)^2 / \text{min}$$

Analysis: In this example, we showed how to use nonlinear regression to find k' and α . The first regression gave $\alpha = 2.04$, which we rounded to 2.00 and then regressed again for the best value of k' for $\alpha = 2.0$, which was $k' = 0.125 (\text{dm}^3/\text{mol})/\text{min}$ giving a value of the true specific reaction rate of $k = 0.25 (\text{dm}^3/\text{mol})^2/\text{min}$. We note that the reaction order is the same as that in [Examples 7-1](#) and [7-2](#); however, the value of k is about 8% larger. The r^2 and other statistics can be found in Polymath's output.

7.5.2 Model Discrimination

One can also determine which model or equation best fits the experimental data by comparing the sums of the squares for each model and then choosing the equation with a smaller sum of squares and/or carrying out an F-test. Alternatively, we can compare the residual plots for each model. These plots show the error associated with each data point, and one looks to see whether the error is randomly distributed or whether there is a trend in the error. When the error is randomly distributed, this is an additional indication that the correct rate law has been chosen. An example of model discrimination using nonlinear regression is given in [Chapter 10, Example 10-3](#).

7.6 REACTION-RATE DATA FROM DIFFERENTIAL REACTORS

Data acquisition using the method of initial rates and a differential reactor is similar in that the rate of reaction is determined for a specified number of predetermined initial or entering reactant concentrations. A differential reactor (PBR) is normally used to determine the rate of reaction as a function of either concentration or partial pressure. It consists of a tube containing a very small amount of catalyst, usually arranged in the form of a thin wafer or disk. A typical arrangement is shown schematically in Figure 7-8. The criterion for a reactor being differential is that the conversion of the reactants in the bed is extremely small, as is the change in temperature and reactant concentration through the bed. As a result, the reactant concentration through the reactor is essentially constant and approximately equal to the inlet concentration. That is, the reactor is considered to be gradientless,⁴ and the reaction rate is considered spatially uniform within the bed.

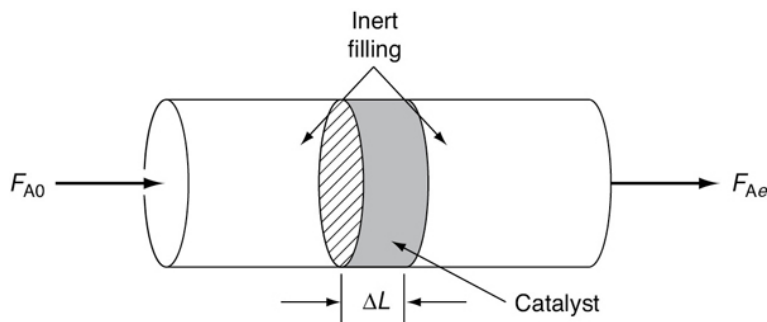


Figure 7-8 Differential reactor.

⁴ B. Anderson, ed., *Experimental Methods in Catalytic Research*, San Diego, CA: Academic Press.

Most commonly used catalytic reactor to obtain experimental data

The differential reactor is relatively easy to construct at a low cost. Owing to the low conversion achieved in this reactor, the heat release per unit volume will be small (or can be made small by diluting the bed with inert solids) so that the reactor operates essentially in an isothermal manner. When operating this reactor, precautions must be taken so that the reactant gas or liquid does not bypass or channel through the packed catalyst, but instead flows uniformly across the catalyst. If the

catalyst under investigation decays rapidly, as discussed in [Chapter 10](#), the differential reactor is not a good choice because the reaction-rate parameters at the start of a run will be different from those at the end of the run. In some cases, sampling and analysis of the product stream may be difficult for small conversions in multicomponent systems.

Limitations of the differential reactor

The differential reactor is operated at steady state.

For the reaction of species A going to product (P)



the volumetric flow rate through the catalyst bed is monitored, as are the entering and exiting concentrations ([Figure 7-9](#)).

Therefore, if the weight of catalyst, ΔW , is known, the rate of reaction per unit mass of catalyst, $-r'_A$, can be calculated.

Since the differential reactor is assumed to be *gradientless*, the design equation will be similar to the CSTR design equation.

A steady-state mole balance on reactant A gives

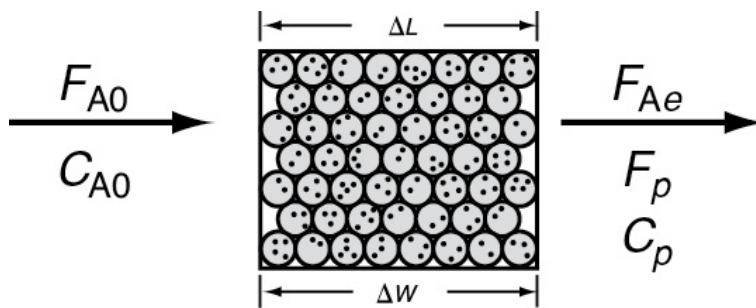


Figure 7-9 Differential catalyst bed.

$$\begin{array}{rclcl}
 \left[\begin{array}{c} \text{Flow} \\ \text{rate} \\ \text{in} \end{array} \right] & - & \left[\begin{array}{c} \text{Flow} \\ \text{rate} \\ \text{out} \end{array} \right] & + & \left[\begin{array}{c} \text{Rate of} \\ \text{generation} \end{array} \right] & = & \left[\begin{array}{c} \text{Rate of} \\ \text{accumulation} \end{array} \right] \\
 [F_{A0}] & - & [F_{Ae}] & + & \left[\left(\frac{\text{Rate of reaction}}{\text{Mass of catalyst}} \right) (\text{Mass of catalyst}) \right] & = & 0 \\
 F_{A0} & - & F_{Ae} & + & (r'_A) (\Delta W) & = & 0
 \end{array}$$

The subscript e refers to the *exit* of the reactor. Solving for $-r'_A$, we have

$$-r'_A = \frac{F_{A0} - F_{Ae}}{\Delta W} \quad (7-26)$$

The mole balance equation can also be written in terms of concentration

$$-r'_A = \frac{v_0 C_{A0} - v C_{Ae}}{\Delta W} \quad (7-27)$$

Differential reactor design equation

or in terms of conversion or product flow rate F_P

$$-r'_A = \frac{F_{A0}X}{\Delta W} = \frac{F_P}{\Delta W} \quad (7-28)$$

The term $F_{A0}X$ gives the rate of formation of product, F_P , when the stoichio-metric coefficients of A and of P are identical. Adjustments to Equation (7-28) must be made when this is not the case.

For constant volumetric flow, Equation (7-28) reduces to

$$-r'_A = \frac{v_0(C_{A0} - C_{Ae})}{\Delta W} = \frac{v_0 C_P}{\Delta W} \quad (7-29)$$

Consequently, we see that the reaction rate, $-r'_A$, can be determined by measuring the product concentration, C_P .

By using very little catalyst and large volumetric flow rates, the concentration difference, $(C_{A0} - C_{Ae})$, can be made quite small. The rate of reaction determined from Equation (7-29) can be obtained as a *function* of the reactant concentration in the catalyst bed, C_{Ab}

$$-r'_A = -r'_A(C_{Ab}) \quad (7-30)$$

by varying the inlet concentration. One approximation of the concentration of A within the bed, C_{Ab} , would be the arithmetic mean of the inlet and outlet concentrations

$$C_{Ab} = \frac{C_{A0} + C_{Ae}}{2} \quad (7-31)$$

However, since very little reaction takes place within the bed, the bed concentration is essentially equal to the inlet concentration

$$C_{Ab} \approx C_{A0}$$

so $-r'_A$ is a function of C_{A0}

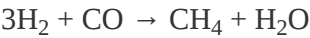
$$-r'_A = -r'_A(C_{A0}) \quad (7-32)$$



As with the method of initial rates (see the CRE Web site, http://www.umich.edu/~elements/6e/software/nonlinear_regression_tutorial.pdf), we find $-r_{A0}$ as a function of C_{A0} and then use various numerical and graphical techniques to determine the appropriate algebraic equation for the rate law. When collecting data for fluid–solid reacting systems, care must be taken that we use high flow rates through the differential reactor and small catalyst particle sizes in order to avoid mass transfer–limitations. If data show the reaction to be first order with a low activation energy, say 8 kcal/mol, one should suspect the data are being collected in the mass transfer–limited regime. We will expand on mass transfer–limitations and how to avoid them in Chapter 10, and also in Chapters 14 and 15.

Example 7–4 Using a Differential Reactor to Obtain Catalytic Rate Data

The formation of methane from carbon monoxide and hydrogen using a nickel catalyst was studied by Pursley.⁵ The reaction



⁵ J. A. Pursley, “An investigation of the reaction between carbon monoxide and hydrogen on a nickel catalyst above one atmosphere,” Ph.D. thesis, University of Michigan.

was carried out at 500°F in a differential reactor where the effluent concentration of methane was measured. The raw data is shown in Table E7-4.1.

TABLE E7-4.1 RAW DATA

R u n	P _{CO} (atm)	P _{H₂} (atm)	C _{CH₄} (mol/dm ³)
1	1	1	1.73 × 10 ^{−4}
2	.8	1	4.40 × 10 ^{−4}
3	.4	1	10.0 × 10 ^{−4}
4	.0	0	1.65 × 10 ^{−4}
5	.0	0	2.47 × 10 ^{−4}
6	.0	4	1.75 × 10 ^{−4}

P_{H_2} is constant in Runs 1, 2, 3.

P_{CO} is constant in Runs 4, 5, 6.

The exit volumetric flow rate from a differential packed bed containing 10 g of catalyst was maintained at $S_0 = 300 \text{ dm}^3/\text{min}$ for each run. The partial pressures of H_2 and CO were determined at the entrance to the reactor, and the methane concentration was measured at the reactor exit.

Determine the rate law and rate-law parameters. To better understand how we will determine the rate law and its parameters, we will break the solution into three parts, **(a)**, **(b)**, and **(c)**, as shown below.

- 1. Relate the rate of reaction to the exit methane concentration.** The reaction-rate law is assumed to be the product of a function of the partial pressure of CO , $f(\text{CO})$, and a function of the partial pressure of H_2 , $g(\text{H}_2)$, that is,

$$r'_{\text{CH}_4} = f(\text{CO}) \cdot g(\text{H}_2) \quad (\text{E7-4.1})$$

- 2. Determine the rate-law dependence on carbon monoxide,** using the data generated in part **(a)**. Assume that the functional dependence of r'_{CH_4} on P_{CO} is of the form

$$r'_{\text{CH}_4} \sim P_{\text{CO}}^\alpha \quad (\text{E7-4.2})$$

- 3. Generate a table of the reaction rate as a function of partial pressures** of carbon monoxide and hydrogen, and then determine the rate-law dependence on H_2 .

Solution

(a) Calculate the Rates of Reaction. In this example the product composition, rather than the reactant concentration, is being monitored. The term $(-r'_{\text{CO}})$ can be written in terms of the flow rate of methane from the reaction

$$-r'_{\text{CO}} = r'_{\text{CH}_4} = \frac{F_{\text{CH}_4}}{\Delta W}$$

Substituting for F_{CH_4} in terms of the volumetric flow rate and the concentration of methane gives

$$r'_{\text{CH}_4} = \frac{v_0 C_{\text{CH}_4}}{\Delta W} \quad (\text{E7-4.3})$$

Since v_0 , C_{CH_4} , and ΔW are known for each run, we can calculate the rate of reaction.

For run 1

$$r'_{\text{CH}_4} = \left(\frac{300 \text{ dm}^3}{\text{min}} \right) \frac{1.73 \times 10^{-4} \text{ mol/dm}^3}{10 \text{ g-cat}} = 5.2 \times 10^{-3} \frac{\text{mol CH}_4}{\text{g-cat} \times \text{min}}$$

The rate for runs 2 through 6 can be calculated in a similar manner (Table E7-4.2).

TABLE E7-4.2 RAW AND CALCULATED DATA

R u n m	P_C o (atm)	P_{H_2} (atm)	C_{CH_4} (mol/dm^3)	r'_{CH_4} $(\frac{\text{mol CH}_4}{\text{g-cat} \cdot \text{min}})$	$(\frac{\text{mol CH}_4}{\text{g-cat} \cdot \text{min}})$
1	1.00	1.00	1.73 $\times 10^{-4}$	5.2 $\times 10^{-3}$	
2	1.08	1.00	4.40 $\times 10^{-4}$	13.2 $\times 10^{-3}$	
3	4.08	1.00	10.0 $\times 10^{-4}$	30.0 $\times 10^{-3}$	
4	1.00	0.01	1.65 $\times 10^{-4}$	4.95 $\times 10^{-3}$	
5	1.00	0.05	2.47 $\times 10^{-4}$	7.42 $\times 10^{-3}$	
6	1.00	0.04	1.75 $\times 10^{-4}$	5.25 $\times 10^{-3}$	

0

(b) Determining the Rate-Law Dependence in CO.

For constant hydrogen concentration (runs 1, 2, and 3), the rate law

$$r'_{\text{CH}_4} = \overbrace{k g(P_{\text{H}_2})}^{k'} p_{\text{CO}}^\alpha$$

can be written as

$$r'_{\text{CH}_4} = k' P_{\text{CO}}^\alpha \quad (\text{E7-4.4})$$

Taking the natural log of Equation (E7-4.4) gives us

$$\ln(r'_{\text{CH}_4}) = \ln k' + \alpha \ln P_{\text{CO}}$$

We now plot $\ln(r'_{\text{CH}_4})$ versus $\ln P_{\text{CO}}$ using runs 1, 2, and 3, for which H_2 the concentration is constant, in Figure E7-4.1. We see from the Excel plot that $\alpha = 1.22$.

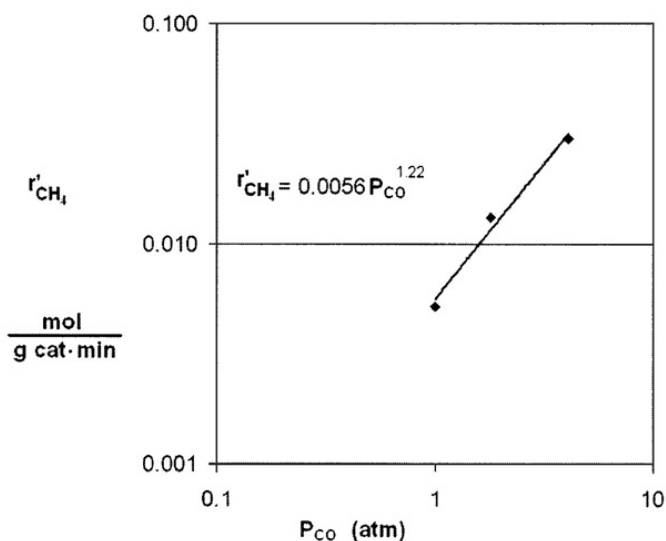


Figure E7-4.1 Reaction rate as a function of concentration.

Had we not been so pressed for time and included more points, we would have found that the reaction is essentially first order with $\alpha = 1$, that is

$$-r'_{\text{CO}} = k' P_{\text{CO}} \quad (\text{E7-4.5})$$

If we had used more data (not given here) we would have found $\alpha = 1$.

From the first three data points in Table E7-4.2 where the partial pressure of H_2 is constant, we see the rate is linear in partial pressure of CO

$$r'_{\text{CH}_4} = k' P_{\text{CO}} \cdot g(\text{H}_2)$$

Now let's look at the hydrogen dependence.

(c) Determining the Rate-Law Dependence on H_2 . It will not be intuitively obvious how to do this analysis until you have studied Chapter 10 where we have rate laws with concentrations or partial pressures in both the numerator **and** denominator of the rate law. From Table E7-4.2 it appears that the dependence of r'_{CH_4} on P_{H_2} cannot be represented by a power law. Comparing run 4 with run 5 and then run 5 with run 6, we see that the reaction rate first increases with increasing partial pressure of hydrogen, and subsequently decreases with increasing P_{H_2} . That is, there appears to be a concentration of hydrogen at which the rate is maximum. One set of rate laws that is consistent with these observations is:

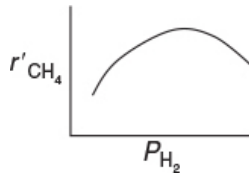
1. At low H_2 concentrations where r'_{CH_4} increases as P_{H_2} increases, the rate law may be of the form

$$r'_{\text{CH}_4} \sim P_{\text{H}_2}^{\beta_1} \quad (\text{E7-4.6})$$

2. At high H_2 concentrations where r'_{CH_4} decreases as P_{H_2} increases, the rate law may be of the form

$$r'_{\text{CH}_4} \sim \frac{1}{P_{\text{H}_2}^{\beta_2}} \quad (\text{E7-4.7})$$

Sketch of r'_{CH_4} as a function of P_{H_2}



We would like to find one rate law that is consistent with reaction-rate data at both high and low hydrogen concentrations. After we have studied heterogeneous reactions in [Chapter 10](#), we would recognize that Equations (E7-4.6) and (E7-4.7) can be combined into the form

$$r'_{\text{CH}_4} \sim \frac{P_{\text{H}_2}^{\beta_1}}{1 + bP_{\text{H}_2}^{\beta_2}} \quad (\text{E7-4.8})$$

We will see in [Chapter 10](#) that this combination and similar rate laws that have reactant concentrations (or partial pressures) in the numerator and denominator are common in *heterogeneous catalysis*.

Let's see if the resulting rate law (E7-4.8) is qualitatively consistent with the rate observed.

1. *For condition 1:* At low P_{H_2} , $[b(P_{\text{H}_2})^{\beta_2} \ll 1]$ and Equation (E7-4.8) reduces to

$$r'_{\text{CH}_4} \sim P_{\text{H}_2}^{\beta_1} \quad (\text{E7-4.9})$$

Equation (E7-4.9) is consistent with the trend in comparing runs 4 and 5.

2. *For condition 2:* At high P_{H_2} , $[b(P_{\text{H}_2})^{\beta_2} \gg 1]$ and Equation (E7-4.8) reduces to

$$r'_{\text{CH}_4} \sim \frac{(P_{\text{H}_2})^{\beta_1}}{(P_{\text{H}_2})^{\beta_2}} \sim \frac{1}{(P_{\text{H}_2})^{\beta_2 - \beta_1}} \quad (\text{E7-4.10})$$

where $\beta_2 > \beta_1$. Equation (E7-4.10) is consistent with the trends in comparing runs 5 and 6.

Combining Equations (E7-4.8) and (E7-4.5)

$$r'_{\text{CH}_4} = \frac{aP_{\text{CO}}P_{\text{H}_2}^{\beta_1}}{1+bP_{\text{H}_2}^{\beta_2}} \quad (\text{E7-4.11})$$

Typical form of the rate law for heterogeneous catalysis

We now use the Polymath regression program to find the parameter values a , b , β_1 , and β_2 . The results are shown in Table E7-4.3.

The corresponding rate law is

$$r'_{\text{CH}_4} = \frac{0.025P_{\text{CO}}P_{\text{H}_2}^{0.61}}{1+2.49P_{\text{H}_2}} \quad (\text{E7-4.12})$$

TABLE E7-4.3 FIRST REGRESSION

POLYMATH Results			
No Title 01-31-2004			
Nonlinear regression (L-M)			
Model: Rate = a*Pco*Ph2^beta1/(1+b*Ph2^beta2)			
Variable	Ini guess	Value	95% confidence
a	1	0.0252715	0.4917749
beta1	1	0.6166542	6.9023286
b	1	2.4872569	68.002944
beta2	1	1.0262047	3.2344414
Nonlinear regression settings			
Max # iterations = 64			



Summary Notes

Polymath and Excel regression tutorials are given in the [Chapter 7 Summary Notes](#) on the [CRE Web site](#).

We could use the rate law given by Equation (E7-4.12) as is, but there are only six data points, and we should

be concerned about extrapolating the rate law over a wider range of partial pressures. We could take more data, and/or we could carry out a theoretical analysis of the type discussed in Chapter 10 for heterogeneous reactions. If we assume hydrogen undergoes dissociative adsorption on the catalyst surface (cf. Figure 10-11), we would expect a dependence on the partial pressure of hydrogen to be to the $\frac{1}{2}$ power. Because 0.61 is close to 0.5, we are going to regress the data again, setting $\beta_1 = \frac{1}{2}$ and $\beta_2 = 1.0$. The results are shown in Table E7-4.4.

TABLE E7-4.4 SECOND REGRESSION

POLYMATH Results				
No Title 01-31-2004				
Nonlinear regression (L-M)				
Model: Rate = $a \cdot P_{CO} \cdot P_{H_2}^{0.5} / (1 + b \cdot P_{H_2})$				
Variable	Ini guess	Value	95% confidence	
a	1	0.018059	0.0106293	
b	1	1.4898245	1.4787491	

After studying the heterogeneous rate laws in Chapter 10, we will become more adept at postulating and analyzing this type of data for heterogeneous reactions.

Note: A complete tutorial of how to enter this example into Polymath can be found on the Web site at http://www.umich.edu/~elements/6e/software/nonlinear_regression_tutorial.pdf.

The rate law is now

$$r'_{CH_4} = \frac{0.018 P_{CO} P_{H_2}^{1/2}}{1 + 1.49 P_{H_2}}$$

where r'_{CH_4} is in (mol/g-cat · s) and the partial pressures are in (atm).

We could also have set $\beta_1 = 1/2$ and $\beta_2 = 1.0$ and rearranged Equation (E7-4.11) in the form

$$\frac{P_{\text{CO}} P_{\text{H}_2}^{1/2}}{r'_{\text{CH}_4}} = \frac{1}{a} + \frac{b}{a} P_{\text{H}_2} \quad (\text{E7-4.13})$$

Linearizing the rate law to determine the rate-law parameters

A plot of $P_{\text{CO}} P_{\text{H}_2}^{1/2} / r'_{\text{CH}_4}$ as a function of P_{H_2} should be a straight line with an intercept of $1/a$ and a slope of b/a . From the plot in Figure E7-4.2, we see that the rate law is indeed consistent with the rate-law data.

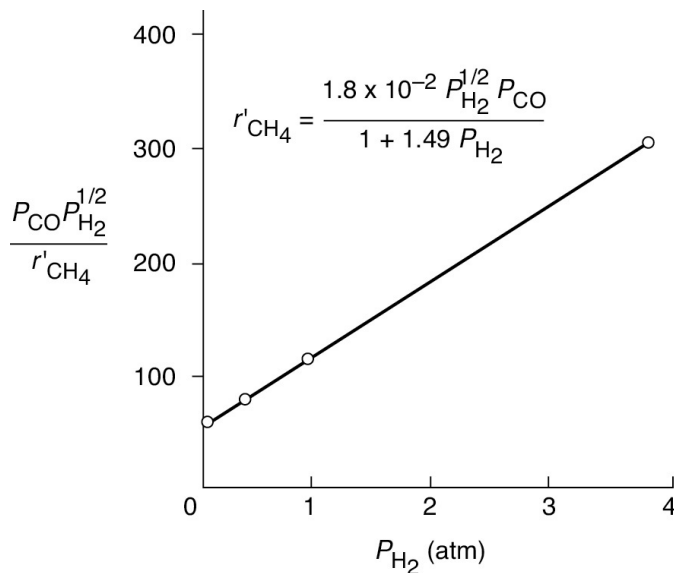


Figure E7-4.2 Linearized plot of data.

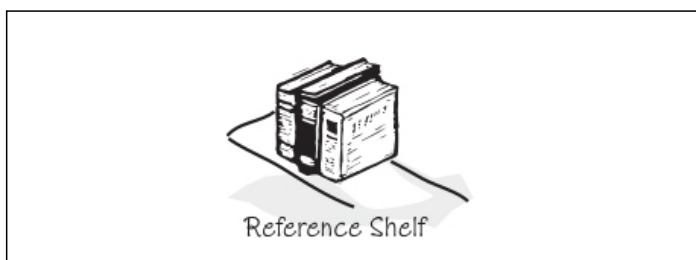
Analysis: The reaction-rate data in this example were obtained at steady state, and as a result, neither the integral method nor differential method of analysis can be used. One of the purposes of this example is to show how to reason out the form of the rate law and to then use regression to determine the rate-law parameters. Once the parameters were obtained, we

showed how to linearize the rate-law (e.g., Equation (E7-4.13)) to generate a single plot of all the data, Figure (E7-4.2).

7.7 EXPERIMENTAL PLANNING

Four to six weeks in the lab can save you an hour in the library.

—G. C. Quarderer, Retired from Dow Chemical Co.



So far, this chapter has presented various methods of analyzing rate data. It is just as important to know in which circumstances to use each method as it is to know the mechanics of these methods. In the Expanded Material and in the *Professional Reference Shelf* (<http://www.umich.edu/~elements/6e/07chap/prof-7-5.html>) on the CRE Web site, we give a thumbnail sketch of a heuristic to plan experiments to generate the data necessary for reactor design. However, for a more thorough discussion, the reader is referred to the books and articles by Box and Hunter.⁶

⁶ G. E. P. Box, W. G. Hunter, and J. S. Hunter, *Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building*, New York: Wiley, 1978.

7.8 AND NOW... A WORD FROM OUR SPONSOR—SAFETY 7 (AWFOS—S7 LABORATORY SAFETY)

This chapter focused on obtaining and analyzing experimental data that is collected safely in both academia and industrial laboratories. To help promote safer laboratory practices, the Web site (<http://umich.edu/~safeche/index.html>), *Process Safety Across the Chemical Engineering Curriculum*, provides

a number of videos on safety. These videos are classified into two types:

1. Video Snippets that are 1–5 minutes instructional videos
2. Case histories of academic accidents that resulted in fatalities or serious injuries and how they may have been prevented.

To access the Snippets Videos, go to the Safety Web site home page and click on *Laboratory and Personal Safety* (http://umich.edu/~safeche/lab_safety.html), which is under *Course Specific Safety Modules*. Upon clicking on *Laboratory and Personal Safety*, you will pull up the menu as shown here:

Safety Snippets Videos

Food in the Lab



The Sloppy Lab



Safety Gear



Evacuate



Videos of Case Histories

After the Rainbow



Experimenting with Danger



Guidelines

Active Attacker

(<https://www.dpss.umich.edu/content/prevention-education/safety-tips/active-attacker/>)

UM Undergraduate Lab Safety Guidelines (PDF)

(<http://umich.edu/~safeche/assets/pdf/LabsSafetyGuidelines.pdf>)

Introduction to Laboratory Safety for Graduate Students (PDF)

(<https://pubs.acs.org/doi/pdfplus/10.1021/acs.jchemed.8b00774>)

ACS Safety Guidelines

(<https://www.acs.org/content/dam/acsorg/about/governance/committees/chemicalsafety/publications/acs-safety-guidelines-academic.pdf?logActivity=true>)

To enhance your laboratory safety prowess, view each of the snippet videos and then write a one-sentence takeaway lesson for each video.

Closure. After reading this chapter, the reader should be able to analyze data to determine the rate law and rate-law parameters using the graphical and numerical techniques, as well as software packages. Nonlinear regression is the easiest method to analyze rate–concentration data to determine the parameters, but the other techniques, such as graphical differentiation, help one get a “feel” for the disparities in the data. The reader should be able to describe the care that needs to be taken in using nonlinear regression to ensure that one does not arrive at a false minimum for σ^2 . Consequently, it is advisable to use more than one method to analyze the data.

SUMMARY

1. Integral method:

1. Guess the reaction order and integrate the mole balance equation.
2. Calculate the resulting function of concentration for the data and plot it as a function of time. If the resulting plot is linear, you have probably guessed the correct reaction order.
3. If the plot is not linear, guess another order and repeat the procedure.

2. Differential method for constant-volume systems:

$$-\frac{dC_A}{dt} = kC_A^\alpha \quad (\text{S7-1})$$

1. Plot $-\Delta C_A/\Delta t$ as a function of t .
2. Determine $-dC_A/dt$ from this plot.
3. Take the \ln of both sides of Equation (S7-1) to get

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k + \alpha \ln C_A \quad (\text{S7-2})$$

Plot $\ln(-dC_A/dt)$ versus $\ln C_A$. The slope will be the reaction order α . We could use finite-difference formulas or software packages to evaluate $(-dC_A/dt)$ as a function of time and concentration.

3. Nonlinear regression: Search for the parameters of the rate law that will minimize the sum of the squares of the difference between the measured rate of reaction and the rate of reaction calculated from the parameter values chosen. For N experimental runs and K parameters to be determined, use Polymath.

$$\sigma^2 = \sum_{i=1}^N \frac{[P_i(\text{measured}) - P_i(\text{calculated})]^2}{N-K} \quad (\text{S7-3})$$

$$s^2 = \sum_{i=1}^N (t_{im} - t_{ic})^2 = \sum_{i=1}^N \left[t_{im} - \frac{C_{A0}^{1-\alpha} - C_{Ai}^{1-\alpha}}{k(1-\alpha)} \right]^2 \quad (\text{S7-4})$$

Caution: Be sure to avoid a false minimum in σ^2 by varying your initial guess.

4. Modeling the differential reactor:

The rate of reaction is calculated from the equation

$$-r'_A = \frac{F_{A0}X}{\Delta W} = \frac{F_P}{\Delta W} = \frac{v_0(C_{A0} - C_{Ae})}{\Delta W} = \frac{C_P v_0}{\Delta W} \quad (\text{S7-5})$$

In calculating the reaction order, α

$$-r'_A = kC_A^\alpha$$

the concentration of A is evaluated either at the entrance conditions or at a mean value between C_{A0} and C_{Ae} . However, power-law models such as

$$-r'_A = kC_A^\alpha C_B^\beta \quad (\text{S7-6})$$

are not the best way to describe heterogeneous reaction-rate laws. Typically, they take the form

$$-r'_A = \frac{kP_A P_B}{1 + K_A P_A + K_B P_B}$$

or a similar form, with the reactant partial pressures in the numerator *and* denominator of the rate law.

CRE WEB SITE MATERIALS

(<http://umich.edu/~elements/6e/07chap/obj.html#/>)

Useful Links

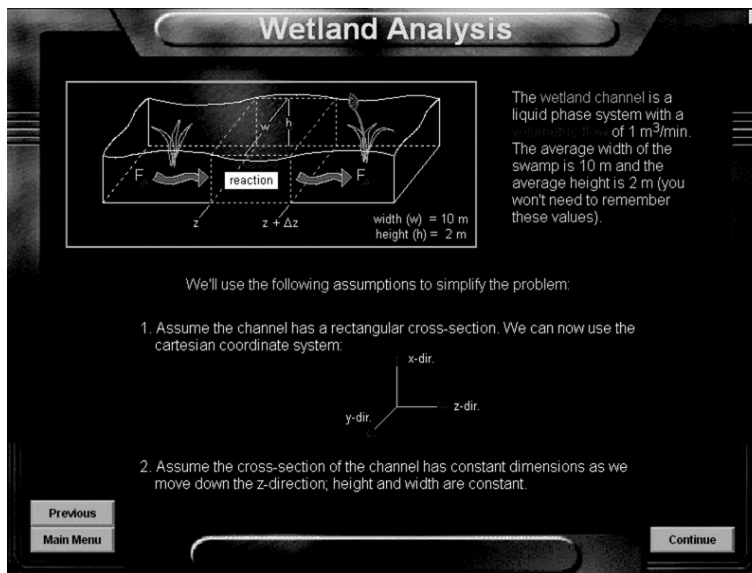


Evaluation



Interactive Computer Games

(<http://umich.edu/~elements/6e/icm/index.html>)

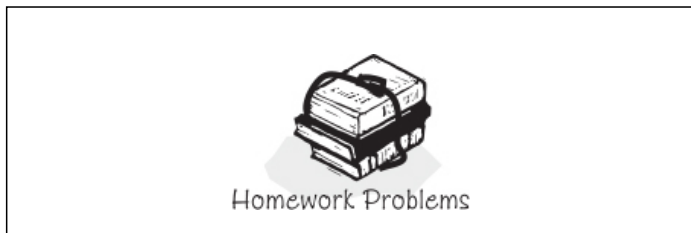


Ecology (<http://umich.edu/~elements/6e/icm/ecology.html>)

QUESTIONS, SIMULATIONS, AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$A = \bullet \quad B = \blacksquare \quad C = \blacklozenge \quad D = \blacklozenge\blacklozenge$$




Questions

Q7-1_A QBR (*Question Before Reading*). If you need to determine the rate law, what methods would you use to collect the data and how would you analyze it?

Q7-2_A i>clicker. Go to the Web site (http://www.umich.edu/~elements/6e/07chap/iclicker_ch7_q1.html) and view at least five i>clicker questions. Choose one that could be used as is, or a variation thereof, to be included on the next exam. You also could consider the opposite case: explaining why the question should *not* be on the next exam. In either case, explain your reasoning.

Q7-3_A

1. Listen to the audios  on the CRE Web site. Pick one and say why it could be eliminated.
2. Create an original problem based on Chapter 7 material.
3. Design an experiment for the undergraduate laboratory that demonstrates the principles of chemical reaction engineering and will cost less than \$500 in purchased parts to build. (From 1998 AIChE National Student Chapter Competition). Rules are provided on the CRE Web site.
4. **K-12 Experiment.** Plant a number of seeds in different pots (corn works well). The plant and soil of each pot will be subjected to different conditions. Measure the height of the plant as a function of time and fertilizer concentration. Other variables might include lighting, pH, and room temperature. (Great grade school or high school science project.)



Q7-4_B Example 7-1. What is the error in assuming the concentration of species B is constant and what limits can you put on the calculated value of k ? (i.e., $k = 0.24 \pm ?$)

Q7-5_A Example 7-3. Explain *why* the regression was carried out twice to find k' and k .

Q7-6_A AWFOS-S. Which of the four Safety Snippets Videos most impressed you with getting across the safety

aspect that the video was trying to highlight? Which of the four 1- to 2-minute Snippets Videos was the most humorous while at the same time getting its point across?

Q7-7_A Go to the LearnChemE screencasts link for Chapter 7

(<http://www.umich.edu/~elements/6e/07chap/learn-cheme-videos.html>).

1. View the two screencasts on nonlinear regression and describe or list any differences between the two videos. Would you recommend these screencasts be assigned to next year's class?
2. In the nonlinear regression screencast, what type of data do you need to regress for the reaction order?

Computer Simulations and Experiments

P7-1_A

1. **LEP Example Problem 7-3_A**. The reaction $A + B \rightarrow C$ occurs in the liquid phase. The proposed empirical rate law is $-r_A = A \exp(-E/RT) C_A^\alpha C_B^\beta$. Look at the values of s^2 as a function of α . At what value of α is s^2 minimized?
 1. Vary β keeping A fixed and describe what you find.
 2. Vary A keeping β fixed and describe what you find.
 3. Suggest a rate law that minimizes s^2 .
2. **Example 7-4: Nonlinear Regression**
Follow the Polymath tutorial to regress the data given in this example to fit the rate law

$$r_{CH_4} = k P_{CO}^\alpha P_{H_2}^\beta$$

What is the difference in the correlation and sums of squares compared with those given in Example 7-4?

Interactive Computer Games

P7-2_A

1. Download the Interactive Computer Game (ICG) from the CRE Web site (<http://www.umich.edu/~elements/6e/icm/ecology.html>). Play the game and then record your performance number for the module that indicates your mastery of the material. Your professor has the key to decode your performance number.
ICM Ecology Performance # _____.
2. Go to Professor Herz's **Reactor Lab** on the Web at www.reactorlab.net. Do (a) one quiz, or (b) two quizzes from Division 1. When you first enter a lab, you see all input values and can vary them. In a lab, click on the Quiz button in the navigation bar to enter the quiz for that lab. In a quiz, you cannot see some of the input values; you need to find those with "???" hiding the values. In the quiz, perform experiments and analyze your data in order to determine the unknown values. See the bottom of the Example Quiz page at www.reactorlab.net for equations

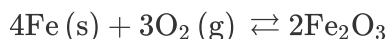
that relate E and k . Click on the “???” next to an input and supply your value. Your answer will be accepted if it is within $\pm 20\%$ of the correct value. Scoring is done with imaginary dollars to emphasize that you should design your experimental study rather than do random experiments. Each time you enter a quiz, new unknown values are assigned. To reenter an unfinished quiz at the same stage you left, click the [i] info button in the Directory for instructions. Turn in copies of your data, your analysis work, and the Budget Report.

Problems

P7-3A Skiing Hand Warmers.[†] Once a year, Professor Dr. Sven Köttlov loves to go skiing with his students in the mountains of Jofostan. Before going, he retires to his basement in his small but adequate university housing to make hand warmers for everyone.

[†] B. Opegrda, A.M.R.P. *Journal of Chemical Elevation on Time*, D01:10.1021/acs.jchemed.8600012. J. Gordon and K. Chancy, *J. Chem. Educ.*, 82(7), 1065 (July 2005).

Here he mixes iron (steel wool), sodium chloride, and a few other proprietary ingredients, then seals them in an airtight Ziploc[®] compartment. When the warmers are needed, the bag is broken and the iron is exposed to air generating heat by the exothermic reaction



To determine the reaction kinetics, a steel wool sample was weighed, cleaned, and put in a sealed container where the percent of oxygen was measured as a function of time and the following data was recorded:

$t(\text{min})$	0	3	5	8	15	20	25
$[\% \text{O}_2]$	21	15	12	10	5	3	2

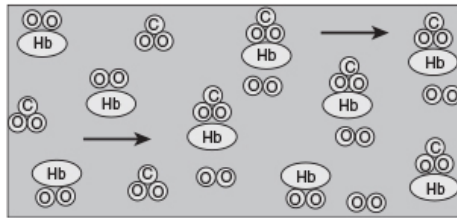
For a specified steel wool weight and surface area, the proposed relationship for the percent oxygen in the bag as

a function of time is

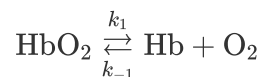
$$[\% \text{O}_2] = 3 \exp(-kt) \quad (\text{P7-3.1})$$

1. Assuming the surface area of steel wool is approximately constant and the bag is sealed, use the CRE algorithm to derive Equation (P7-3.1).
2. Compare the rate law and data. By inspection, without carrying out any data analysis, can you determine immediately that the rate law is correct or not? Explain.
3. Use the data to determine the rate law and rate-law parameters.
4. The data shows the reaction is virtually complete after 25 minutes, while the students will be skiing for 5–7 hours. Professor Köttlov had finger nail polish removed from his nails with acetic acid immediately before performing the experiment. It is known that acid accelerates the reaction. Can you take this information into account? If so, how would you do it?

P7-4_A When arterial blood enters a tissue capillary, it exchanges oxygen and carbon dioxide with its environment, as shown in this diagram.



The kinetics of this deoxygenation of hemoglobin in blood was studied with the aid of a **tubular reactor** by Nakamura and Staub (*J. Physiol.*, 173, 161).



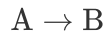
Although this is a reversible reaction, measurements were made in the initial phases of the decomposition so that the reverse reaction could be neglected. Consider a system similar to the one used by Nakamura and Staub: the solution enters a tubular reactor (0.158 cm in diameter) that has oxygen electrodes placed at 5-cm intervals down the tube. The solution flow rate into the reactor is 19.6 cm³/s with $C_{A0} = 2.33 \times 10^{-6}$ mol/cm³.

Electrode position	1	2	3	4	5	6	7
--------------------	---	---	---	---	---	---	---

Percent decomposition of HbO ₂	0	1	3	5	7	9	11
4	.2	.0
	0	9	8	6	8	5	0
	0	3	2	8			

1. Using the method of differential analysis of rate data, determine the reaction order and the forward specific reaction-rate constant k_1 for the deoxygenation of hemoglobin.
2. Repeat using regression.

P7-5_A The irreversible isomerization



was carried out in a constant-volume **batch** reactor and the following concentration–time data were obtained:

t (min)	0	5	8	10	12	15	17.5	20
C_A (mol/dm ³)	4.0	2.25	1.45	1.0	0.65	0.25	0.06	0.008

Determine the reaction order = and the specific reaction rate k in appropriate units.

P7-6_B OEQ (*Old Exam Question*). The liquid-phase irreversible reaction



is carried out in a CSTR. To learn the rate law, the volumetric flow rate, v_0 , (hence $\tau = V/v_0$) is varied and the effluent concentrations of species A are recorded as a function of the space time τ . Pure A enters the reactor at a concentration of 2 mol/dm³. Steady-state conditions exist when the measurements are recorded.

Run	1	2	3	4	5
τ (min)	15	38	100	300	1200
C_A (mol/dm ³)	1.5	1.25	1.0	0.75	0.5

1. Determine the reaction order and specific reaction-rate constant.
2. What experiments would you do to determine the activation energy?
3. If you were to take more data, where would you place the measurements (e.g., τ)?
4. It is believed that the technician may have made a dilution factor-of-10 error in one of the concentration measurements. What do you think?

Note: All measurements were taken at steady-state conditions. Be careful; this problem is sneaky.

P7-7_A The reaction



was carried out in a constant-volume batch reactor where the following concentration measurements were recorded as a function of time.

t (min)	0	5	9	15	22	30	40	60
C_A (mol/dm ³)	2	1.6	1.35	1.1	0.87	0.70	0.53	0.35

1. Use nonlinear least squares (i.e., regression) and one other method to determine the reaction order, α , and the specific reaction rate, k .
2. Nicolas Bellini wants to know, if you were to take more data, where would you place the points? Why?
3. Prof. Dr. Sven Köttlov from Jofostan University always asks his students, if you were to repeat this experiment to determine the kinetics,

what would you do differently? Would you run at a higher, lower, or the same temperature? Take different data points? Explain what you think he is expecting them to say and why.

- It is believed that the technician made a dilution error in the concentration measured at 60 min. What do you think? How do your answers compare using regression (Polymath or other software) with those obtained by graphical methods?

P7-8_A OEQ (Old Exam Question). The following data were reported (from C. N. Hinshelwood and P. J. Ackey, *Proc. R. Soc. [Lond]*, A115, 215) for a gas-phase constant-volume decomposition of dimethyl ether at 504°C in a *batch reactor*. Initially, only $(\text{CH}_3)_2\text{O}$ was present.

<i>Time (s)</i>	39 0	77 7	119 5	315 5	∞
<i>Total Pressure (mmHg)</i>	40 8	48 8	562	799	93 1

- Why do you think the total pressure measurement at $t = 0$ is missing? Can you estimate it?
- Assuming that the reaction

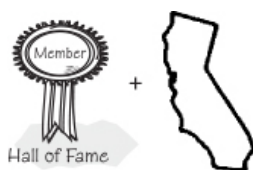
$$(\text{CH}_3)_2\text{O} \rightarrow \text{CH}_4 + \text{H}_2 + \text{CO}$$
 is irreversible and goes virtually to completion, determine the reaction order and specific reaction rate k . (**Ans:** $k = 0.00048 \text{ min}^{-1}$)
- What experimental conditions would you suggest if you were to obtain more data?
- How would the data and your answers change if the reaction were run at a higher temperature? A lower temperature?

P7-9_A OEQ (Old Exam Question). In order to study the photochemical decay of aqueous bromine in bright sunlight, a small quantity of liquid bromine was dissolved in water contained in a glass battery jar and placed in direct sunlight. The following data were obtained at 25°C:

<i>Time (min)</i>	10	20	30	40	50	60
-------------------	----	----	----	----	----	----

ppm Br ₂	2.4	1.7	1.23	0.88	0.62	0.44
	5	4				

1. Determine whether the reaction rate is zero, first, or second order in bromine, and calculate the reaction-rate constant in units of your choice.
2. Assuming identical exposure conditions, calculate the required hourly rate of injection of bromine (in pounds per hour) into a sunlit body of water, 25000 gal in volume, in order to maintain a sterilizing level of bromine of 1.0 ppm. (**Ans:** 0.43 lb/h)



3. Apply to this problem one or more of the six ideas discussed in Table P-4 in the Complete Preface-Introduction on the Web site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>).

Note: ppm = parts of bromine per million parts of brominated water by weight. In dilute aqueous solutions, 1 ppm \equiv 1 milligram per liter. (From California Professional Engineers' Exam.)

P7-10_C The reactions of ozone were studied in the presence of alkenes (from R. Atkinson et al., *Int. J. Chem. Kinet.*, 15(8), 721). The data in Table P7-10_C are for one of the alkenes studied, *cis*-2-butene. The reaction was carried out isothermally at 297 K. Determine the rate law and the values of the rate-law parameters.

TABLE P7-10_C RATE AS A FUNCTION OF OZONE AND BUTENE CONCENTRATIONS

R_u n	Ozone Rate (mol/s · dm ³ × 10 ⁷)		Ozone Concentration (mol/dm ³)	Butene Concentration (mol/dm ³)
1	1.5	0.01	10 ⁻¹²	
2	3.2	0.02	10 ⁻¹¹	

3	3.5	0.015	10^{-10}
4	5.0	0.005	10^{-9}
5	8.8	0.001	10^{-8}
6	4.7*	0.018	10^{-9}

*Hint: Ozone also decomposes by collision with the wall.

P7-11_A OEQ (Old Exam Question). Tests were run on a small experimental reactor used for decomposing nitrogen oxides in an automobile exhaust stream. In one series of tests, a nitrogen stream containing various concentrations of NO_2 was fed to a reactor, and the kinetic data obtained are shown in Figure P7-11_A. Each point represents one complete run. The reactor operates essentially as an *isothermal backmix reactor (CSTR)*. What can you deduce about the apparent order of the reaction over the temperature range studied?

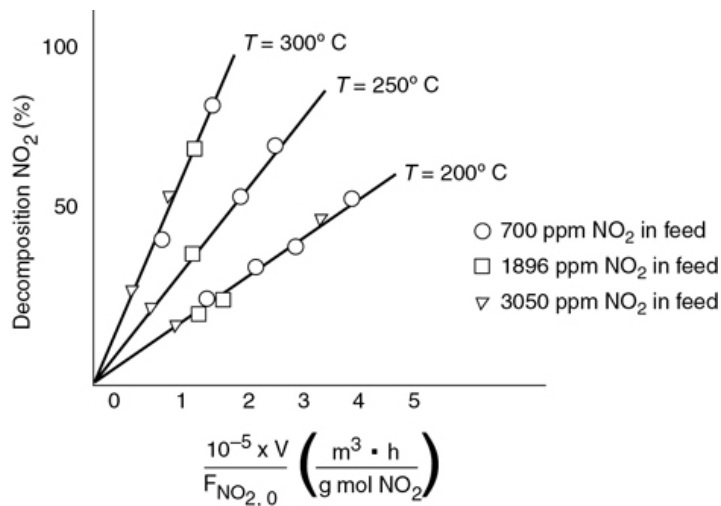


Figure P7-11_A Auto exhaust data.

The plot gives the fractional decomposition of NO_2 fed versus the ratio of reactor volume V (in cm^3) to the NO_2 feed rate, $F_{\text{NO}_2,0}$ (g mol/h), at different feed concentrations of NO_2 (in parts per million by weight). Determine as many rate-law parameters as you can.

P7-12_A The thermal decomposition of isopropyl isocyanate was studied in a *differential packed-bed reactor*. From the data in Table P7-12_A, determine the reaction-rate-law parameters.

TABLE P7-12_A RAW DATA[†]

Run	Rate (mol/s · dm ³)	Concentration (mol/dm ³)	Temperature (K)
1	4.9×10^{-4}	0.2	700
2	1.1×10^{-4}	0.02	750
3	2.4×10^{-3}	0.05	800
4	2.2×10^{-2}	0.08	850
5	1.18×10^{-1}	0.1	900
6	1.82×10^{-2}	0.06	950

[†] Jofostan Journal of Chemical Engineering, Vol. 15, page 743 (1995).

SUPPLEMENTARY READING

1. A wide variety of techniques for measuring the concentrations of the reacting species may or may not be found in

THORNTON W. BURGESS, *Mr. Toad and Danny the Meadow Mouse Take a Walk*. New York: Dover Publications, Inc., 1915.

H. SCOTT FOGLER AND STEVEN E. LEBLANC, with BENJAMIN RIZZO, *Strategies for Creative Problem Solving*, 3rd ed. Upper Saddle River, NJ: Pearson, 2014.

CHESTER L. KARRASS, *In Business As in Life, You Don't Get What You Deserve, You Get What You Negotiate*. Hill, CA: Stanford Street Press, 1996.

J. W. ROBINSON, *Undergraduate Instrumental Analysis*, 5th ed.
New York: Marcel Dekker, 1995.

DOUGLAS A. SKOOG, F. JAMES HOLLER, and TIMOTHY A.
NIEMAN, *Principles of Instrumental Analysis*, 5th ed.
Philadelphia: Saunders College Publishers, Harcourt Brace
College Publishers, 1998.

2. The design of laboratory catalytic reactors for obtaining rate data is presented in

H. F. RASE, *Chemical Reactor Design for Process Plants*, Vol. 1.
New York: Wiley, 1983, Chap. 5.

3. The sequential design of experiments and parameter estimation is covered in

G. E. P. BOX, J. S. HUNTER, and W. G. HUNTER, *Statistics for Experimenters: Design, Innovation, and Discovery*, 2nd ed.
Hoboken, NJ: Wiley, 2005.

8. *Multiple Reactions*

Sometimes you just have to jump and build your wings on the way down.

—Carol Craig, entrepreneur

Overview. Seldom is the reaction of interest the *only one* that occurs in a chemical reactor. Typically, multiple reactions will occur, some desired and some undesired. One of the key factors in the economic success of a chemical plant is the minimization of undesired side reactions that occur along with the desired reaction.

In this chapter, we discuss reactor selection and general mole balances, net rates, and relative rates for multiple reactions.

First, we describe the four basic types of multiple reactions:

- Series
- Parallel
- Independent
- Complex

Next, we define the selectivity parameter and discuss how it can be used to minimize unwanted side reactions by proper choice of operating conditions and reactor selection.

We then show how to modify our CRE algorithm to solve reaction engineering problems when multiple reactions are involved. The modification builds on the algorithm presented in [Chapter 6](#) by numbering all reactions and expanding the *Rates Building Block* into three parts:

- Rate laws
- Relative rates
- Net rates

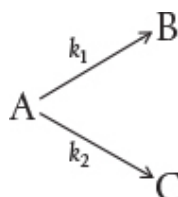
Finally, a number of examples are given that show how the algorithm is applied to real reactions.

8.1 DEFINITIONS

8.1.1 Types of Reactions

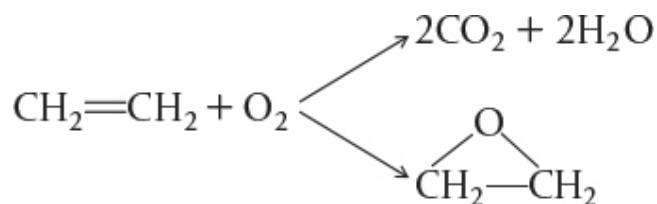
There are four basic types of multiple reactions: series, parallel, independent, and complex. These types of multiple reactions can occur by themselves, in pairs, or all together. When there is a combination of parallel and series reactions, they are often referred to as *complex reactions*.

Parallel reactions (also called *competing reactions*) are reactions where the reactant is consumed by two different reaction pathways to form different products:



Parallel reactions

An example of an industrially significant parallel reaction is the oxidation of ethylene to ethylene oxide while avoiding complete combustion to carbon dioxide and water:



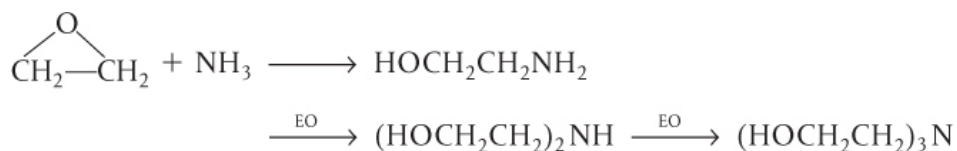
Serious chemistry

Series reactions (also called *consecutive reactions*) are reactions where the reactant forms an intermediate product, which reacts further to form another product:



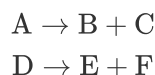
Series reactions

An example of a series reaction is the reaction of ethylene oxide (EO) with ammonia to form mono-, di-, and triethanolamine:



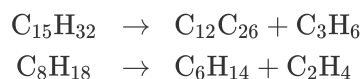
In recent years, the shift has been toward the production of diethanolamine as the *desired* product rather than triethanolamine.

Independent reactions are reactions that occur at the same time but neither the products nor the reactants react with themselves or one another.

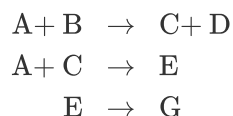


Independent reactions

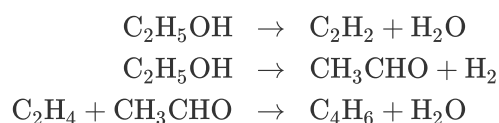
An example is the cracking of crude oil to form gasoline, where two of the many reactions occurring are



Complex reactions are multiple reactions that involve combinations of series and independent parallel reactions, such as

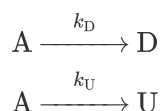


An example of a combination of parallel and series reactions is the formation of butadiene from ethanol:



8.1.2 Selectivity

Desired and Undesired Reactions. Of particular interest are reactants that are consumed in the formation of a *desired product*, D, and the formation of an *undesired product*, U, in a competing or side reaction. In the parallel reaction sequence



or in the series reaction sequence



The economic incentive

we want to minimize the formation of U and maximize the formation of D because the greater the amount of undesired product U formed, the greater the cost of separating the

undesired product U from the desired product D (see Figure 8-1).

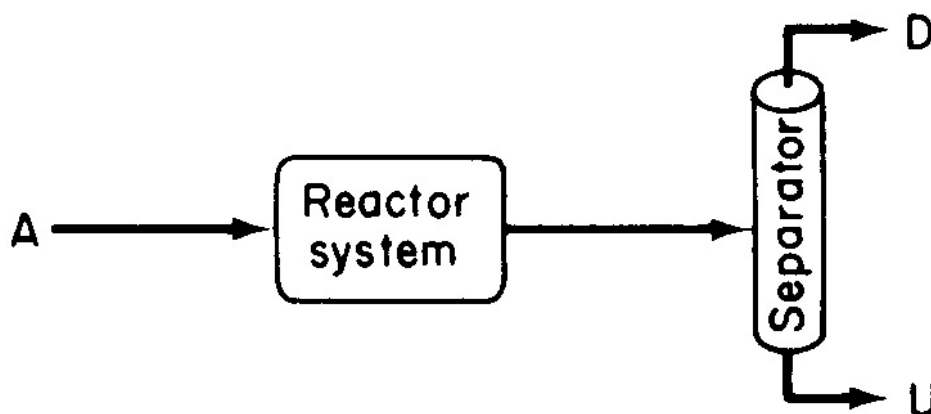


Figure 8-1 Reaction–separation system producing both desired and undesired products.

Selectivity tells us how one product is favored over another when we have multiple reactions. We can quantify the formation of D with respect to U by defining the *selectivity* and the *yield* of the system. The **instantaneous selectivity** of D with respect to U is the ratio of the rate of formation of D to the rate of formation of U.

Instantaneous selectivity

$$S_{D/U} = \frac{r_D}{r_U} = \frac{\text{rate of formation of D}}{\text{rate of formation of U}} \quad (8-1)$$

In Section 8.3, we will see how evaluating $S_{D/U}$ will guide us in the design and selection of our reaction system to maximize the selectivity.

Another definition of selectivity used in the current literature, $\tilde{S}_{D/U}$, is given in terms of the flow rates leaving the reactor. $\tilde{S}_{D/U}$ is the **overall selectivity**.

Overall selectivity

$$\tilde{S}_{D/U} = \frac{F_D}{F_U} = \frac{\text{Exit molar flow rate of desired product}}{\text{Exit molar flow rate of undesired product}} \quad (8-2a)$$

Using a CSTR mole balance on species D and on species U, it is easily shown that for a CSTR the instantaneous and overall selectivities are identical, that is, $S_{D/U} = \tilde{S}_{D/U}$; see the [Chapter 8 Expanded Material on the CRE Web site](http://www.umich.edu/~elements/6e/08chap/expanded.html) (<http://www.umich.edu/~elements/6e/08chap/expanded.html>).

For a batch reactor, the overall selectivity is given in terms of the number of moles of D and U at the end of the reaction time.

$$\tilde{S}_{D/U} = \frac{N_D}{N_U} \quad (8-2b)$$

8.1.3 Yield

Reaction yield, like selectivity, has two definitions: one based on the ratio of reaction rates and one based on the ratio of molar flow rates. In the first case, the yield at a point can be defined as the ratio of the reaction rate of a given product to the reaction rate of the *key* reactant A, usually the basis of calculation. This yield is referred to as the *instantaneous yield* Y_D .

$$Y_D = \frac{r_D}{-r_A} \quad (8-3)$$

Two definitions for selectivity and yield are found in the literature.

Instantaneous yield based on reaction rates

The *overall yield*, \tilde{Y}_D , is based on molar flow rates and defined as the ratio of moles of product formed at the end of the reaction to the number of moles of the key reactant, A, that have been consumed.

For a batch system

$$\tilde{Y}_D = \frac{N_D}{N_{A0} - N_A} \quad (8 - 4a)$$

Overall yield based on moles

For a flow system

$$\tilde{Y}_D = \frac{F_D}{F_{A0} - F_A} \quad (8 - 4b)$$

Overall yield based on molar flow rates

As with selectivity, the instantaneous yield and the overall yield are identical for a CSTR (i.e., $\tilde{Y}_D = Y_D$). From an economic standpoint, the overall selectivities, \tilde{S} , and yields, \tilde{Y} , are important in determining profits, while the instantaneous selectivities give insights in choosing reactors, operating conditions, and reaction schemes that will help maximize the profit. There often is a conflict between selectivity and conversion because you want to make the maximum amount of your desired product (D) as possible and at the same time have the minimum of the undesired product (U), and it may not be possible to do both at the same time. However, in many instances, the greater the conversion you achieve, not only do you make more D, but you also form more U.

#Conflict!

8.1.4 Conversion

While we will not code or solve multiple reaction problems using conversion, it sometimes gives insight to calculate it from the molar flow rates or the number of moles. However, to do this we need to give conversion X a subscript to refer to one of the reactants fed.

For species A

$$\begin{array}{c} \text{Flow} \\ X_A = \frac{F_{A0} - F_A}{F_{A0}} \end{array} \quad \text{or} \quad \begin{array}{c} \text{Batch} \\ X_A = \frac{N_{A0} - N_A}{N_{A0}} \end{array} \quad (8-5a)$$

and for species B

$$\begin{array}{c} \text{Flow} \\ X_B = \frac{F_{B0} - F_B}{F_{B0}} \end{array} \quad \text{or} \quad \begin{array}{c} \text{Batch} \\ X_B = \frac{N_{B0} - N_B}{N_{B0}} \end{array}$$

For a semibatch reactor where B is fed to A

$$X_A = \frac{C_{A0}V_0 - C_A V}{C_{A0}V_0} \quad (8-5b)$$

$$X_B = \frac{F_{B0}t - C_B V}{F_{B0}t}, \text{ for example, } t > 0.001 \text{ s} \quad (8-5c)$$

The conversion for the different species fed is easily included in the numerical software solutions.

8.2 ALGORITHM FOR MULTIPLE REACTIONS

The multiple-reaction algorithm can be applied to parallel reactions, series reactions, independent reactions, and complex reactions. The availability of software packages (ODE solvers)

makes it much easier to solve problems using moles N_j or molar flow rates F_j rather than conversion. For liquid systems, concentration is usually the preferred variable used in the mole balance equations.

After numbering each and every reaction involved we carry out a mole balance on *each* and *every* species. The mole balances for the various types of reactors we have been studying are shown in Table 8-1. The rates shown in Table 8-1, for example, r_A , are the *net rates* of formation and are discussed in detail in Table 8-2. The resulting coupled differential mole balance equations can be easily solved using an ODE solver. In fact, this section has been developed to take advantage of the vast number of computational techniques now available on laptop computers (e.g., Polymath, MATLAB, Wolfram, or Python).

“Each and Every”

TABLE 8-1 MOLE BALANCES FOR MULTIPLE REACTIONS

General Mole Balance	
$\frac{dN_j}{dt} = F_{j0} - F_j + \int^V r_j dV$	
Molar Quantities (Gas or Liquid)	Concentration (Liquid)
B a t	

c h	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A$
	$\frac{dN_B}{dt} = r_B V$	$\frac{dC_B}{dt} = r_B$
	\vdots	\vdots
P F R / P B R	$\frac{dF_A}{dV} = r_A$	$\frac{dC_A}{dV} = \frac{r_A}{v_0}$
	$\frac{dF_B}{dV} = r_B$	$\frac{dC_B}{dV} = \frac{r_B}{v_0}$
	\vdots	\vdots
C S T R	$V = \frac{F_{A0} - F_A}{(-r_A)_{\text{exit}}}$	$V = \frac{v_0 [C_{A0} - C_A]}{(-r_A)_{\text{exit}}}$
	$V = \frac{F_{B0} - F_B}{(-r_B)_{\text{exit}}}$	$V = \frac{v_0 [C_{B0} - C_B]}{(-r_B)_{\text{exit}}}$
	\vdots	\vdots
M e m b r a n e : C d i f f u s e s o	$\frac{dF_A}{dV} = r_A$	$\frac{dF_A}{dV} = r_A$
	$\frac{dF_B}{dV} = r_B$	$\frac{dF_B}{dV} = r_B$
	$\frac{dF_C}{dV} = r_C - R_C$	$\frac{dF_C}{dV} = r_C - R_C$
	\vdots	\vdots

u t		
S e m i b a t c h B a d d e d t o A	$\frac{dN_A}{dt} = r_A V$ $\frac{dN_B}{dt} = F_{B0} + r_B V$ \vdots	$\frac{dC_A}{dt} = r_A - \frac{v_0 C_A}{V}$ $\frac{dC_B}{dt} = r_B + \frac{v_0 [C_{B0} - C_B]}{V}$ \vdots

Mole balances on each and every species

8.2.1 Modifications to the Chapter 6 CRE Algorithm for Multiple Reactions

Just a very few changes to our CRE algorithm for multiple reactions

There are a few small changes to the CRE algorithm presented in Table 6-2, and we will describe these changes in detail when we discuss complex reactions in Section 8.5. However, before discussing parallel and series reactions, it is necessary to point

out some of the modifications to our algorithm. These changes are highlighted by brackets in Table 8-2. When analyzing multiple reactions, we first *number every reaction*. Next, we must perform a mole balance on each and every species, just as we did in Chapter 6 to analyze reactions in terms of the mole balances for different reactor types. The rates of formation shown in the mole balances in Table 6-2 (e.g., r_A , r_B , r_j) are the *net rates* of formation. The main change in the CRE algorithm in Table 6-2 is that the **Rate Law** step in our algorithm has now been replaced by the step **Rates**, which includes three substeps:

- Rate Laws
- Net Rates
- Relative Rates

“Each and Every Reaction”

The concentrations identified in the lower bracket in Table 8-2 are the same concentrations that were discussed in Chapter 6.

TABLE 8-2 MODIFICATION TO THE CRE ALGORITHM

<div><div>r_{ij}</div><div><div>└ Species</div><div>└ Reaction number</div></div></div>
--

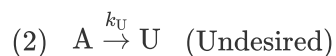
Identify	1. Number Each and Every Reaction Separately
Mole Balance	2. Mole Balance on Each and Every Species
3. Rates	a. Rate Law for Every Reaction For example, $-r_i = k_i f(C_A, C_B, \dots, C_i)$ The subscript "i" refers to the reaction number and the subscript "j" refers to the species.
	b. Net Rates of Reaction for Each Species, for example, j $r_j = \sum_{i=1}^N r_{ij}$ <div style="text-align: center;"> r_{ij} \downarrow Species \downarrow Reaction number </div>
	For N reactions, the net rate of formation of species A is: $r_A = \sum_{i=1}^N r_{iA} = r_{1A} + r_{2A} + \dots + r_{NA}$
	c. Relative Rates for Every Reaction For a given reaction i: $a_i A + b_i B \rightarrow c_i C + d_i D$ <div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 10px auto;"> $\frac{r_{iA}}{-a_i} = \frac{r_{iB}}{-b_i} = \frac{r_{iC}}{c_i} = \frac{r_{iD}}{d_i}$ </div>
The remaining steps to the algorithm in Table 6-2 remain unchanged, for example,	
Stoichiometry	Gas Phase
	$C_j = C_{T0} \frac{F_j}{F_T} \frac{P}{P_0} \frac{T_0}{T}$
	$F_T = \sum_{j=1}^n F_j$
	Liquid Phase
	$C_j = \frac{F_j}{u_0}$

8.3 PARALLEL REACTIONS

8.3.1 Selectivity

In this section, we discuss various ways of minimizing the undesired product, U, through the selection of reactor type and operating conditions. We also discuss the development of efficient reactor schemes.

For the competing reactions such as



the rate laws are

$$r_D = k_D C_A^{\alpha_1} \quad (8-6)$$

$$r_U = k_U C_A^{\alpha_2} \quad (8-7)$$

Rate laws for formation of desired and undesired products

The net rate of disappearance of A for this reaction sequence is the sum of the rates of formation of U and D:

$$-r_A = r_D + r_U \quad (8-8)$$

$$-r_A = k_D C_A^{\alpha_1} + k_U C_A^{\alpha_2} \quad (8-9)$$

where α_1 and α_2 are positive reaction orders. We want the rate of formation of D, r_D , to be high with respect to the rate of formation of U, r_U . Taking the ratio of these rates (i.e., Equations (8-6) and (8-7)), we obtain the **instantaneous selectivity**, $S_{D/U}$, which is to be maximized:

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2} \quad (8-10)$$

Instantaneous selectivity

8.3.2 Maximizing the Desired Product for One Reactant

In this section, we examine ways to maximize the instantaneous selectivity, $S_{D/U}$, for different reaction orders of the desired and undesired products.

Case 1: $\alpha_1 > \alpha_2$. The reaction order of the desired product, α_1 , is greater than the reaction order of the undesired product, α_2 .

Let a be a positive number that is the difference between these reaction orders ($a > 0$):

$$\alpha_1 > \alpha_2 = a$$

Then, upon substitution into Equation (8-10), we obtain

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^a \quad (8-11)$$

For $\alpha_1 > \alpha_2$, make C_A as large as possible by using a **PFR** or **BR**.

To make this ratio as large as possible, we want to carry out the reaction in a manner that will keep the concentration of reactant A as high as possible during the reaction. If the reaction is carried out in the gas phase, we should run it without inerts and at high pressures to keep high. If the reaction is in the liquid phase, the use of diluents should be kept to a minimum.¹

¹ For a number of liquid-phase reactions, the proper choice of a solvent can enhance selectivity. See, for example, *Ind. Eng. Chem.*, 62(9), 16. In gas-phase heterogeneous catalytic reactions, selectivity is an important parameter of any particular catalyst.

A batch or plug-flow reactor should be used in this case because, in these two reactors, the concentration of A starts at a high value and drops progressively during the course of the reaction. In a *perfectly mixed* CSTR, the concentration of reactant within the reactor is always at its lowest value (i.e., that of the outlet concentration) and therefore the CSTR should not be chosen under these circumstances.

Case 2: $\alpha_2 > \alpha_1$. The reaction order of the undesired product is greater than that of the desired product. Let $b = \alpha_2 - \alpha_1$, where b is a positive number; then

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_D C_A^{\alpha_1}}{k_U C_A^{\alpha_2}} = \frac{k_D}{k_U C_A^{\alpha_2 - \alpha_1}} = \frac{k_D}{k_U C_A^b} \quad (8-12)$$

For the ratio r_D/r_U to be high, the concentration of A should be as low as possible.

This low concentration may be accomplished by diluting the feed with inerts and running the reactor at low concentrations of species A. A CSTR should be used because the concentrations of reactants are maintained at a low level. A recycle reactor in which the product stream acts as a diluent could be used to maintain the entering concentrations of A at a low value.

For $\alpha_2 > \alpha_1$ use a **CSTR** and dilute the feed stream.

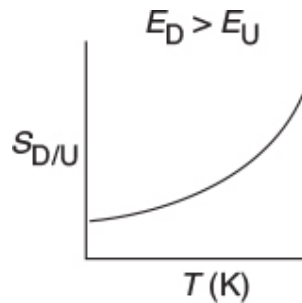
Temperature: Because the activation energies of the two reactions in cases 1 and 2 are not given, it cannot be determined whether the reaction should be run at high or low temperatures. The sensitivity of the rate selectivity parameter to temperature can be determined from the ratio of the specific reaction rates

$$S_{D/U} \sim \frac{k_D}{k_U} = \frac{A_D}{A_U} e^{-[(E_D - E_U)/RT]} \quad (8-13)$$

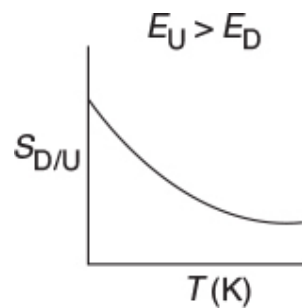
Effect of temperature on selectivity

where A is the frequency factor and E the activation energy, and the subscripts D and U refer to desired and undesired product, respectively.

Case 3: $E_D > E_U$. In this case, the specific reaction rate of the desired reaction k_D (and therefore the overall rate r_D) increases more rapidly with increasing temperature, T , than does the specific rate of the undesired reaction k_U . Consequently, the reaction system should be operated at the highest possible temperature to maximize $S_{D/U}$.



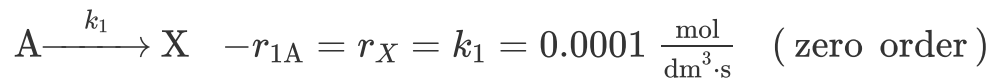
Case 4: $E_U > E_D$. In this case, the reaction should be carried out at a low temperature to maximize $S_{D/U}$, *but not* so low that the desired reaction does not proceed to any significant extent.



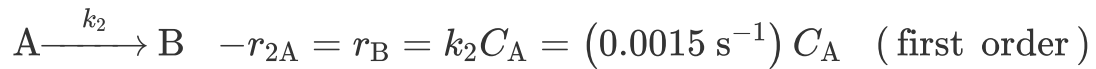
Example 8–1 Maximizing the Selectivity for the Famous Trambouze Reactions

Reactant A decomposes by three simultaneous reactions to form three products, one that is desired, B, and two that are undesired, X and Y. These liquid-phase reactions, along with the appropriate rate laws, are called the *Trambouze reactions* (AIChE J., 5, 384).

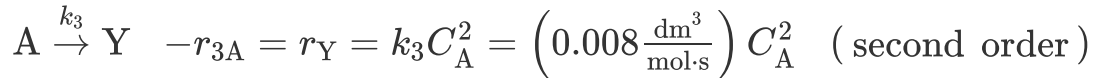
1)



2)



3)



The Famous Trambouze Reactions

The specific reaction rates are given at 300 K and the activation energies for reactions (1), (2), and (3) are $E_1 = 10000 \text{ cal/mole}$, $E_2 = 15000 \text{ cal/mole}$, and $E_3 = 20000 \text{ cal/mole}$.

1. How, and under what conditions (e.g., reactor type(s), temperature, concentrations), should the reaction be carried out to maximize the selectivity of species B for an entering concentration of species A of 0.4 M and a volumetric flow rate of $2.0 \text{ dm}^3/\text{s}$?
2. How could the conversion of B be increased and still keep selectivity relatively high?

Solution

Part (a)

The instantaneous selectivity of species B with respect to species X and Y is

$$S_{B/XY} = \frac{r_B}{r_X + r_Y} = \frac{k_2 C_A}{k_1 + k_3 C_A^2} \quad (\text{E8-1.1})$$

We immediately observe the selectivity, $S_{B/XY}$, is low at very low reactant concentrations of A [$k_1 \gg k_3 C_A^2$ thus $S_{B/XY} \sim C_A$] also very low at very high concentrations of A [$k_1 \ll k_3 C_A^2$ thus $S_{B/XY} \sim \frac{1}{C_A}$].

When we plot $S_{B/XY}$ versus C_A , we see that there is a maximum, as shown in Figure E8-1.1.

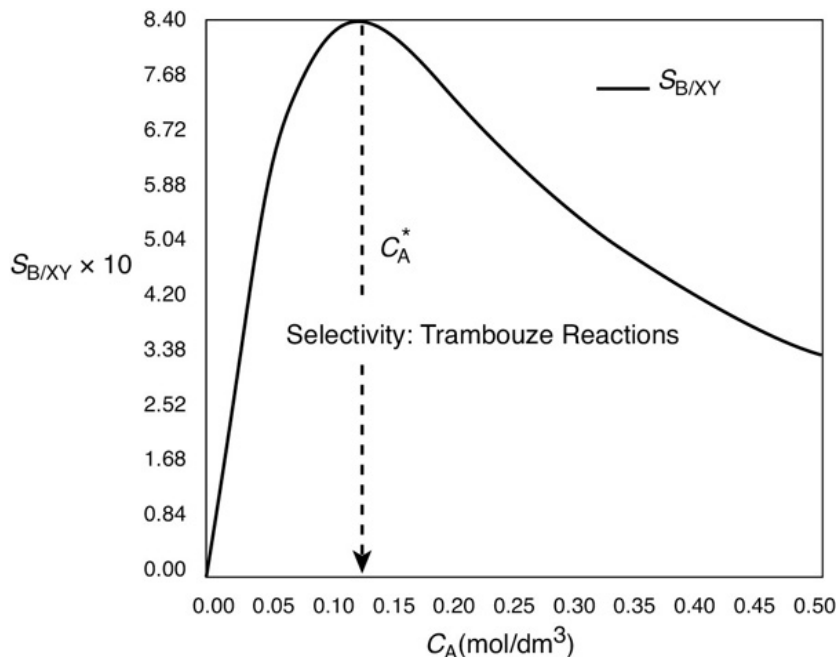


Figure E8-1.1 Selectivity as a function of the concentration of A.

$$S_{B/XY} = \frac{r_B}{r_X + r_Y} = \frac{k_2 C_A}{k_1 + k_3 C_A^2}$$

As we can see, the selectivity $S_{B/XY}$ reaches a maximum at a concentration C_A^* . Because the concentration changes down the length of a PFR, we cannot operate the PFR at this maximum. Consequently, we must use a CSTR and design it to operate at this maximum of $S_{B/XY}$. To find the maximum, C_A^* , we differentiate $S_{B/XY}$ with respect to C_A , set the derivative to zero, and solve for C_A^* . That is,

$$\frac{dS_{B/XY}}{dC_A} = 0 = \frac{k_2 [k_1 + k_3 C_A^{*2}] - k_2 C_A^* [2k_3 C_A^*]}{[k_1 + k_3 C_A^{*2}]^2} \quad (\text{E8-1.2})$$

Solving for C_A^*

$$C_A^* = \sqrt{\frac{k_1}{k_3}} = \sqrt{\frac{0.0001 (\text{mol/dm}^3 \cdot \text{s})}{0.008 (\text{dm}^3/\text{mol} \cdot \text{s})}} = 0.112 \text{ mol/dm}^3 \quad (\text{E8-1.3})$$

Operate at this CSTR reactant concentration:

$$C_A^* = 0.112 \text{ mol/dm}^3.$$

We see from [Figure E8-1.1](#) that the selectivity is indeed a maximum at $C_A^* = 0.112 \text{ mol/dm}^3$.

$$C_A^* = \sqrt{\frac{k_1}{k_3}} = 0.112 \text{ mol/dm}^3$$

Therefore, to maximize the selectivity $S_{B/XY}$, we want to carry out our reaction in such a manner that the

CSTR concentration of A is always at C_A^* . The corresponding selectivity at C_A^* is

$$S_{B/XY} = \frac{k_2 C_A^*}{k_1 + k_3 C_A^{*2}} = \frac{k_2 \sqrt{\frac{k_1}{k_3}}}{k_1 + k_1} = \frac{k_2}{2\sqrt{k_1 k_3}} = \frac{0.0015}{2[(0.0001)(0.008)]^{1/2}} \quad (\text{E8-1.4})$$

$$S_{B/XY} = 0.84$$

We now calculate the CSTR volume when the exit concentration is C_A^* . The **net rate** of formation of A is a sum of the reaction rates from Equations (1), (2), and (3)

$$r_A = r_{1A} + r_{2A} + r_{3A} = -k_1 - k_2 C_A - k_3 C_A^2 \quad (\text{E8-1.5})$$

$$-r_A = k_1 + k_2 C_A + k_3 C_A^2$$

Using Equation (E8-1.5) in the **mole balance** on a CSTR for this liquid-phase reaction ($v = v_0$) to **combine** it with the **net rate** we obtain

$$V = \frac{v_0 [C_{A0} - C_A^*]}{-r_A^*} = \frac{v_0 [C_{A0} - C_A^*]}{[k_1 + k_2 C_A^* + k_3 C_A^{*2}]} \quad (\text{E8-1.6})$$

$$\tau = \frac{V}{v_0} = \frac{C_{A0} - C_A^*}{-r_A^*} = \frac{C_{A0} - C_A^*}{k_1 + k_2 C_A^* + k_3 C_A^{*2}} \quad (\text{E8-1.7})$$

$$\tau = \frac{(0.4 - 0.112)}{(0.0001) + (0.0015)(0.112) + 0.008(0.112)^2} = 782 \text{ s}$$

$$V = v_0 \tau = (2 \text{ dm}^3/\text{s})(782 \text{ s})$$

$$V = 1564 \text{ dm}^3 = 1.564 \text{ m}^3$$

CSTR volume to maximize selectivity

$$\tilde{S}_{B/XY} = S_{B/XY}$$

For an entering volumetric flow rate of $2 \text{ dm}^3/\text{s}$, we must have a CSTR volume of 1564 dm^3 to maximize the selectivity, $S_{B/XY}$.

Maximize the selectivity with respect to temperature.

We now substitute C_A^* in Equation (E8-1.1) and then substitute for C_A^* in terms of k_1 and k_3 (compare Equation (E8-1.3)) to get $S_{B/XY}$ in terms of k_1 , k_2 , and k_3 .

$$S_{B/XY} = \frac{k_2 C_A^*}{k_1 + k_3 C_A^*} = \frac{k_2 \sqrt{\frac{k_1}{k_3}}}{k_1 + k_1} = \frac{k_2}{2\sqrt{k_1 k_3}} \quad (\text{E8-1.4})$$

$$S_{B/XY} = \frac{A_2}{2\sqrt{A_1 A_3}} \exp \left[\frac{\frac{E_1 + E_3}{2} - E_2}{RT} \right] \quad (\text{E8-1.8})$$

At what temperature should we operate the CSTR?

Case 1 : If $\frac{E_1 + E_3}{2} < E_2$ $\left\{ \begin{array}{l} \text{Run at as high a temperature as possible with existing} \\ \text{equipment and watch out for other side reactions that} \\ \text{might occur at higher temperatures} \end{array} \right.$

Case 2 : If $\frac{E_1 + E_3}{2} > E_2$ $\left\{ \begin{array}{l} \text{Run at low temperatures but not so low that a significant} \\ \text{conversion is not achieved} \end{array} \right.$

For the activation energies given in this example

$$\frac{E_1 + E_3}{2} - E_2 = \frac{10000 + 20000}{2} - 15000 = 0 \quad (\text{E8-1.9})$$

#Seriously

So the selectivity for this combination of activation energies is independent of temperature!

What is the conversion of A in the CSTR operated at C_A^* ?

$$X^* = \frac{C_{A0} - C_A^*}{C_{A0}} = \frac{0.4 - 0.112}{0.4} = 0.72$$

Part (b)

If a greater than 72% conversion of A is required, say 90%, then the CSTR operated with a reactor concentration of 0.112 mol/dm^3 should be followed by a PFR because the conversion will increase continuously as we move down the PFR (see Figure E8-1.2(b)). However, as can be seen in Figure E8-1.2, the concentration will decrease continuously from C_A^* , as will the selectivity $S_{B/XY}$ as we move down the PFR to an exit concentration C_{Af} . Consequently the system

$$\left[\text{CSTR} \Big|_{C_A^*} + \text{PFR} \Big|_{C_A^*}^{C_{Af}} \right]$$

How can we increase the conversion and still have a high selectivity $S_{B/XY}$?

would give a higher conversion than the single CSTR. However, the selectivity, while still high, would be less than that of a single CSTR. This CSTR and PFR arrangement would give the smallest total reactor volume when forming more of the desired product B, beyond what was formed at C_A^* in a single CSTR.

Figure E8-1.2 illustrates how, as the conversion is increased above X^* by adding the PFR reactor volume; however, the selectivity decreases.

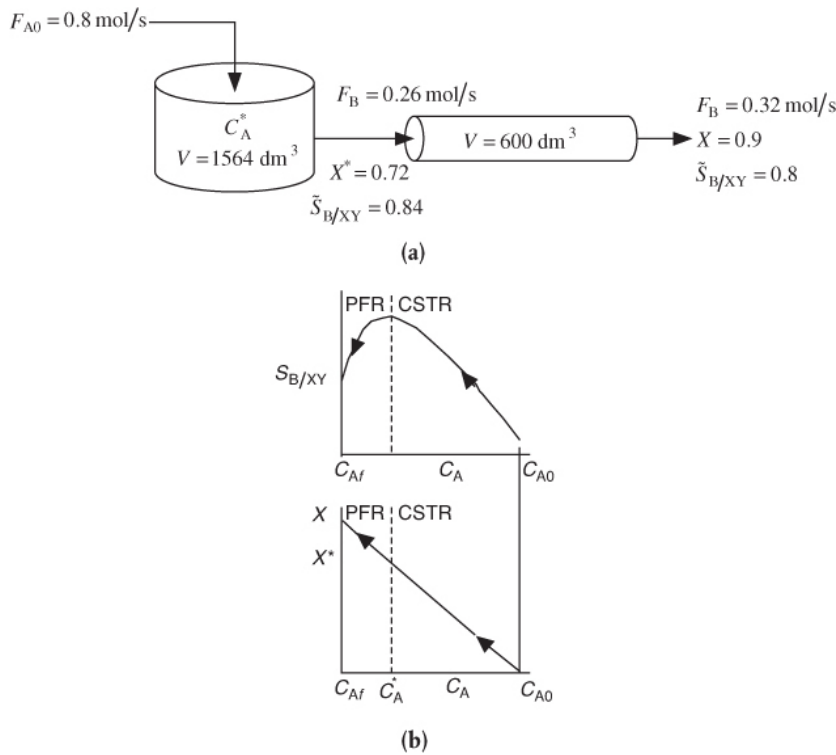


Figure E8-1.2 Effect of adding a PFR to increase conversion. **(a)** Reactor arrangement; **(b)** Selectivity and conversion trajectories.

This calculation for the PFR is carried out in the Chapter 8 *Expanded Material* on the CRE Web site (<http://www.umich.edu/~elements/6e/08chap/expanded.html>). The results of this calculation show that at the exit of the PFR, the molar flow rates are $F_X = 0.22 \text{ mol/s}$, $F_B = 0.32 \text{ mol/s}$, and $F_Y = 0.18 \text{ mol/s}$ corresponding to a conversion of $X = 0.9$. The corresponding selectivity at a conversion of 90% is

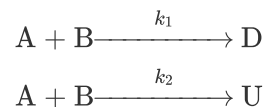
$$\tilde{S}_{B/xy} = \frac{F_B}{F_X + F_Y} = 0.8$$

Do you really want to add the PFR?

Analysis: One now has to make a decision as to whether adding the PFR to increase the conversion of A from 0.72 to 0.9 and the molar flow rate of the desired product B from 0.26 to 0.32 mol/s is worth not only the added cost of the PFR, but also the decrease in selectivity from 0.84 to 0.8. In this example, we used the *Trambouze reactions* to show how to optimize the selectivity to species B in a CSTR. Here, we found the optimal exit conditions ($C_A = 0.112 \text{ mol/dm}^3$), conversion ($X = 0.72$), and selectivity ($S_{B/XY} = 0.84$). The corresponding CSTR volume was $V = 1564 \text{ dm}^3$. If we wanted to increase the conversion to 90%, we could use a PFR to follow the CSTR, but we would find that the selectivity decreased.

8.3.3 Reactor Selection and Operating Conditions

Next, consider two simultaneous reactions in which two reactants, A and B, are being consumed to produce a desired product, D, and an unwanted product, U, resulting from a side reaction. The rate laws for the reactions



are

$$r_D = k_1 C_A^{\alpha_1} C_B^{\beta_1} \quad (8-14)$$

$$r_U = k_2 C_A^{\alpha_2} C_B^{\beta_2} \quad (8-15)$$

The instantaneous selectivity

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_1}{k_2} C_A^{\alpha_1 - \alpha_2} C_B^{\beta_1 - \beta_2} \quad (8-16)$$

Instantaneous selectivity

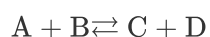
is to be maximized. Shown in Figure 8-2 are various reactor schemes and conditions that might be used to maximize $S_{D/U}$.

The two reactors with recycle shown in Figures 8-2 (i) and (j) can also be used for highly exothermic reactions. Here, the recycle stream is cooled and returned to the reactor to dilute and cool the inlet stream, thereby avoiding hot spots and *runaway reactions*. The PFR with recycle is used for exothermic gas-phase reactions, and the CSTR is used for exothermic liquid-phase reactions.



Runaway Reactions

The last two reactors in Figure 8-2, (k) and (l), are used for thermodynamically limited reactions where the equilibrium lies far to the left (reactant side)



and one of the products must be removed (e.g., C) for the reaction to continue to completion. The membrane reactor (k) is used for thermodynamically limited gas-phase reactions,

while reactive distillation (I) is used for liquid-phase reactions when one of the products has a higher volatility (e.g., C) than the other species in the reactor.

In making our selection of a reactor, the criteria are *safety*, *selectivity*, *yield*, *temperature control*, and *cost*.

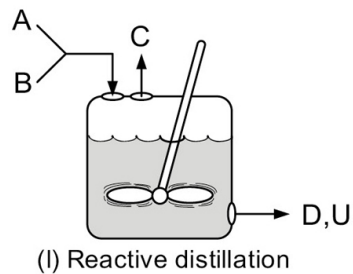
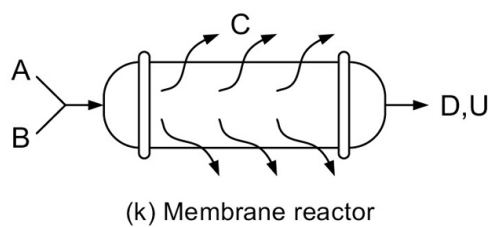
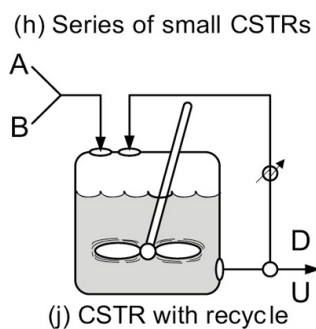
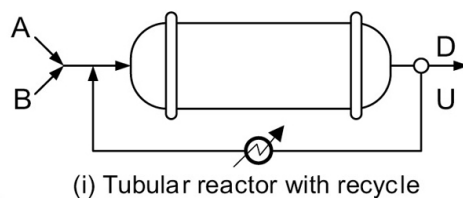
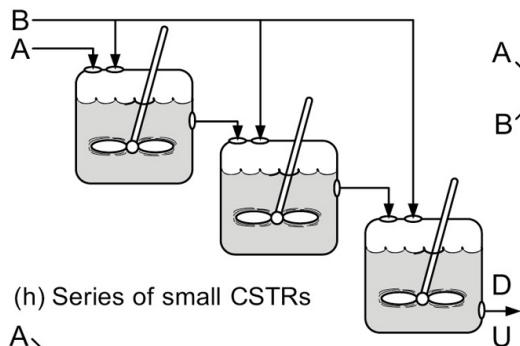
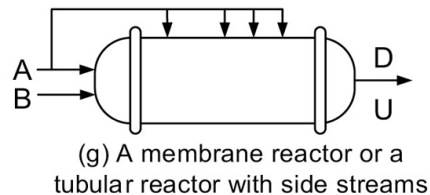
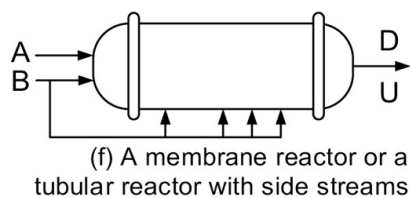
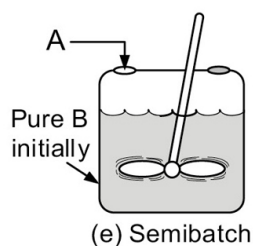
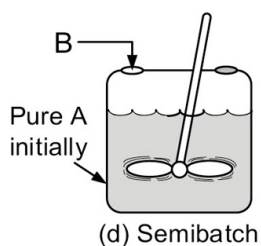
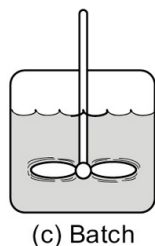
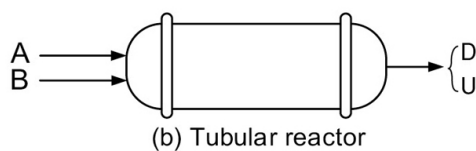
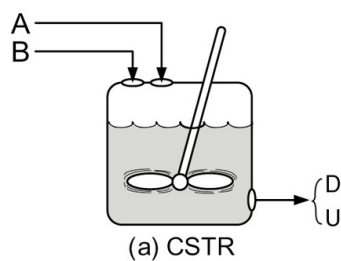


Figure 8-2 Different reactors and schemes for maximizing $S_{D/U}$ in Equation (8-16). Note unreacted A and B also exit the reactor along with D and U.

Reactor schemes to improve selectivity

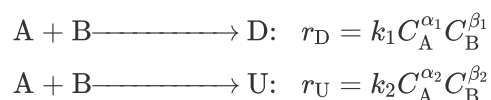
Reactor Selection

Criteria:

- Safety
- Selectivity
- Yield
- Temperature control
- Cost

Example 8–2 Choice of Reactor and Conditions to Minimize Unwanted Products

For the parallel reactions



consider all possible combinations of reaction orders and select the reaction scheme that will maximize $S_{\text{D/U}}$.

Solution

Case 1: $\alpha_1 > \alpha_2$, $\beta_1 > \beta_2$. Let $a = \alpha_1 - \alpha_2$ and $b = \beta_1 - \beta_2$, where a and b are positive constants. Using these definitions, we can write Equation (8-16) in the form

$$S_{\text{D/U}} = \frac{r_{\text{D}}}{r_{\text{U}}} = \frac{k_1}{k_2} C_{\text{A}}^a C_{\text{B}}^b \quad (\text{E8-2.1})$$

Decisions, decisions!

To maximize the ratio $r_{\text{D}}/r_{\text{U}}$, maintain the concentrations of both A and B as high as possible. To do this, use

- A tubular reactor, Figure 8-2(b).
- A batch reactor, Figure 8-2(c).
- High pressures (if gas phase), and reduce inerts.

Use BR or PFR

Case 2: $\alpha_1 > \alpha_2$, $\beta_1 < \beta_2$. Let $a = \alpha_1 - \alpha_2$ and $b = \beta_1 - \beta_2$, where a and b are positive constants. Using these

definitions, we can write Equation (8-16) in the form

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_1 C_A^a}{k_2 C_B^b} \quad (\text{E8-2.2})$$

To make $S_{D/U}$ as large as possible, we want to make the concentration of A high and the concentration of B low. To achieve this result, use

- A semibatch reactor in which B is fed slowly into a large amount of A as in Figure 8-2(d).
- A membrane reactor or a tubular reactor with side streams of B continually fed to the reactor as in Figure 8-2(f).
- A series of small CSTRs with A fed only to the first reactor and small amounts of B fed to each reactor. In this way, B is mostly consumed before the CSTR exit stream flows into the next reactor as in Figure 8-2(h).

Use semibatch *or* membrane reactor *or* side fed PFR *or* CSTRs in series each with a feed stream.

Case 3: $\alpha_1 < \alpha_2$, $\beta_1 < \beta_2$. Let $a = \alpha_1 - \alpha_2$ and $b = \beta_1 - \beta_2$, where a and b are positive constants. Using these definitions, we can write Equation (8-16) in the form

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_1}{k_2 C_A^a C_B^b} \quad (\text{E8-2.3})$$

To make $S_{D/U}$ as large as possible, the reaction should be carried out at low concentrations of A and of B. Use

- A CSTR as in Figure 8-2(a).
- A tubular reactor in which there is a large recycle ratio as in Figure 8-2(i).
- A feed diluted with inerts.

- Low pressure (if gas phase).

Use CSTR *or* PFR with recycle

Case 4: $\alpha_1 < \alpha_2$, $\beta_1 > \beta_2$. Let $a = \alpha_1 - \alpha_2$ and $b = \beta_1 - \beta_2$, where a and b are positive constants. Using these definitions, we can write Equation (8-16) in the form

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_1 C_B^b}{k_2 C_A^a} \quad (\text{E8-2.4})$$

To maximize $S_{D/U}$, run the reaction at high concentrations of B and low concentrations of A. Use

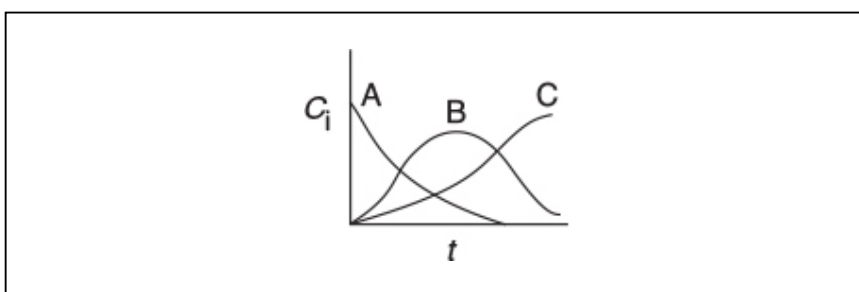
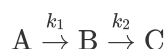
- A semibatch reactor with A slowly fed to a large amount of B as in Figure 8-2(e).
- A membrane reactor or a tubular reactor with side streams of A as in Figure 8-2(g).
- A series of small CSTRs with fresh A fed to each reactor.

Use semibatch *or* membrane reactor *or* side fed PFR *or* CSTRs in series each with a feed stream.

Analysis: In this very important example we showed how to use the instantaneous selectivity, $S_{D/U}$, to guide the initial selection of the type of reactor and reactor system to maximize the selectivity with respect to the desired species D. The final selection should be made after one calculates the overall selectivity $\tilde{S}_{D/U}$ for the reactors and operating conditions chosen.

8.4 REACTIONS IN SERIES

In Section 8.1, we saw that the undesired product could be minimized by adjusting the reaction conditions (e.g., concentration, temperature) and by choosing the proper reactor. For series (i.e., consecutive) reactions, the most important variable is time: space time for a flow reactor and real time for a batch reactor. To illustrate the importance of the time factor, we consider the sequence



in which species B is the desired product.

If the first reaction is slow and the second reaction is fast, it will be extremely difficult to produce a significant amount of species B. If the first reaction (formation of B) is fast and the reaction to form C is slow, a large yield of B can be achieved. However, if the reaction is allowed to proceed for a long time in a batch reactor, or if the tubular flow reactor is too long, the desired product B will eventually be converted to the undesired product C. In no other type of reaction is exactness in the calculation of the time needed to carry out the reaction more important than in series reactions.

Example 8–3 Series Reactions in a Batch Reactor

The elementary liquid-phase series reaction



is carried out in a batch reactor. The reaction is heated very rapidly to the reaction temperature, where it is held at this temperature until the time it is quenched by rapidly lowering the temperature.

1. Plot and analyze the concentrations of species A, B, and C as a function of time.
2. Calculate the time to quench the reaction when the concentration of B will be a maximum.
3. What are the overall selectivity and yields at this quench time?

Additional Information

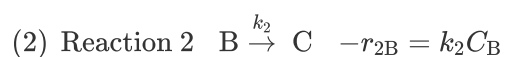
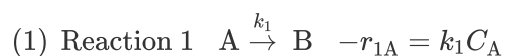
$$C_{A0} = 2 \text{ M}, k_1 = 0.5 \text{ h}^{-1}, k_2 = 0.2 \text{ h}^{-1}$$

Solution

Part (a) Follow the algorithm to plot and analyze $C_A(t)$, $C_B(t)$ and $C_C(t)$.

0. Number the Reactions:

The preceding series reaction can be written as two reactions

**1. Mole Balances on Each and Every Species:**

1A. Mole Balance on A:

$$\frac{dN_A}{dt} = r_A V$$

- 1. Mole balance** in terms of concentration for $V = V_0$ becomes

$$\frac{dC_A}{dt} = r_A \quad (\text{E8-3.1})$$

- 2. Rate law for Reaction 1:** Reaction is elementary

$$r_A = r_{1A} = k_1 C_A \quad (\text{E8-3.2})$$

- 3. Combining** the mole balance and rate law

$$\frac{dC_A}{dt} = -k_1 C_A \quad (\text{E8-3.3})$$

Integrating with the initial condition $C_A = C_{A0}$ at $t = 0$

$$\ln \frac{C_A}{C_{A0}} = -k_1 t \quad (\text{E8-3.4})$$

Solving for C_A

$$\boxed{C_A = C_{A0} e^{-k_1 t}} \quad (\text{E8-3.5})$$

**1B. Mole Balance on B:**

- 1. Mole balance** for a constant-volume batch reactor becomes

$$\frac{dC_B}{dt} = r_B \quad (\text{E8-3.6})$$

- 2. Rates:**

Rate Laws

Elementary reactions

$$r_{2B} = -k_2 C_B \quad (\text{E8-3.7})$$

Relative Rates

Rate of formation of B in Reaction 1 equals the rate of disappearance of A in Reaction 1.

$$r_{1B} = -r_{1A} = k_1 C_A \quad (\text{E8-3.8})$$

Net Rates

The net rate of reaction of B will be the rate of formation of B in reaction (1) plus the rate of formation of B in reaction (2).

$$r_B = r_{1B} + r_{2B} \quad (\text{E8-3.9})$$

$$r_B = k_1 C_A - k_2 C_B \quad (\text{E8-3.10})$$

3. Combining the mole balance and rate law

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B \quad (\text{E8-3.11})$$

Rearranging and substituting for C_A

$$\frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} e^{-k_1 t} \quad (\text{E8-3.12})$$

Using the integrating factor gives

$$\frac{d(C_B e^{k_2 t})}{dt} = k_1 C_{A0} e^{(k_2 - k_1)t} \quad (\text{E8-3.13})$$

At time $t = 0$, $C_B = 0$. Solving Equation (E8-3.13) gives

$$C_B = k_1 C_{A0} \left[\frac{e^{-k_1 t} - e^{-k_2 t}}{k_2 - k_1} \right] \quad (\text{E8-3.14})$$

There is a tutorial on the integrating factor in [Appendix A](#) and on the CRE Web site.

1C. Mole Balance on C:

The mole balance on C is similar to Equation (E8-3.1).

$$\frac{dC_c}{dt} = r_c \quad (\text{E8-3.15})$$

The rate of formation of C is just the rate of disappearance of B in reaction (2), that is, $r_C = -r_{2B} = k_2 C_B$

$$\frac{dC_C}{dt} = k_2 C_B \quad (\text{E8-3.16})$$

Substituting for C_B

$$\frac{dC_C}{dt} = \frac{k_1 k_2 C_{A0}}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

and integrating with $C_C = 0$ at $t = 0$ gives

$$C_C = \frac{C_{A0}}{k_2 - k_1} [k_2 [1 - e^{-k_1 t}] - k_1 [1 - e^{-k_2 t}]] \quad (\text{E8-3.17})$$

Note that as $t \rightarrow \infty$, then $C_C = C_{A0}$ as expected.

We also note the concentration of C, C_C , could have been obtained more easily from an overall balance.

$$C_C = C_{A0} - C_A - C_B \quad (\text{E8-3.18})$$

Calculating the concentration of C the easy way

The concentrations of A, B, and C are shown as a function of time in Figure E8-3.1.

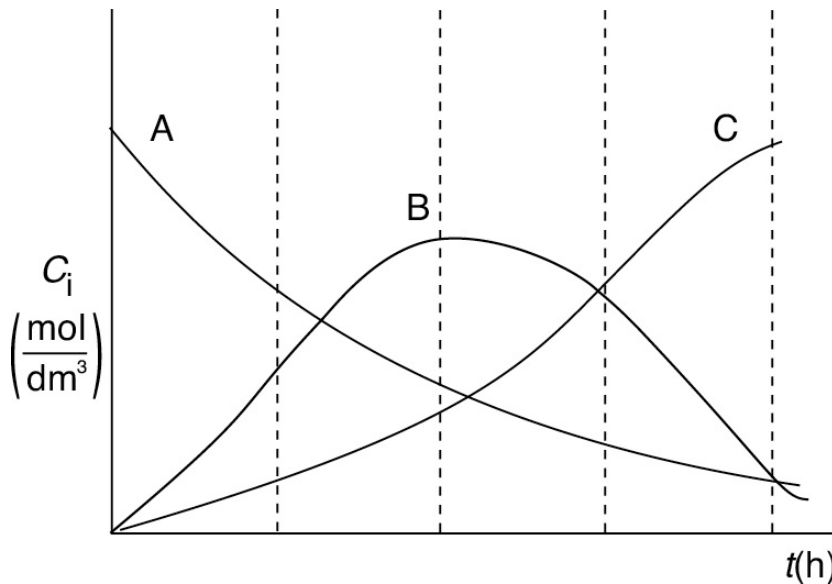


Figure E8-3.1 Concentration trajectories in a batch reactor.

Part (b)

1. **Concentrations and Time at the Maximum:** We note from Figure E8-3.1 that the concentration of B goes through a maximum. Consequently, to find the maximum we need to differentiate Equation (E8-3.14) and set it to zero.

$$\frac{dC_B}{dt} = 0 = \frac{k_1 C_{A0}}{k_2 - k_1} [-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}] \quad (\text{E8-3.19})$$

Solving for t_{\max} gives

$$t_{\max} = \frac{1}{k_2 - k_1} \ln \frac{k_2}{k_1} \quad (\text{E8-3.20})$$

Substituting Equation (E8-3.20) into Equation (E8-3.5), we find the concentration of A at the maximum for C_B is

$$C_A = C_{A0} e^{-k_1 \left(\frac{1}{k_2 - k_1} \ln \frac{k_2}{k_1} \right)} \quad (\text{E8-3.21})$$

$$C_A = C_{A0} \left[\frac{k_1}{k_2} \right]^{\frac{k_1}{k_2 - k_1}} \quad (\text{E8-3.22})$$

Series Reaction

Similarly, the concentration of B at the maximum is

$$C_B = \frac{k_1 C_{A0}}{k_2 - k_1} \left[\left(\frac{k_1}{k_2} \right)^{\frac{k_1}{k_2 - k_1}} - \left(\frac{k_1}{k_2} \right)^{\frac{k_1}{k_2 - k_1}} \right] \quad (\text{E8-3.23})$$

2. **Evaluate:** Substituting for $C_{A0} = 2 \text{ mol/dm}^3$, $k_1 = 0.5 \text{ h}^{-1}$, and $k_2 = 0.2 \text{ h}^{-1}$ in Equations (E8-3.5), (E8-3.14), and (E8-3.18), the concentrations as a function of time are

$$C_A = 2 \text{ mol/dm}^3 (e^{-0.5t})$$

$$C_B = \frac{2(\text{mol/dm}^3)}{(0.2-0.5)} (0.5) [e^{-0.5t} - e^{-0.2t}]$$

$$C_B = 3.33 (\text{mol/dm}^3) [e^{-0.2t} - e^{-0.5t}]$$

$$C_c = 2 \text{ mol/dm}^3 - 2 (\text{mol/dm}^3) e^{-0.5t} - 3.33 \text{ mol/dm}^3 [e^{-0.2t} - e^{-0.5t}]$$

Substituting in Equation (E8-3.20)

$$t_{\max} = \frac{1}{0.2-0.5} \ln \frac{0.2}{0.5} = \frac{1}{0.3} \ln \frac{0.5}{0.2}$$

$$t_{\max} = 3.05 \text{ h}$$

The time to quench the reaction is at 3.05 h.

Batch
At $t_{\max} = 3.05 \text{ h}$
$C_A = 0.43 \frac{\text{mol}}{\text{dm}^3}$
$C_B = 1.09 \frac{\text{mol}}{\text{dm}^3}$
$C_C = 0.48 \frac{\text{mol}}{\text{dm}^3}$
$X = 0.785$
$S_{B/C} = 2.3$
$Y_B = 0.69$

At $t_{\max} = 3.05 \text{ h}$, the concentrations of A, B, and C are

$$C_A = 2 \frac{\text{mol}}{\text{dm}^3} \left[\left(\frac{0.5}{0.2} \right)^{\left(\frac{0.5}{0.2-0.5} \right)} \right] = 0.43 \frac{\text{mol}}{\text{dm}^3}$$

$$C_B = 2 \frac{\text{mol}}{\text{dm}^3} \frac{(0.5)}{(0.2-0.5)} \left[\left(\frac{0.5}{0.2} \right)^{\left(\frac{0.5}{0.2-0.5} \right)} - \left(\frac{0.5}{0.2} \right)^{\left(\frac{0.2}{0.2-0.5} \right)} \right] = 1.09 \frac{\text{mol}}{\text{dm}^3}$$

$$X = \frac{C_{A0} - C_A}{C_{A0}} = \frac{2 - 0.43}{2} = 0.785$$

The concentration of C at the time we quench the reaction is

$$C_C = C_{A0} - C_A - C_B = 2 - 0.44 - 1.07 = 0.48 \text{ mol/dm}^3$$

Part (c) Calculate the overall selectivity and yield at the reaction quench time. The selectivity is

$$\tilde{S}_{B/C} = \frac{C_B}{C_C} = \frac{1.09}{0.48} = 2.3$$

The yield is

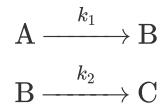
$$\tilde{Y}_B = \frac{C_B}{C_{A0} - C_A} = \frac{1.09}{2 - 0.44} = 0.69$$

Analysis: In this example, we applied our CRE algorithm for multiple reactions to the series reaction $A \rightarrow B \rightarrow C$. Here, we obtained an analytical solution to find the time at which the concentration of the desired product B was a maximum and, consequently, the time to quench the reaction. We also calculated the concentrations of A, B, and C at this time, along with the selectivity and yield.

We will now carry out this same series reaction in a CSTR.

Example 8–4 Series Reaction in a CSTR

The reactions discussed in Example 8-3 are now to be carried out in a CSTR.



1. Determine the exit concentrations from the CSTR.
2. Find the value of the space time τ that will maximize the concentration of B.

*Solution***Part (a) Follow the CRE Algorithm to Find the Exit Concentrations**

1.

1. Mole Balance on A:

$$\begin{array}{rcccccccl} \text{IN} & - & \text{OUT} & + & \text{GENERATION} & = & 0 \\ F_{A0} & - & F_A & + & r_A V & = & 0 \\ v_0 C_{A0} & - & v_0 C_A & + & r_A V & = & 0 \end{array}$$

Dividing by v_0 , rearranging and recalling that $\tau = V/v_0$, we obtain

$$C_{A0} - C_A + r_A \tau = 0 \quad (\text{E8-4.1})$$

2. Rates

The laws and net rates are the same as in Example 8-3.

$$\text{Reaction 1: } r_A = -k_1 C_A \quad (\text{E8-4.2})$$

3. **Combining** the mole balance of A with the rate of disappearance of A

$$C_{A0} - C_A - k_1 C_A \tau = 0 \quad (\text{E8-4.3})$$

Solving for C_A

$$C_A = \frac{C_{A0}}{1 + \tau k_1} \quad (\text{E8-4.4})$$

We now use the same algorithm for species B we did for species A to solve for the concentration of B.

2.

1. Mole Balance on B:

$$\begin{array}{rclclcl} \text{IN} & - & \text{OUT} & + & \text{GENERATION} & = & 0 \\ 0 & - & F_B & + & r_B V & = & 0 \\ & - & v_0 C_B & + & r_B V & = & 0 \end{array}$$

Dividing by v_0 and rearranging

$$-C_B + r_B \tau = 0 \quad (\text{E8-4.5})$$

2. Rates

The laws and net rates are the same as in Example 8-3.

Net Rates

$$r_B = k_1 C_A - k_2 C_B \quad (\text{E8-4.6})$$

3. Combine

$$-C_B + (k_1 C_A - k_2 C_B) \tau = 0$$

$$C_B = \frac{k_1 C_A \tau}{1 + k_2 \tau} \quad (\text{E8-4.7})$$

Substituting for C_A

$$C_B = \frac{\tau k_1 C_{A0}}{(1 + k_1 \tau)(1 + k_2 \tau)} \quad (\text{E8-4.8})$$

3. Mole Balance on C:

$$0 - v_0 C_C + r_C V = 0$$

$$-C_C + r_C \tau = 0 \quad (\text{E8-4.9})$$

Rates

$$r_C = -r_{2B} = k_2 C_B$$

$$C_C = r_C \tau = k_2 C_B \tau$$

$$C_C = \frac{\tau^2 k_1 k_2 C_{A0}}{(1+k_1\tau)(1+k_2\tau)} \quad (\text{E8-4.10})$$

Part (b) Optimum Concentration of B

To find the maximum concentration of B, we set the differential of Equation (E8-4.8) with respect to τ equal to zero

$$\frac{dC_B}{d\tau} = \frac{k_1 C_{A0}(1+\tau k_1)(1+\tau k_2) - \tau k_1 C_{A0}(k_1 + k_2 + 2\tau k_1 k_2)}{[(1+k_1\tau)(1+k_2\tau)]^2} = 0$$

Solving for τ at which the concentration of B is a maximum at

$$\tau_{\max} = \frac{1}{\sqrt{k_1 k_2}} \quad (\text{E8-4.11})$$

Finding the optimum space time τ to maximize the concentration of our desired product B.

The exiting concentration of B at the optimum value of τ is

$$C_B = \frac{\tau_{\max} k_1 C_{A0}}{(1+\tau_{\max} k_1)(1+\tau_{\max} k_2)} = \frac{\tau_{\max} k_1 C_{A0}}{1+\tau_{\max} k_1 + \tau_{\max} k_2 + \tau_{\max}^2 k_1 k_2} \quad (\text{E8-4.12})$$

Substituting Equation (E8-4.11) for τ_{\max} in Equation (E8-4.12)

$$C_B = \frac{C_{A0} \frac{k_1}{\sqrt{k_1 k_2}}}{1 + \frac{k_1}{\sqrt{k_1 k_2}} + \frac{k_2}{\sqrt{k_1 k_2}} + 1} \quad (\text{E8-4.13})$$

Rearranging, we find the concentration of B at the optimum space time is

$$C_B = \frac{C_{A0} k_1}{2\sqrt{k_1 k_2} + k_1 + k_2} \quad (\text{E8-4.14})$$

Evaluation

$$\tau_{\max} = \frac{1}{\sqrt{(0.5)(0.2)}} = 3.16 \text{ h}$$

At τ_{\max} , the concentrations of A, B, and C are

$$C_A = \frac{C_{A0}}{1+\tau_{\max}k_1} = \frac{2 \frac{\text{mol}}{\text{dm}^3}}{1+\left(3.16 \text{ h}\right)\left(\frac{0.5}{\text{h}}\right)} = 0.78 \frac{\text{mol}}{\text{dm}^3}$$

$$C_B = 2 \frac{\text{mol}}{\text{dm}^3} \frac{0.5}{2\sqrt{(0.2)(0.5)}+0.2+0.5} = 0.75 \frac{\text{mol}}{\text{dm}^3}$$

$$C_C = C_{A0} - C_A - C_B = \left(2-0.78-0.75 \frac{\text{mol}}{\text{dm}^3}\right) = 0.47 \frac{\text{mol}}{\text{dm}^3}$$

The conversion is

$$X = \frac{C_{A0}-C_A}{C_{A0}} = \frac{2-0.78}{2} = 0.61$$

The selectivity is

$$\widetilde{S}_{B/C} = \frac{C_B}{C_C} = \frac{0.75}{0.47} = 1.60$$

The yield is

$$\widetilde{Y}_B = \frac{C_B}{C_{A0}-C_A} = \frac{0.75}{2-0.78} = 0.61$$

SUMMARY TABLE

TimeX $\widetilde{S}_{B/C}$ \widetilde{Y}_B				
BR	$t_{\max} = 3.05 \text{ h}$	0.785	2.3	0.69
CSTR	$\tau_{\max} = 3.16 \text{ h}$	0.61	1.6	0.61

Real data compared with real theory.

Analysis: The CRE algorithm for multiple reactions was applied to the series reaction $A \rightarrow B \rightarrow C$ in a CSTR to find the CSTR space time necessary to maximize the concentration of B, that is, $\tau = 3.16$ h. The conversion at this space time is 61%, the selectivity, $\tilde{S}_{B/C}$, is 1.60, and the yield, \tilde{Y}_B , is 0.61. The conversion and selectivity are less for the CSTR than those for the batch reactor at the time of quenching.

PFR If the series reaction were carried out in a PFR, the results would essentially be those of a batch reactor where we replaced the time variable “ t ” with the space time, “ τ ”. Data for the series reaction



is compared for different values of the specific reaction rates, k_1 and k_2 , in Figure 8-3.

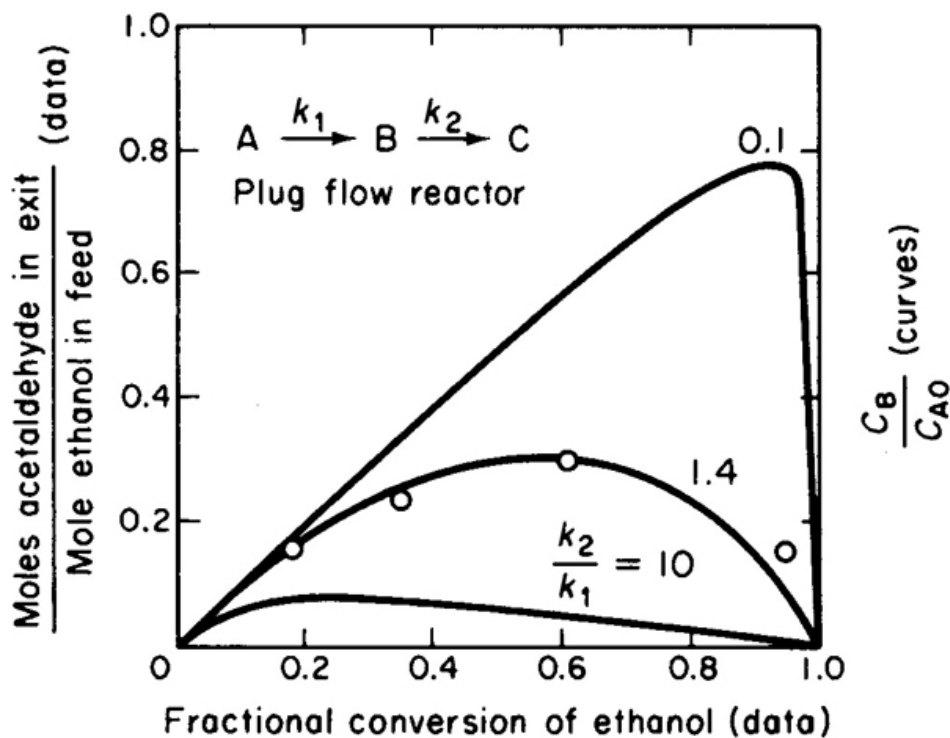


Figure 8-3 Yield of acetaldehyde as a function of ethanol conversion. Data were obtained at 518 K. Data points (in order of increasing ethanol conversion) were obtained at space velocities of 26,000; 52,000; 104,000; and 208,000 h⁻¹. The curves were calculated for a first-order series reaction in a plug-flow reactor and show yield of the intermediate species B as a function of the conversion of reactant for various ratios of rate constants k_2 and k_1 . (Robert W. McCabe and Patricia J. Mitchell. "Oxidation of ethanol and acetaldehyde over alumina-supported catalysts." *Ind. Eng. Chem. Prod. Res. Dev.*, 22(2), 212–217 (1983). Copyright © 1963, American Chemical Society. Reprinted by permission.)

#RealLiveData!

A complete analysis of this reaction carried out in a PFR is given on the CRE Web site.

Side Note: Blood Clotting

Many metabolic reactions involve a large number of sequential reactions, such as those that occur in the coagulation of blood.

Cut → Blood → Clotting

Blood coagulation (see Figure A) is part of an important host defense mechanism called *hemostasis*, which causes the cessation of blood loss from a damaged vessel. The clotting process is initiated when a nonenzymatic lipoprotein (called the *tissue factor*) contacts blood plasma because of cell damage. The tissue factor (TF) is normally not in contact with plasma (see Figure B) because of an intact endothelium. The rupture (e.g., cut) of the endothelium exposes the plasma to TF and a cascade* of series reactions proceeds (Figure C). These series reactions ultimately result in the conversion of fibrinogen (soluble) to fibrin (insoluble), which produces the clot. Later, as wound healing occurs, mechanisms that restrict formation of fibrin clots, necessary to maintain the fluidity of the blood, start working.

If you are squeamish, you might want to skip this side note!

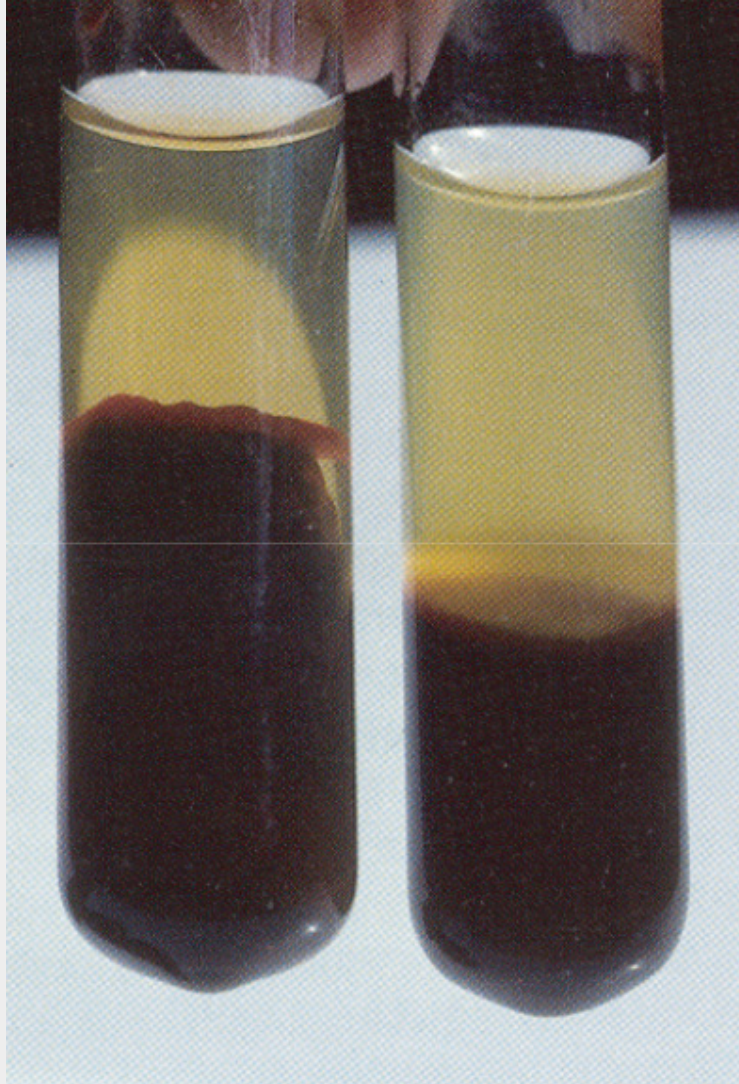


Figure A Normal clot coagulation of blood. (Dietrich Mebs, *Venomous and Poisonous Animals*, Stuttgart: Medpharm, 2002, p. 305. Reprinted by permission of the author.)

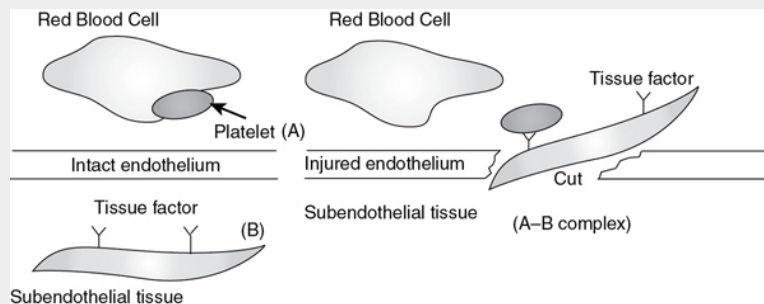


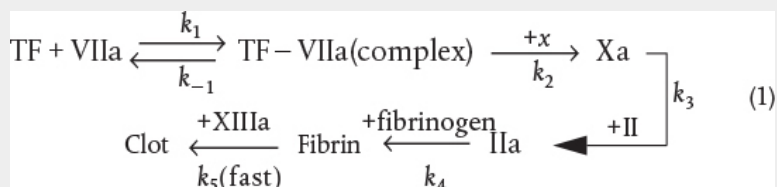
Figure B Schematic of separation of TF (A) and plasma (B) before cut occurs.

Figure C Cut allows contact of plasma to initiate coagulation. (A + B → Cascade)

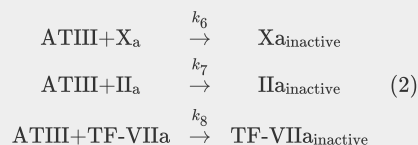
²Platelets provide procoagulant, phospholipids-equivalent surfaces upon which the complex-dependent reactions of the blood coagulation cascade are localized.

#Ouch!

An abbreviated form (1) of the initiation and following cascade metabolic reactions that can capture the clotting process is

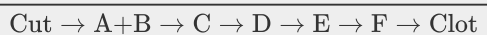


In order to maintain the fluidity of the blood, the clotting sequence (2) must be moderated. The reactions that attenuate the clotting process are



where TF = tissue factor, VIIa = factor novoseven, X = Stuart Prower factor, Xa = Stuart Prower factor activated, II = prothrombin, IIa = thrombin, ATIII = antithrombin, and XIIIa = factor XIIIa.

Symbolically, the clotting equations can be written as



#ER. The next time you have to go to the emergency room for a serious cut, discussing the clotting mechanism should impress the doctor as you are stitched up.

One can model the clotting process in a manner identical to the series reactions by writing a mole balance and rate law for each species, such as

$$\begin{aligned}
 \frac{dC_{\text{TF}}}{dt} &= -k_1 \cdot C_{\text{TF}} \cdot C_{\text{VIIa}} + k_{-1} \cdot C_{\text{TF-VIIa}} \\
 \frac{dC_{\text{VIIa}}}{dt} &= -k_1 \cdot C_{\text{TF}} \cdot C_{\text{VIIa}} + k_{-1} \cdot C_{\text{TF-VIIa}}
 \end{aligned}$$

, and so on,

and then using Polymath to solve the coupled equations to predict the thrombin (shown in Figure D) and other species concentration as a function of time, as well as to determine the clotting time. Laboratory data are also shown below for a TF concentration of 5 pM. One notes that when the complete set of equations is used, the Polymath output is identical to Figure E. The complete set of equations, along with the Polymath Living Example Problem LEP code (<http://www.umich.edu/~elements/6e/08chap/live.html>) is given in the Solved Problems on the CRE Web site

(<http://www.umich.edu/~elements/6e/08chap/pdf/BloodCoagulation.pdf>). You can load the program directly and vary some of the parameters.

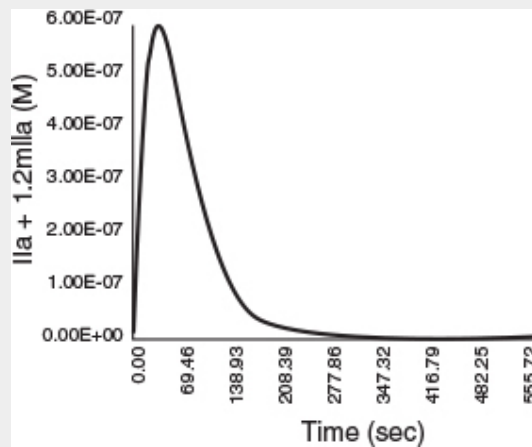


Figure D Total thrombin as a function of time with an initiating TF concentration of 25 pM (after running Polymath) for the abbreviated blood-clotting cascade.

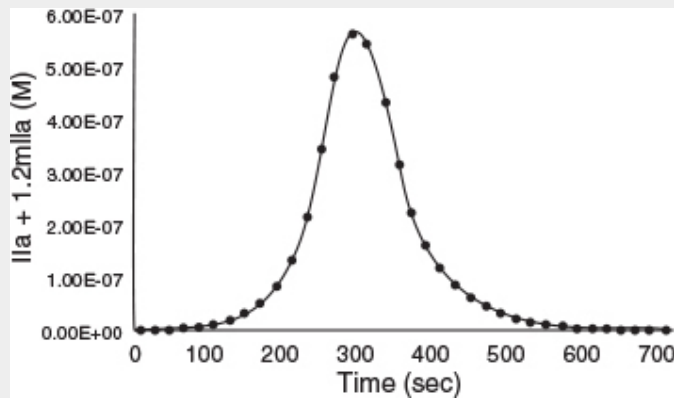


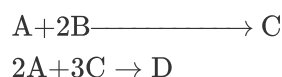
Figure E Total thrombin as a function of time with an initiating TF concentration of 25 pM. Full blood-clotting cascade. (Enzyme Catalysis and Regulation: Mathew F. Hockin, Kenneth C. Jones, Stephen J. Everse, and Kenneth G. Maan. A Model for the Stoichiometric Regulation of Blood Coagulation. J. Biol. Chem. 2002, 277: 18322–18333. First published on March 13, 2002. Copyright © 2002, by the American Society for Biochemistry and Molecular Biology.)

8.5 COMPLEX REACTIONS

A *complex reaction* system consists of a combination of interacting series and parallel reactions. Overall, this algorithm

is very similar to the one given in [Chapter 6](#) for writing the mole balances in terms of molar flow rates and concentrations (i.e., [Figure 6-1](#)). After numbering each reaction, we write a mole balance on *each and every* species, similar to those in [Figure 6-1](#). The major difference between the two algorithms is in the rate-law step. As shown in [Table 8-2](#), we have three steps (3, 4, and 5) to find the net rate of reaction for each species in terms of the concentration of the reacting species. As an example, we shall study the following complex reactions

In business, it is usually important to keep your reactions proprietary.



This important complex reaction, which has been coded as A, B, C, and D for reasons of industrial propriety and National security, embodies virtually **all the nuances** needed to gain a thorough understanding of multiple reactions occurring in common industrial reactors. The following three examples model this reaction in a PBR, a CSTR, and a semibatch reactor, respectively.

8.5.1 Complex Gas-Phase Reactions in a PBR

We now apply the algorithms in [Tables 8-1](#) and [8-2](#) to a very important complex reaction carried out in a PBR. As mentioned, in order to protect the confidential nature of this reaction the chemicals have been given the names A, B, C, and D.

Example 8–5 Multiple Gas-Phase Reactions in a PBR

The following solid catalyzed complex gas-phase reactions follow elementary rate laws



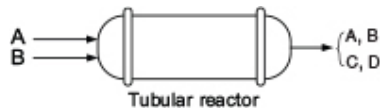
and take place isothermally in a PBR. The feed is equimolar in A and B with $F_{A0} = 10 \text{ mol/min}$ and the volumetric flow rate is $100 \text{ dm}^3/\text{min}$. The catalyst weight is 1000 kg, the pressure drop is $\alpha = 0.0019 \text{ kg}^{-1}$, and the total entering concentration is $C_{T0} = 0.2 \text{ mol/dm}^3$.

$$k_{1A} = 100 \left(\frac{\text{dm}^9}{\text{mol}^2 \cdot \text{kg} \cdot \text{cat} \cdot \text{min}} \right) \text{ and } k_{2C} = 1,500 \left(\frac{\text{dm}^{15}}{\text{mol}^4 \cdot \text{kg} \cdot \text{cat} \cdot \text{min}} \right)$$

Plot and analyze F_A , F_B , F_C , F_D , p , and $S_{C/D}$ as a function of catalyst weight, W .

Solution

Following the algorithm in Table 8-2 and having numbered our reactions, we now proceed to carry out a mole balance on each and every species in the reactor.



Gas-Phase PBR

1. Mole Balances

$$\frac{dF_A}{dw} = r'_A \quad \left(F_{A0} = 10 \frac{\text{mol}}{\text{min}} \right) \quad W_f = 1000 \text{ kg} \quad (\text{E8-5.1})$$

$$(2) \quad \frac{dF_B}{dw} = r'_B \quad \left(F_{B0} = 10 \frac{\text{mol}}{\text{min}} \right) \quad (\text{E8-5.2})$$

$$(3) \quad \frac{dF_C}{dW} = r'_C \quad (\text{E8-5.3})$$

$$(4) \quad \frac{dF_D}{dW} = r'_D \quad (\text{E8-5.4})$$

2. Rates

Net Rates

$$(5) \quad r'_A = r'_{1A} + r'_{2A} \quad (\text{E8-5.5})$$

$$(6) \quad r'_B = r'_{1B} \quad (\text{E8-5.6})$$

$$(7) \quad r'_C = r'_{1C} + r'_{2C} \quad (\text{E8-5.7})$$

$$(8) \quad r'_D = r'_{2D} \quad (\text{E8-5.8})$$

Rate Laws

$$(9) \quad r'_{1A} = -k_{1A} C_A C_B^2 \quad (\text{E8-5.9})$$

$$(10) \quad r'_{2C} = -k_{2C} C_A^2 C_C^3 \quad (\text{E8-5.10})$$

Relative Rates

$$\text{Reaction 1: } A + 2B \longrightarrow C \quad \frac{r'_{1A}}{-1} = \frac{r'_{1B}}{-2} = \frac{r'_{1C}}{1}$$

$$(11) \quad r'_{1B} = 2r'_{1A} \quad (\text{E8-5.11})$$

$$(12) \quad r'_{1C} = r'_{1A} \quad (\text{E8-5.12})$$

$$\text{Reaction 2: } 2A + 3C \rightarrow D \quad \frac{r'_{2A}}{-2} = \frac{r'_{2C}}{-3} = \frac{r'_{2D}}{1}$$

$$(13) \quad r'_{2A} = \frac{2}{3} r'_{2C} \quad (\text{E8-5.13})$$

$$(14) \quad r'_{2D} = -\frac{1}{3} r'_{2C} \quad (\text{E8-5.14})$$



The net rates of reaction for species A, B, C, and D are

$$\begin{aligned} r'_A &= r'_{1A} + r'_{2A} = -k_{1A} C_A C_B^2 - \frac{2}{3} k_{2C} C_A^2 C_C^3 \\ r'_B &= r'_{1B} = -2k_{1A} C_A C_B^2 \\ r'_C &= r'_{1C} + r'_{2C} = k_{1A} C_A C_B^2 - k_{2C} C_A^2 C_C^3 \\ r'_D &= r'_{2D} = \frac{1}{3} k_{2C} C_A^2 C_C^3 \end{aligned}$$

Selectivity

$$\tilde{S}_{C/D} = \frac{F_C}{F_D}$$

Tricks of the Trade

One observes that at $W = 0$, $F_D = 0$ causing $S_{C/D}$ to go to infinity and thus causing the ODE solver to crash. Therefore, we set $S_{C/D} = 0$ between $W = 0$ and a very small number, $W = 0.0001$ kg, to prevent Polymath, as well as other ODE solvers such as MATLAB and Excel, from crashing. In Polymath, this condition is written

$$(15) \quad S_{C/D} = \text{if } (W > 0.0001) \text{ then } \left(\frac{F_C}{F_D} \right) \text{ else } (0) \quad (\text{E8-5.15})$$

3. Stoichiometry Isothermal $T = T_0$

$$(16) \quad C_A = C_{T0} \left(\frac{F_A}{F_T} \right) p \quad (\text{E8-5.16})$$

$$(17) C_B = C_{T0} \left(\frac{F_B}{F_T} \right) p \quad (\text{E8-5.17})$$

$$(18) C_C = C_{T0} \left(\frac{F_C}{F_T} \right) p \quad (\text{E8-5.18})$$

$$(19) C_D = C_{T0} \left(\frac{F_D}{F_T} \right) p \quad (\text{E8-5.19})$$

$$(20) \frac{dp}{dW} = -\frac{\alpha}{2p} \left(\frac{F_T}{F_{T0}} \right) \quad (\text{E8-5.20})$$

$$(21) F_T = F_A + F_B + F_C + F_D \quad (\text{E8-5.21})$$

$$(22) X_A = \frac{F_{A0} - F_A}{F_{A0}} \quad (\text{E8-5.22A})$$

$$(23) X_B = \frac{F_{B0} - F_B}{F_{B0}} \quad (\text{E8-5.22B})$$

4. Parameters

$$(24) C_{T0} = 0.2 \text{ mol/dm}^3$$

$$(25) \alpha = 0.0019 \text{ kg}^{-1}$$

$$(26) v_0 = 100 \text{ dm}^3/\text{min}$$

$$(27) k_{1A} = 100 (\text{dm}^9/\text{mol}^2)/\text{min/kg-cat}$$

$$(28) k_{2C} = 1500 (\text{dm}^{15}/\text{mol}^4)/\text{min/kg-cat}$$

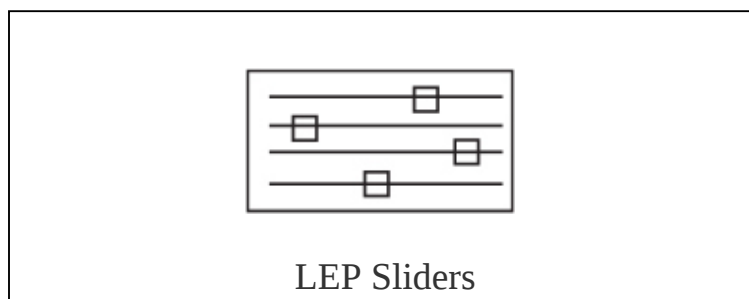
$$(29) F_{T0} = 20 \text{ mol/min}$$

$$(30) F_{A0} = 10$$

$$(31) F_{B0} = 10$$

Entering the above equations into Polymath's ODE solver, we obtain the following results in Table E8-5.1 and Figures E8-5.1 and E8-5.2.

Analysis: This example is a very important one as it shows, step by step, how to handle isothermal complex reactions. For complex reactions occurring in any of the reactors shown in [Figure 8-2](#), a numerical solution is virtually always required. The Polymath program and sample results are shown in [Table E8-5.1](#). This problem is a Living Example Problem, *LEP*, so the reader can download the Polymath code or perhaps better use the LEP sliders to vary the reaction parameters (e.g., k_{1A} , α , and k_{2C}) to learn how [Figures E8-5.1](#) and [E8-5.2](#) change (<http://www.umich.edu/~elements/6e/08chap/live.html>).



Decision: Selectivity *versus* Product Molar Flow Rate

In looking at the solution we note from [Figure E8-5.2](#) that the selectivity reaches a maximum very close to the entrance ($W \approx 60$ kg) and then drops rapidly. However, 90% of A is not consumed until 200 kg, the catalyst weight at which the desired product C reaches its maximum flow rate. If the activation energy for reaction (1) is greater than that for reaction (2), try increasing the temperature to increase the molar flow rate of C and selectivity. However, if that does not help, then one has to decide which is more important,

selectivity or the molar flow rate of the desired product. In the former case, the PBR catalyst weight will be 60 kg. In the latter case, the PBR catalyst weight will be 200 kg.

TABLE E8-5.1 POLYMATH PROGRAM AND OUTPUT

Differential equations

1. $d(F_a)/d(W) = r_a$
2. $d(F_b)/d(W) = r_b$
3. $d(F_c)/d(W) = r_c$
4. $d(F_d)/d(W) = r_d$
5. $d(p)/d(W) = -\alpha/2 \cdot p \cdot (F_t/F_{t0})$

Explicit equations

1. $F_{t0} = 20$
2. $\alpha = 0.0019$
3. $F_t = F_a + F_b + F_c + F_d$
4. $k_{1a} = 100$
5. $k_{2c} = 1500$
6. $C_{t0} = 0.2$
7. $C_a = C_{t0} \cdot (F_a/F_t)^p$
8. $C_b = C_{t0} \cdot (F_b/F_t)^p$
9. $C_c = C_{t0} \cdot (F_c/F_t)^p$
10. $r_{1a} = -k_{1a} \cdot C_a \cdot C_b^2$

$$11. r_{1b} = 2 * r_{1a}$$

$$12. r_b = r_{1b}$$

$$13. r_{2c} = -k_{2c} * C_a^2 * C_c^3$$

$$14. r_{2a} = 2/3 * r_{2c}$$

$$15. r_{2d} = -1/3 * r_{2c}$$

$$16. r_{1c} = -r_{1a}$$

$$17. r_d = r_{2d}$$

$$18. r_a = r_{1a} + r_{2a}$$

$$19. r_c = r_{1c} + r_{2c}$$

$$20. v = 100$$

$$21. F_{bo} = 10$$

$$22. F_{ao} = 10$$

$$23. X_b = (F_{bo} - F_b) / F_{bo}$$

$$24. X_a = (F_{ao} - F_a) / F_{ao}$$

$$25. C_d = C_{to} * (F_d / F_t) * p$$

$$26. S_{cd} = \text{if}(W > 0.0001) \text{ then } (F_c / F_d) \text{ else } (0)$$

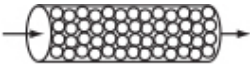
Calculated values of DEQ variables

	Variable	Initial value	Final value
1	alpha	0.0019	0.0019

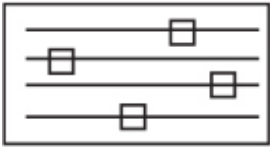
2	Ca	0.1	0.0257858
3	Cb	0.1	0.0020471
4	Cc	0	0.0211051
5	Cd	0	0.0026336
6	Cto	0.2	0.2
7	Fa	10.	4.293413
8	Fao	10.	10.
9	Fb	10.	0.3408417
10	Fbo	10.	10.
11	Fc	0	3.514068
12	Fd	0	0.4385037
13	Ft	20.	8.586827
14	Fto	20.	20.

15	k1a	100.	100.
16	k2c	1500.	1500.
17	p	1.	0.2578577
18	r1a	-0.1	-1.081E-05
19	r1b	-0.2	-2.161E-05
20	r1c	0.1	1.081E-05
21	r2a	0	-6.251E-06
22	r2c	0	-9.376E-06
23	r2d	0	3.126e-06
24	ra	-0.1	-1.706E-05
25	rb	-0.2	-2.161E-05
26	rc	0.1	1.429E-06

27	rd	0	3.126e-06
28	Scd	0	8.01377
29	v	100.	100.
30	W	0	1000.
31	Xa	0	0.5706587
32	Xb	0	0.9659158



PBR Results



LEP Sliders

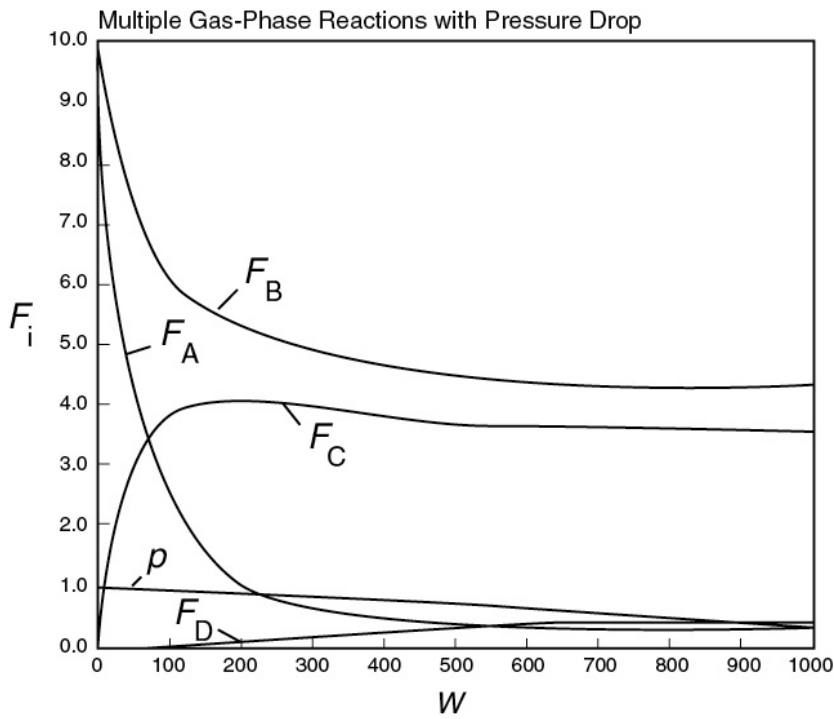


Figure E8-5.1 Molar flow rate profiles.

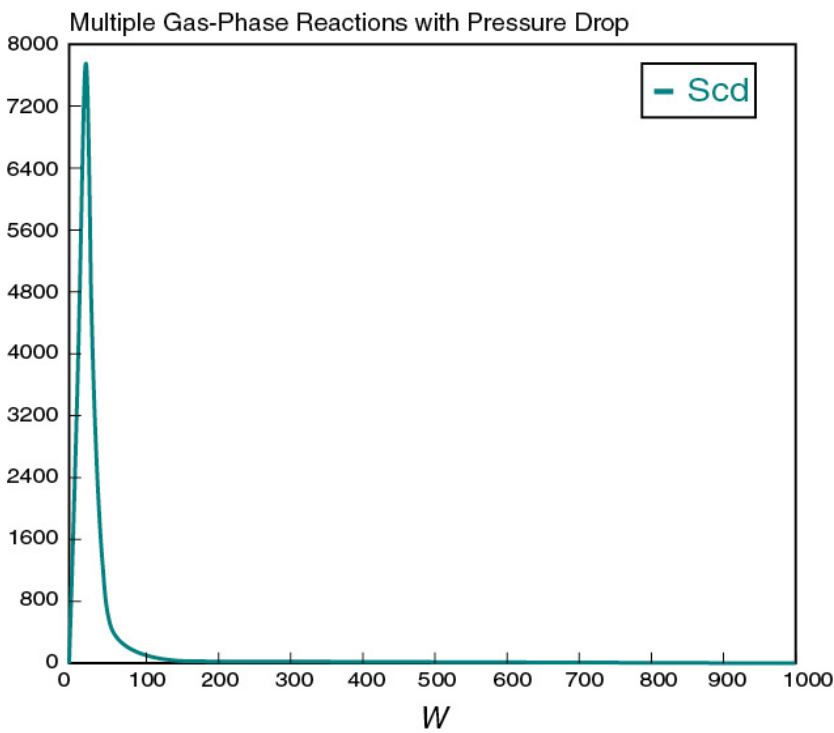


Figure E8-5.2 Selectivity profile.

Go to this LEP on the CRE Web site and use Wolfram or Python Sliders to vary parameters to gain a full understanding of this reaction and reactor.

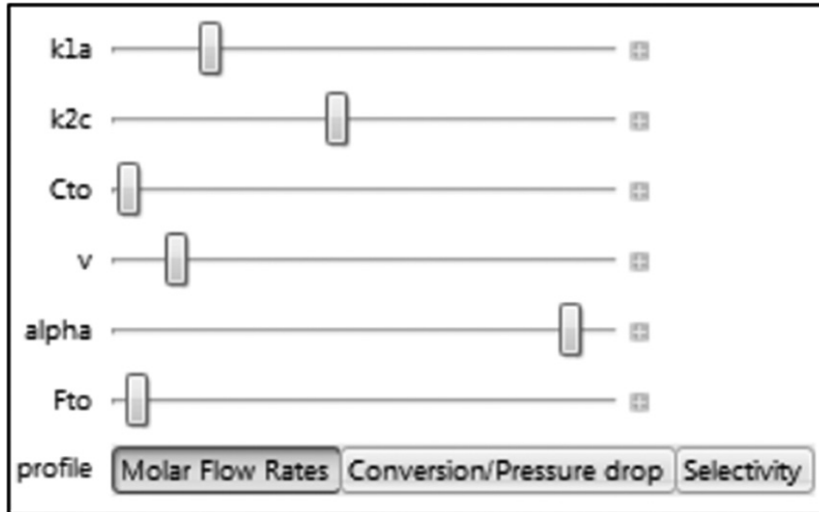


Figure E8-5.3 Wolfram sliders.

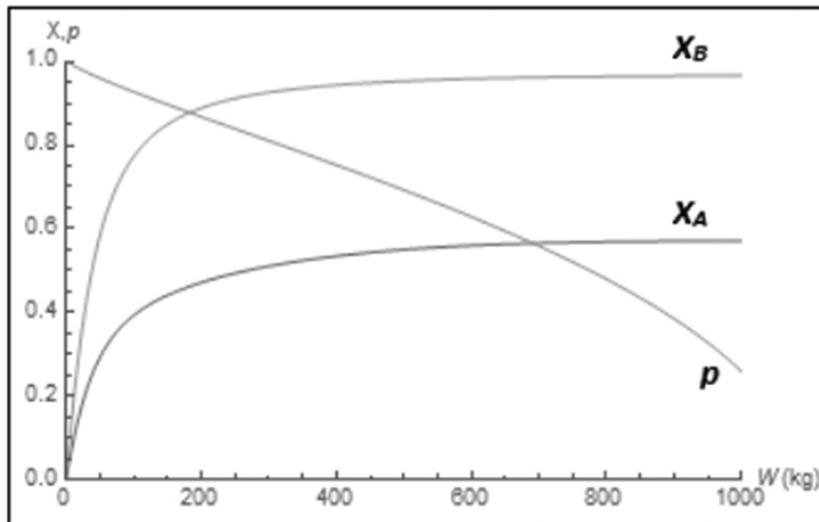


Figure E8-5.4 Wolfram conversion profiles.

The molar flow rate profiles are shown in [Figure E8-5.1](#), while the selectivity and conversion profiles are

shown in Figures E8-5.2 and E8-5.4, respectively.

8.5.2 Complex Liquid-Phase Reactions in a CSTR

For a CSTR, a coupled set of algebraic equations analogous to the PFR differential equations must be solved. These equations are arrived at from a mole balance on CSTR for every species which are then coupled with the rates step and stoichiometry.

For q liquid-phase reactions occurring where N different species are present, we have the following set of algebraic equations:

$$F_{10} - F_1 = -r_1 V = V \sum_{i=1}^q -r_{i1} = V \cdot f_1(C_1, \dots, C_N) \quad (8-17)$$

$$\vdots$$

$$F_{j0} - F_j = -r_j V = V \cdot f_j(C_1, \dots, C_N) \quad (8-18)$$

$$\vdots$$

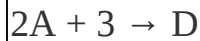
$$F_{N0} - F_N = -r_N V = V \cdot f_N(C_1, \dots, C_N) \quad (8-19)$$

We can use a nonlinear algebraic equation solver (NLE) in Polymath or a similar program to solve Equations (8-17)–(8-19).

Example 8–6 Complex Reactions in a Liquid-Phase CSTR

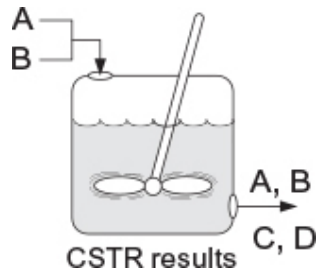
The complex reactions discussed in [Example 8-5](#) now take place in the liquid phase in a 2500 dm³ CSTR. The feed is equimolar in A and B with $F_{A0} = 200$ mol/min and the volumetric flow rate is 100 dm³/min. The rate constants are

$$k_{1A} = 10 \left(\frac{\text{dm}^3}{\text{mol}} \right)^2 / \text{min} \quad \text{and} \quad k_{2C} = 15 \left(\frac{\text{dm}^3}{\text{mol}} \right)^4 / \text{min}$$



Find the concentrations of A, B, C, and D exiting the reactor, along with the exiting selectivity, $\tilde{S}_{C/D}$.

$$\tilde{S}_{C/D} = \frac{C_C}{C_D}$$



Solution

Liquid-Phase CSTR: $v = v_0$ (Polymath Formulation)

Mole Balances

(1)

$$f(C_A) = v_0 C_{A0} - v_0 C_A + r_A V \quad (\text{E8-6.1})$$

(2)

$$f(C_B) = v_0 C_{B0} - v_0 C_B + r_B V \quad (\text{E8-6.2})$$

$$(3) \quad f(C_C) = -v_0 C_C + r_C V \quad (\text{E8-6.3})$$

$$(4) \quad f(C_D) = -v_0 C_D + r_D V \quad (\text{E8-6.4})$$

The **Rate Laws**, **Relative Rates**, and **Net Rates** are the same as in Example 8-5. In addition, Steps (5)–(14) (i.e., Equations (E8-5.5)–(E8-5.14) from Example 8-5) remain unchanged for this example. This fact is going to save us a lot of time in solving this example problem.

Selectivity

Tricks of the Trade. Note: We add a very small number (0.001 mol/min) to the term in the denominator to prevent $S_{C/D}$ from going to infinity when $F_D = 0$.

(15)

$$\tilde{S}_{C/D} = \frac{F_C}{(F_D + 0.001)} \quad (\text{E8-6.5})$$

Parameters

$$(16) \quad v_0 = 100 \text{ dm}^3/\text{min}$$

$$(17) \quad k_{1A} = 10 (\text{dm}^3/\text{mol})^2/\text{min}$$

$$(18) \quad k_{2C} = 15 (\text{dm}^3/\text{mol})^4/\text{min}$$

$$(19) \quad V = 2500 \text{ dm}^3$$

$$(20) \quad C_{A0} = 2.0 \text{ mol/dm}^3$$

$$(21) \quad C_{B0} = 2.0 \text{ mol/dm}^3$$

These equations are now used to solve for the exit concentrations using Polymath's nonlinear equation solver as shown in Table E8-6.1.

Liquid-Phase CSTR

TABLE E8-6.1 POLYMATH PROGRAM AND OUTPUT

Nonlinear equations

- 1 $f(Ca) = v \cdot C_{a0} - v \cdot Ca + r_a \cdot V = 0$
- 2 $f(Cb) = v \cdot C_{b0} - v \cdot Cb + r_b \cdot V = 0$
- 3 $f(Cc) = -v \cdot Cc + r_c \cdot V = 0$
- 4 $f(Cd) = -v \cdot Cd + r_d \cdot V = 0$

Explicit equations

- 1 $k_{1a} = 10$
- 2 $k_{2c} = 15$
- 3 $r_{2c} = -k_{2c} \cdot Ca^2 \cdot Cc^3$
- 4 $r_{1a} = -k_{1a} \cdot Ca \cdot Cb^2$
- 5 $r_{1b} = 2 \cdot r_{1a}$
- 6 $r_{2a} = 2/3 \cdot r_{2c}$
- 7 $r_{1c} = -r_{1a}$
- 8 $r_{2d} = -1/3 \cdot r_{2c}$
- 9 $r_b = r_{1b}$
- 10 $r_a = r_{1a} + r_{2a}$
- 11 $C_{a0} = 2$
- 12 $C_{b0} = 2$
- 13 $r_c = r_{1c} + r_{2c}$
- 14 $r_d = r_{2d}$
- 15 $V = 2500$
- 16 $v = 100$
- 17 $S_{cd} = Cc / (Cd + 0.001)$

POLYMATH Report

Nonlinear Equations

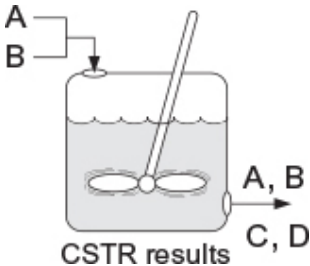
Calculated values of NLE variables

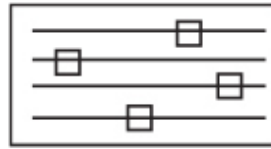
	Variable	Value	f(x)	Initial Guess
1	Ca	0.5326529	-3.979E-13	2.
2	Cb	0.0848008	8.527E-14	1.
3	Cc	0.1929784	-7.354E-13	1.
4	Cd	0.2548737	2.345E-13	0.1

Results

	Variable	Value
1	Cao	2.
2	Cbo	2.
3	k1a	10.
4	k2c	15.
5	r1a	-0.038304
6	r1b	-0.076608
7	r1c	0.038304
8	r2a	-0.0203899
9	r2c	-0.0305848
10	r2d	0.0101949
11	ra	-0.0586939
12	rb	-0.076608
13	rc	0.0077191
14	rd	0.0101949
15	Scd	0.7541941
16	v	100.
17	V	2500.

Selectivity





LEP Sliders

#UseLEPSliders ToPlayWithThis ReactionSystem

The exit concentrations are $C_A = 0.53$ M, $C_B = 0.085$ M, $C_C = 0.19$ M, and $C_D = 0.25$ M with $\tilde{S}_{C/D} = 0.75$. The corresponding conversion of A is

$$X = \frac{C_{A0} - C_A}{C_{A0}} = \frac{2 - 0.533}{2} = 0.73$$

$C_A = 0.53$ M
 $C_B = 0.085$ M
 $C_C = 0.19$ M
 $C_D = 0.25$ M
 $S_{C/D} = 0.75$
 $X = 0.73$

Analysis: The CRE algorithm for a complex reaction carried out in a CSTR was solved using the nonlinear equation solver. The CSTR exit concentrations shown in the results table correspond to a selectivity $\tilde{S}_{C/D} = 0.75$, as shown in the Polymath report. While the CSTR conversion is reasonable, the selectivity is rather low. The PFR is a better choice for these reactions to maximize selectivity.

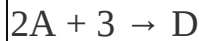
8.5.3 Complex Liquid-Phase Reactions in a Semibatch Reactor

Next up is the application of Tables 8-1 and 8-2 to a complex reaction carried out in a semibatch reactor.

Example 8–7 Complex Reactions in a Semibatch Reactor

The complex liquid-phase reactions discussed in [Example 8-6](#) now take place in a semibatch reactor where A is fed to B with $F_{A0} = 3 \text{ mol/min}$. The volumetric flow rate is $10 \text{ dm}^3/\text{min}$ and the initial reactor volume is 1000 dm^3 . The rate constants are

$$k_{1A} = 10 \left(\frac{\text{dm}^3}{\text{mol}} \right)^2 / \text{min} \quad \text{and} \quad k_{2C} = 15 \left(\frac{\text{dm}^3}{\text{mol}} \right)^4 / \text{min}$$



The maximum volume is 2000 dm^3 . The inlet concentration of A is $C_{A0} = 0.3 \text{ mol/dm}^3$ and the initial concentration of B is $C_{Bi} = 0.2 \text{ mol/dm}^3$.

(a) Plot and analyze N_A , N_B , N_C , N_D , and $S_{C/D}$ as a function of time.

Solution

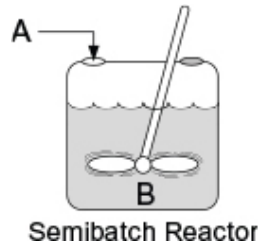
Mole Balances

$$(1) \quad \frac{dN_A}{dt} = r_A V + F_{A0} \quad (N_{Ai} = 0) \quad (\text{E8-7.1})$$

$$(2) \quad \frac{dN_B}{dt} = r_B V \quad (N_{Bi} = C_{Bi} V_0 = 200 \text{ moles}) \quad (\text{E8-7.2})$$

$$(3) \quad \frac{dN_C}{dt} = r_C V \quad (N_{Ci} = 0) \quad (\text{E8-7.3})$$

$$(4) \quad \frac{dN_D}{dt} = r_D V \quad (N_{Di} = 0) \quad (\text{E8-7.4})$$



Net Rates, Rate Laws, and Relative Rates are the same as liquid-phase CSTR.

Same as Step 2 in Example 8-5, that is, Steps (5)–(14), Equations (E8-5.5)–(E8-5.14).

Stoichiometry

$$(15) \quad C_A = N_A/V \quad (\text{E8-7.5})$$

$$(16) \quad C_B = N_B/V \quad (\text{E8-7.6})$$

$$(17) \quad C_C = N_C/V \quad (\text{E8-7.7})$$

$$(18) \quad C_D = N_D/V \quad (\text{E8-7.8})$$

$$(19) \quad V = V_0 + v_0 t \quad (\text{E8-7.9})$$

$$(20) \quad X_B = \frac{N_{B0} - N_B}{N_{B0}} \quad (\text{E8-7.10})$$

Selectivity

Tricks of the Trade. Because N_D is 0 at time $t = 0$, the selective goes to infinity so we again use an “if” statement.

(21)

$$\tilde{S}_{C/D} = \text{if } (t > 0.0001 \text{ min}) \text{ then } \left(\frac{N_C}{N_D} \right) \text{ else } (0) \quad (\text{E8-7.11})$$

Parameters

New Parameters

$$(22) v_0 = 10 \text{ dm}^3/\text{min}$$

$$(23) V_0 = 1000 \text{ dm}^3$$

$$(24) F_{A0} = 3 \text{ mol/min}$$

Putting this information into Polymath's ODE solver, we obtain the following results.

Liquid-Phase Multiple Reactions in a Semibatch Reactor

Differential equations

$$1. d(N_b)/d(t) = r_b \cdot V$$

$$2. d(N_a)/d(t) = r_a \cdot V + F_{A0}$$

$$3. d(N_d)/d(t) = r_d \cdot V$$

$$4. d(N_c)/d(t) = r_c \cdot V$$

Explicit equations

$$1. k_{1a} = 10$$

$$2. k_{2c} = 15$$

$$3. V_0 = 1000$$

$$4. v_0 = 10$$

$$5. V = V_0 + v_0 \cdot t$$

$$6. C_a = N_a/V$$

$$7. C_b = N_b/V$$

$$8. r_{1a} = -k_{1a} \cdot C_a \cdot C_b^2$$

$$9. C_c = N_c/V$$

$$10. r1b = 2 * r1a$$

$$11. rb = r1b$$

$$12. r2c = -k2c * Ca^2 * Cc^3$$

$$13. Fao = 3$$

$$14. r2a = 2/3 * r2c$$

$$15. r2d = -1/3 * r2c$$

$$16. rlc = -r1a$$

$$17. rd = r2d$$

$$18. ra = r1a + r2a$$

$$19. Cd = Nd/V$$

$$20. rc = rlc + r2c$$

$$21. Scd = \text{if}(t > 0.0001) \text{ then } (Nc/Nd) \text{ else } (0)$$

$$22. Nbo = 200$$

$$23. X = 1 - Nb/Nbo$$

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	Ca	0	0.1034461
2	Cb	0.2	0.0075985

3	Cc	0	0.0456711
4	Cd	0	0.0001766
5	Fao	3.	3.
6	k1a	10.	10.
7	k2c	15.	15.
8	Na	0	206.8923
9	Nb	200.	15.197
10	Nbo	200.	200.
11	Nc	0	91.34215
12	Nd	0	0.3531159
13	r1a	0	-5.973E-05
14	r1b	0	-0.0001195
15	rlc	0	5.973E-05

16	r2a	0	-1.019E-05
17	r2c	0	-1.529E-05
18	r2d	0	5.097E-06
19	ra	0	-6.992E-05
20	rb	0	-0.0001195
21	rc	0	4.444E-05
22	rd	0	5.097E-06
23	Scd	0	258.6747
24	t	0	100.
25	V	1000.	2000.
26	Vo	1000.	1000.
27	vo	10.	10.

28	X	0	0.924015
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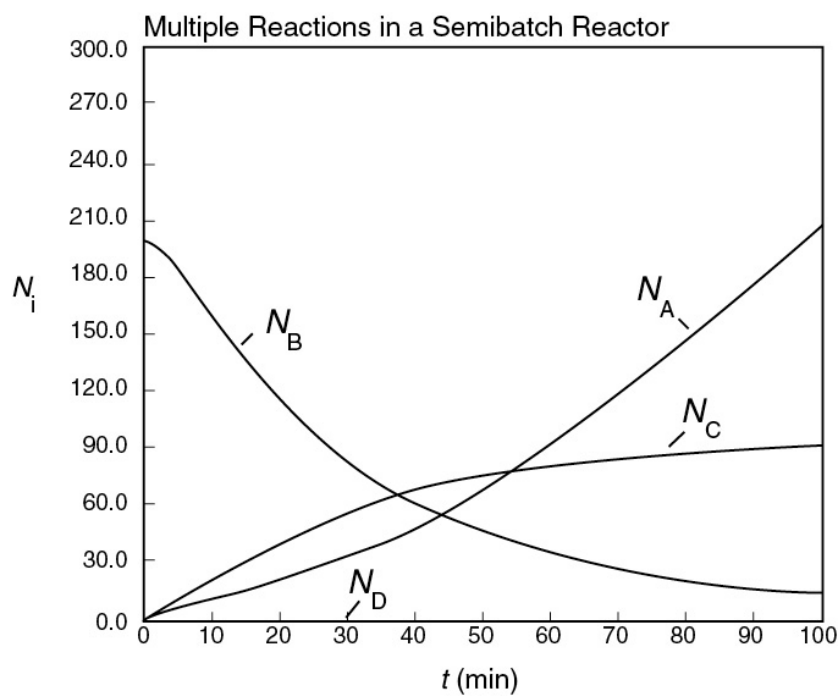
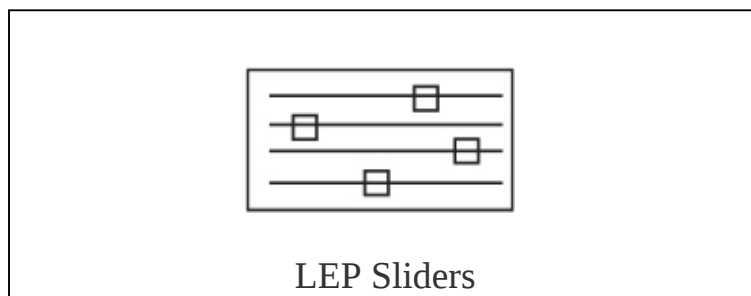
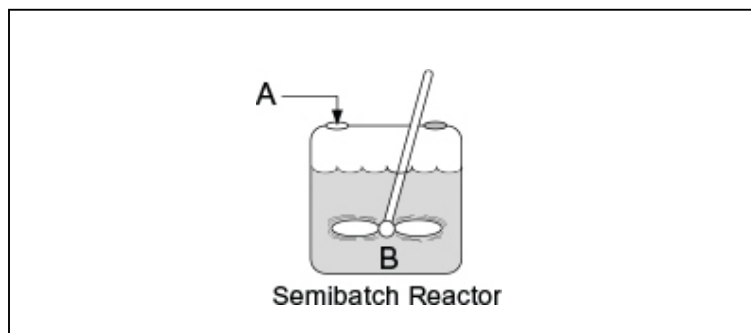


Figure E8-7.1 Number of moles as a function of time.

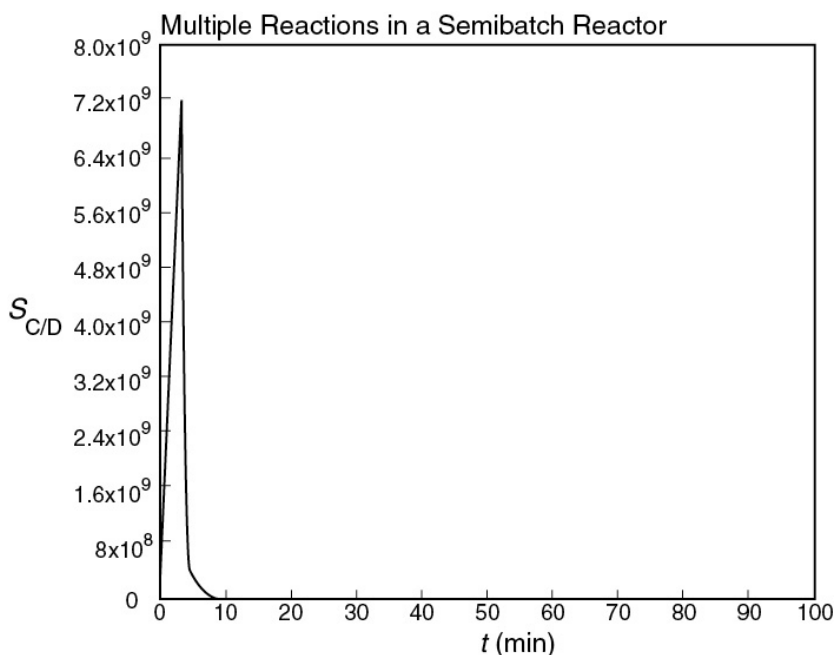


Figure E8-7.2 Selectivity as a function of time.

#LEPSliders

Analysis: The CRE algorithm for a complex reaction was applied to a semibatch reactor and solved using the ODE solver Polymath. The maximum in the selectivity occurs after only 6.5 minutes (as shown in Figure E8-7.2); however, very little of the desired product, C, has been formed at this time. If $E_D > E_U$, first try changing the temperature to see whether that will improve the amount of product formed while keeping the selectivity high. If that does not work, an economical decision needs to be made. Are selectivity and the cost of separating C and D more important than making more C to sell?

One notes in Figure E8-7.1 that after 70 minutes, very little change in the number of moles of species B, C, and D takes place; however, the number of moles of A

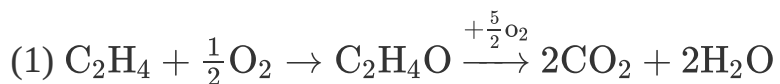
continue to increase because it is continually fed and there isn't sufficient B to react with A. The number of moles of D produced is so small that it is indistinguishable from the x-axis in Figure E8-7.1. Finally, we note that these times, 6.5 and 10 minutes, are **far too short to use a semibatch** reactor and, consequently, one should consider another reactor scheme such as Figure 8-2(g), where A is fed along the length of the reactor, or analogous to that shown in Figure 8-2(h), where A is fed to each of the CSTRs.

Takeaway lesson: Reaction time is far too short for a batch or semibatch reactor

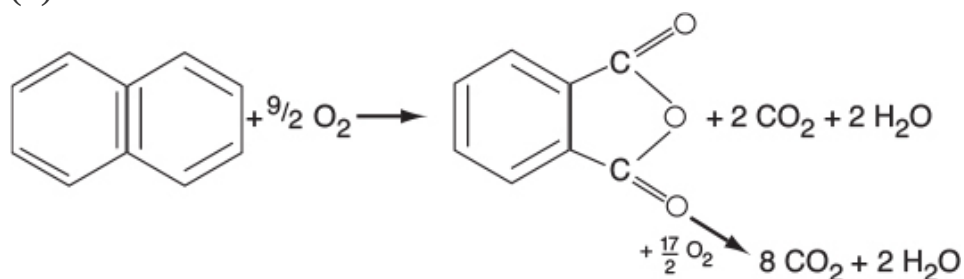
8.6 MEMBRANE REACTORS TO IMPROVE SELECTIVITY IN MULTIPLE REACTIONS

In addition to using membrane reactors (MRs) to remove a reaction product in order to shift the equilibrium toward completion, we can use membrane reactors to increase selectivity in multiple reactions. This increase can be achieved by injecting one of the reactants along the length of the reactor. It is particularly effective in partial oxidation of hydrocarbons, as well as chlorination, ethoxylation, hydrogenation, nitration, and sulfonation reactions, to name a few.²

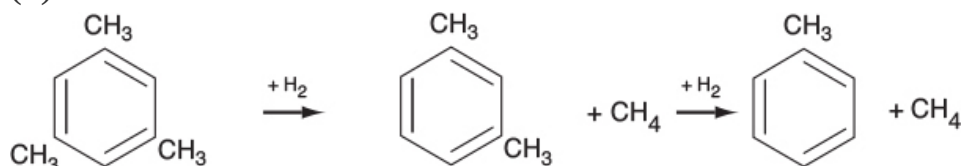
² W. J. Asher, D. C. Bomberger, and D. L. Huestis, *Evaluation of SRI's Novel Reactor Process Permixon™*, New York: AIChE, 2000.



(2)



(3)



In reactions (1) and (2), the desired product is the intermediate (e.g., $\text{C}_2\text{H}_4\text{O}$). However, because there is oxygen present, the reactants and intermediates can be completely oxidized to form undesired products, CO_2 and water. The desired product in Reaction (3) is xylene. We can enhance selectivity by keeping one of the reactants at a low concentration, which can be achieved by feeding it through the sides of a membrane reactor.

In the solved example problem in the *Chapter 8 Expanded Material* on the CRE Web site

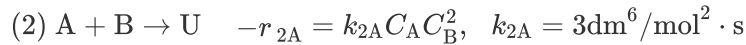
(http://www.umich.edu/~elements/6e/08chap/expanded_08chap_1.pdf), we have used a membrane reactor (MR) for the hydrodealkylation of mesitylene reaction. In some ways, this CRE Web site example parallels the use of MRs for partial oxidation reactions. We will now do an example for a different reaction to illustrate the advantages of an MR for certain types of reactions.



Solved Problem Mesitylene Reactions

Example 8–8 Membrane Reactor (MR) to Improve Selectivity in Multiple Reactions

The reactions



take place in the gas phase. The overall selectivities, $\tilde{S}_{D/U}$, are to be compared for a membrane reactor (MR) and a conventional PFR.[†] First, we use the instantaneous selectivity to determine which species should be fed through the membrane

$$S_{D/U} = \frac{k_1 C_A^2 C_B}{k_2 C_B^2 C_A} = \frac{k_1 C_A}{k_2 C_B}$$

[†] Prof. Dr. Sven Köttlov in the chemical engineering department at Jofostan University in RiÖa, Jofostan, is one of the best membrane analysts in that area of the world.

We see that to maximize $S_{D/U}$, we need to keep the concentration of A high and the concentration of B low; therefore, we feed small amounts of B along the reactor through the membrane. The molar flow rate of A entering the reactor is 4 mol/s and that of B entering through the membrane is 4 mol/s, as shown in Figure E8-8.1. For the PFR, B enters along with A.

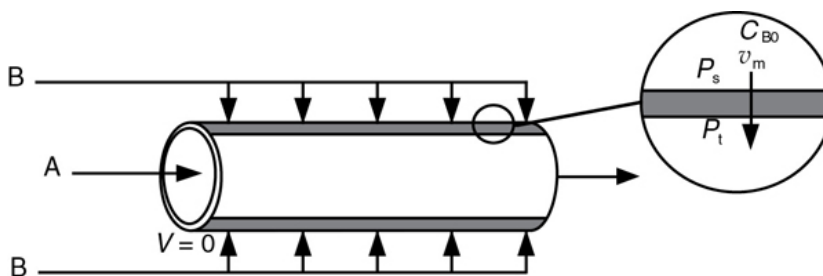


Figure E8-8.1 Membrane reactor with one reactant fed through the sides.

The reactor volume is 50 dm³ and the entering total concentration is 0.8 mol/dm³.

Plot and analyze the molar flow rates and the overall selectivity, $\tilde{S}_{D/U}$, as a function of reactor volume for both the MR and PFR.

Solution

1. Mole Balances for Both the PFR and the MR

PFR	MR
Species A: $\frac{dF_A}{dV} = r_A$ (E8-8.1[a])	$\frac{dF_A}{dV} = r_A$ (E8-8.1[b])
Species B: $\frac{dF_B}{dV} = r_B$ (E8-8.2[a])	$\frac{dF_B}{dV} = r_B + R_B$ (E8-8.2[b])
Species D: $\frac{dF_D}{dV} = r_D$ (E8-8.3[a])	$\frac{dF_D}{dV} = r_D$ (E8-8.3[b])
Species U: $\frac{dF_U}{dV} = r_U$ (E8-8.4[a])	$\frac{dF_U}{dV} = r_U$ (E8-8.4[b])



2. Net Rates and Rate Laws (same for PFR and MR)

$$r_A = r_{1A} + r_{2A} = -k_{1A}C_A^2C_B - k_{2A}C_AC_B^2 \quad (\text{E8-8.5})$$

$$r_B = r_{1B} + r_{2B} = -k_{1A}C_A^2C_B - k_{2A}C_AC_B^2 \quad (\text{E8-8.6})$$

$$r_D = r_{1D} = k_{1A}C_A^2C_B \quad (\text{E8-8.7})$$

$$r_U = r_{2U} = k_{2A}C_AC_B^2 \quad (\text{E8-8.8})$$

3. Transport Law (MR)

We now discuss the rate of transport of B into the reactor, R_B . From fluid mechanics we know that the volumetric flow rate through the membrane, v_m , is given by Darcy's Law.³

$$v_m = K[P_s - P_t]A_t \quad (\text{E8-8.9})$$

³ J. O. Wilkes, *Fluid Mechanics for Chemical Engineers with Microfluidics and CFD*, 2nd ed. Upper Saddle River, NJ: Prentice Hall, 2006.

where K is the membrane permeability ($\text{m/s} \cdot \text{kPa}$), P_s (kPa) and P_t (kPa) are the shell-side and tube-side pressures, and A_t is the membrane surface area (m^2). The flow rate through the membrane can be controlled by adjusting the pressure drop across the membrane ($P_s - P_t$). Recall from Equation (6-5) that “a” is the membrane surface area per unit volume of reactor

$$A_t = aV_t \quad (\text{E8-8.10})$$

The total molar flow rate of B through the sides of the reactor is

$$F_{B0} = C_{B0} v_m = \underbrace{C_{B0} K [P_s - P_t] a}_{R_B} \cdot V_t = R_B V_t \quad (\text{E8-8.11})$$

The total molar flow rate of B through the sides of the reactor is

$$R_B = \frac{F_{B0}}{V_t} \quad (\text{E8-8.12})$$

4. Stoichiometry (same for **PFR** and **MR**)

Isothermal ($T = T_0$) and neglect pressure drop down the length of the reactor ($P = P_0, p = 1.0$).

For no pressure drop down the length of the reactor and isothermal operation, the concentrations for both the PFR and MR are

$$C_A = C_{T0} \frac{F_A}{F_T} \quad (\text{E8-8.13})$$

$$C_B = C_{T0} \frac{F_B}{F_T} \quad (\text{E8-8.14})$$

$$C_D = C_{T0} \frac{F_D}{F_T} \quad (\text{E8-8.15})$$

$$C_U = C_{T0} \frac{F_U}{F_T} \quad (\text{E8-8.16})$$

$$X = \frac{F_{A0} - F_A}{F_{A0}} \quad (\text{E8-8.17})$$

Here, $T = T_0$ and $\Delta P = 0$.

5. Combine

The Polymath program will combine the mole balance, net rates, and stoichiometric equations to solve for the

molar flow rate and selectivity profiles for both the conventional PFR and the MR.

A note of caution on calculating the overall selectivity

$$\tilde{S}_{D/U} = \frac{F_D}{F_U} \quad (E8-8.18)$$

We again have to use tricks of the trade to fool Polymath because at the entrance of the reactor $F_U = 0$, Polymath will look at Equation (E8-8.18) and will not run because it will say you are dividing by zero. Therefore, we need to add a very small number to the denominator, say 0.0000001 mol/s (or smaller); that is

Fool Polymath!

$$\tilde{S}_{D/U} = \frac{F_D}{F_U + 0.0000001} \quad (E8-8.19)$$

Table E8-8.1 shows the Polymath program and report sheet.

Sketch the trends or results you expect **before** working out the details of the problem.

TABLE E8-8.1 POLYMATH PROGRAM

Polymath Program and Report Sheet content

Differential equations

- 1 $d(F_A)/d(V) = r_A$
- 2 $d(F_B)/d(V) = r_B + R_B$
- 3 $d(F_D)/d(V) = r_D$
- 4 $d(F_U)/d(V) = r_U$

Explicit equations

- 1 $F_t = F_A + F_B + F_D + F_U$
- 2 $C_{t0} = 0.8$
- 3 $k_1 a = 2$
- 4 $k_2 a = 3$
- 5 $C_b = C_{t0} \cdot F_b / F_t$
- 6 $C_a = C_{t0} \cdot F_a / F_t$
- 7 $r_A =$
 $-k_1 a \cdot C_a^2 \cdot C_b - k_2 a \cdot C_a \cdot C_b^2$
- 8 $r_B = r_A$
- 9 $C_d = C_{t0} \cdot F_d / F_t$
- 10 $C_u = C_{t0} \cdot F_u / F_t$
- 11 $r_d = k_1 a \cdot C_a^2 \cdot C_b$
- 12 $r_u = k_2 a \cdot C_a \cdot C_b^2$
- 13 $V_t = 50$
- 14 $F_{b0} = 4$
- 15 $R_b = F_{b0} / V_t$
- 16 $S_d u =$
 $F_d / (F_u + .000000000000001)$

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	Ca	0.8	0.2020242
2	Cb	0	0.2020242
3	Cd	0	0.2855303
4	Ct0	0.8	0.8
5	Cu	0	0.1104213
6	Fa	4.	1.351387
7	Fao	4.	4.
8	Fb	0	1.351387
9	Fbo	4.	4.
10	Fd	0	1.909979
11	Ft	4.	5.351387
12	Fu	0	0.7386336
13	k1a	2.	2.
14	k2a	3.	3.
15	ra	0	-0.0412269
16	Rb	0.08	0.08
17	rb	0	-0.0412269
18	rd	0	0.0164908
19	ru	0	0.0247361
20	Sdu	0	2.585827
21	V	0	50.
22	Vt	50.	50.
23	X	0	0.6621531

← Selectivity

We can easily modify the program, shown in Table E8-8.1, for the PFR simply by setting R_B equal to zero ($R_B = 0$) and the initial condition for B to be 4.0.

Figures E8-8.2(a) and E8-8.2(b) show the molar flow rate profiles for the conventional PFR and MR, respectively.

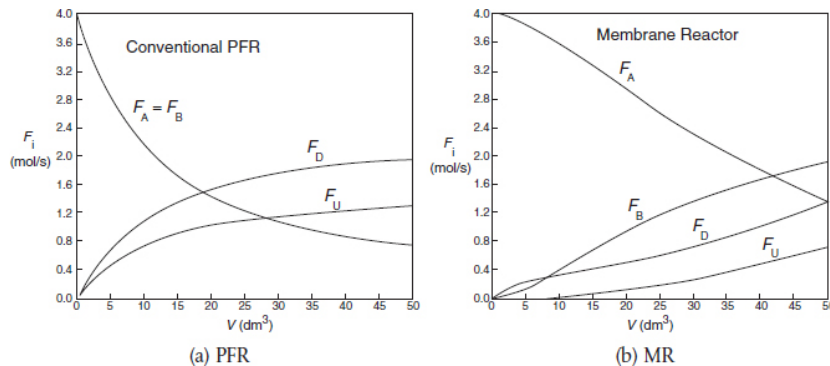
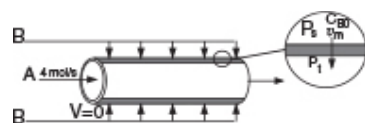


Figure E8-8.2 Molar flow rates.



Figures E8-8.3(a) and E8-8.3(b) show the selectivity for the PFR and MR. One notices the enormous enhancement in selectivity the MR has over the PFR.

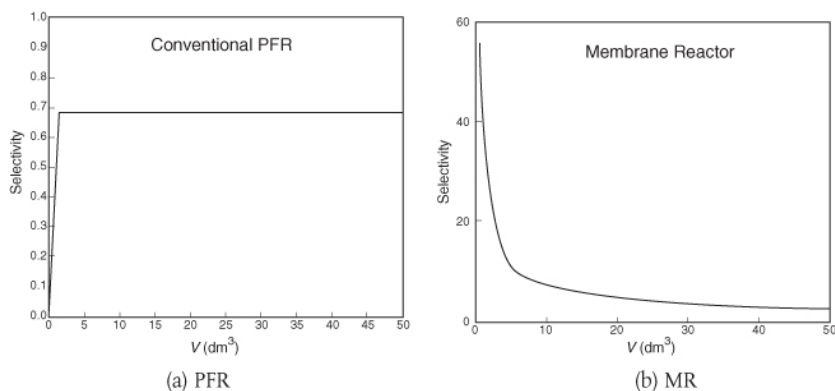


Figure E8-8.3 Selectivity.

LEP:

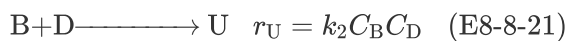
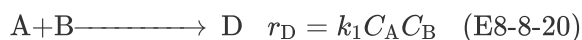
<http://www.umich.edu/~elements/6e/08chap/live.html>

Selectivities at $V = 5 \text{ dm}^3$

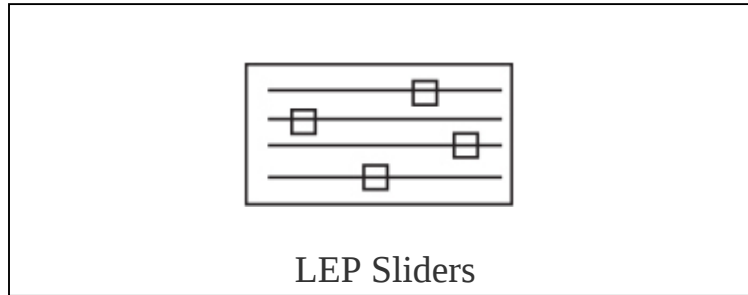
MR: $S_{D/U} = 14$

PFR: $S_{D/U} = 0.65$

Be sure to download this Living Example Problem (**LEP**) from the CRE Web site and use Wolfram to “play” with the reactions and reactors. With minor modifications, you can explore reactions analogous to partial oxidations



where oxygen (B) is fed through the side of the membrane (see Problem P8-15_C).



*#WithLEPYouCan BecomeAnExpert
OnSelectivityIn MembraneReactors*

Analysis: One notes that A is consumed more rapidly in the PFR than in the side-fed MR and that more of the desired product is also formed in the PFR. However, the selectivity is much higher in the MR than the PFR. One also notes, when comparing the molar flow rates, that the rates in the side-fed MR continue to change significantly after 30 dm³ down the reactor, while those in the PFR do not change significantly after 30 dm³. Again, one has to decide which is more important $S_{D/U}$ or X !

8.7 SORTING IT ALL OUT

In Example 8-5, we were given the rate laws and asked to calculate the product distribution profiles. The *inverse* of the problem described in Example 8-5 must frequently be solved. Specifically, the rate laws often must be determined from the variation in the product distribution profiles generated by changing the feed concentrations. In some instances, this determination may not be possible without carrying out

independent experiments on some of the reactions in the sequence. The best strategy to use to *sort out* all of the rate-law parameters will vary from reaction sequence to reaction sequence. Consequently, the strategy developed for one system may not be the best approach for other multiple-reaction systems. One general rule is to start an analysis by looking for species produced in only one reaction; next, study the species involved in only two reactions, then three, and so on.

When some of the intermediate products are free radicals, it may not be possible to perform independent experiments to determine the rate-law parameters. Consequently, we must deduce the rate-law parameters from changes in the distribution of reaction products with feed conditions. Under these circumstances, the analysis turns into an optimization problem to estimate the best values of the parameters that will minimize the sums of the squares between the calculated variables and measured variables. This process is basically the same as that described in [Section 7.5](#), but more complex, owing to the larger number of parameters to be determined. We begin by estimating the parameter values using some of the methods just discussed. Next, we use these estimates in nonlinear regression techniques to determine the best estimates of our parameter values from the data for all of the experiments.⁴ Polymath as well as other software packages are available for an analysis such as this one.

⁴ See, for example, Y. Bard, *Nonlinear Parameter Estimation*, San Diego, CA: Academic Press, 1974.

Nonlinear least squares

8.8 THE FUN PART



Once you get into it, it really is lots of fun.

I'm not talking about the fun you can have at an amusement park, but CRE fun. Now that we have an understanding on how to solve for the exit concentrations of multiple reactions in a CSTR and how to plot the species concentrations down the length of a PFR or PBR, we can address one of the most important and fun areas of chemical reaction engineering. This area, discussed in [Section 8.3](#), is learning how to maximize the desired product and minimize the undesired product. It is this area that can make or break a chemical process financially. It is also an area that requires creativity in designing the reactor schemes and feed conditions that will maximize profits. Here, you can mix and match reactors, feed streams, and side streams, as well as vary the ratios of feed concentration in order to maximize or minimize the selectivity of a particular species. Problems of this type are what I call *digital-age problems* because almost always one needs to use ODE solvers, along with critical and creative thinking skills, to find the best answer.^{5,6} A number of problems at the end of this chapter will allow you to practice these critical and creative thinking skills. These problems offer the opportunity to explore many different solution alternatives to enhance selectivity and have fun doing it. The chemical reaction engineering students at Jofostan University in Riça, Jofostan, have often commented on how much they enjoy the LEPs and

using Wolfram or Python to vary the parameters as they explore the problems and maximize the selective.

⁵ H. Scott Fogler, *Teaching Critical Thinking, Creative Thinking, and Problem Solving in the Digital Age*, Phillips Lecture, Stillwater, OK: OSU Press, 1997.

⁶ H. S. Fogler and S. E. LeBlanc, with B. Rizzo, *Strategies for Creative Problem Solving*, 3rd Ed. Upper Saddle River, NJ: Prentice Hall, 2014.

However, to carry CRE to the next level and to have a lot more fun solving multiple-reaction problems, we will have to be patient a little longer. The reason is that in this chapter we consider only isothermal multiple reactions, and it is nonisothermal multiple reactions where things really get interesting. Consequently, we will have to wait to carry out schemes to maximize the desired product in nonisothermal multiple reactions until we study heat effects in Chapters 11–13. After studying these chapters, we will add a new dimension to multiple reactions, as we now have another variable, temperature, that we may or may not be able to use to affect selectivity and yield. In one particularly interesting problem (**P12-26C**), we will study the production of styrene from ethylbenzene in which two side reactions, one endothermic and one exothermic, must be taken into account. Here, we may vary a whole slew of variables, such as entering temperature, diluent rate, and observed optima, in the production of styrene. However, we will have to delay gratification of the styrene study until we have mastered Chapters 11–13.

Multiple reactions with heat effects is unique to this book.

8.9 AND NOW... A WORD FROM OUR SPONSOR—SAFETY 8 (AWFOS—S8 THE FIRE TRIANGLE)

The fire triangle shown in [Figure 8-4](#), also referred to as the combustion triangle, is a visual representation of the three essential ingredients needed for the ignition of a fire. Why do we need this triangle? The triangle helps us visually to understand how an initiating incident and that all three sides are necessary to cause a fire/explosion to occur. It offers preventative information and gives a simple model to focus our attention on each of the sides to see how each component could be reduced or eliminated.



Figure 8-4 The fire triangle.

8.9.1 The Fire Triangle

Oxygen: An oxidizing agent is any substance in the combustion reaction that reacts with the fuel to yield an exothermic reaction. The most common oxidizing agent for combustion is oxygen because of its abundance in air. Other

oxidizers include such compounds as fluorine gas, perchlorate salts, and chlorine trifluoride.

Fuel: The fuel of the fire is any material that can burn. It can be any combustible material, such as wood, paper, flammable liquids or gases, rubber, or fabrics. The more fuel, the longer the fire can burn and spread.

A fuel usually needs to be “primed,” or heated to a minimum temperature, before it can ignite. Flammable vapor mixtures occur at, or above, the *flash point* temperature of the liquid. The *flash point* is the temperature at which a vapor-air mixture above a liquid is capable of sustaining combustion after ignition from an energy source. One exception is a fine droplet mist which can be flammable below the flash point of the liquid. Flammable gas mixtures can form at any temperature.

8.9.2 Defining Some Important Terms

Ignition Source: An ignition source is needed to either start the fire, preheat the fuel, and/or keep the fire alight. About 98% of all ignitions come from open flames, hot surfaces, hot gases, sparks from mechanical or electrical equipment, static electricity, and chemical reactions. Other ignition sources can include lightning strikes, electromagnetic radiation, or stray electrical currents.

Flammability Limit: Vapor in mixtures will only ignite and burn over a well-specified range of compositions.[†]

[†] The mixture is only combustible between the LFL and the UFL.

Lower Flammability Limit (LFL): Below the LFL the mixture will not burn as it is below the lower flammability

limit; that is, the mixture is too lean (e.g., insufficient fuel) for combustion.

Upper Flammability Limit (UFL): Above the UFL the mixture will not be combustible as the composition is too rich (e.g., insufficient oxygen).

Flash Point: Temperature at which a vapor-air mixture above a liquid is capable of sustaining combustion after ignition from an energy source.

8.9.3 Ways to Prevent Fires

To stop a fire only one of the three components need to be removed. There are many ways to reduce the risk of a fire, and a few are listed below:

- Eliminate ignition sources:
 - Do not weld (hot work) on or near containers that have contained or are containing flammable substances.
 - Make sure metal parts are grounded to reduce formation and accumulation of static electricity, which can cause a spark.
 - Avoid using electrical equipment around flammable liquids and gases as that heightens risk of fire and explosion.
- Reduce quantity of fuel:
 - Limit the amount of a flammable substance being stored.
 - Avoid storing large amounts of flammable substances near each other to prevent a fire from growing.
- Limit the oxidant concentration:

- Have a certified fire extinguisher on hand near open flames as well as flammable substances.
- Use nitrogen gas to dilute the concentration of flammable substances so they remain outside of their flammability limits.

8.9.4 Ways to Protect from Fires

Steps to take to protect people and facilities from fire damage:

- Use explosion-resistant vessels when designing a chemical process.
- Ensure adequate pressure relief devices are in place.
- Isolate high-temperature equipment (which can become an ignition source) from flammable materials.
- Install explosion-suppression devices.

Further Reading:

County Fire Protection. *Understanding Fire: The Fire Triangle*. (<https://county-fire.com/understanding-fire-the-fire-triangle>)

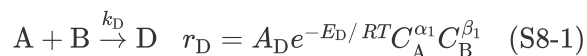
Closure. After completing this chapter, the reader should be able to describe the different types of multiple reactions (series, parallel, independent, and complex) and to select a reaction system that maximizes the selectivity. The reader should be able to write down and use the algorithm for solving CRE problems with multiple reactions. The reader should also be able to point out the major differences in the CRE algorithm for the multiple reactions from that for the single reactions, and then discuss why care must be taken when writing the rate law and stoichiometric steps to account for the rate laws for each reaction, the relative rates, and the net rates of reaction.

Finally, readers should feel a sense of accomplishment by knowing they have now reached a level where they can solve realistic CRE problems with complex kinetics.

SUMMARY

1. For the competing reactions

Reaction 1:



Reaction 2:



the instantaneous selectivity parameter is defined as

$$S_{D/U} = \frac{r_D}{r_U} = \frac{A_D}{A_U} \exp\left(-\frac{(E_D - E_U)}{RT}\right) C_A^{\alpha_1 - \alpha_2} C_B^{\beta_1 - \beta_2} \quad (\text{S8-3})$$

1. If $E_D > E_U$, the selectivity parameter $S_{D/U}$ will increase with increasing temperature.
2. If $\alpha_1 > \alpha_2$ and $\beta_2 > \beta_1$, the reaction should be carried out at high concentrations of A and low concentrations of B to maintain the selectivity parameter $S_{D/U}$ at a high value. Use a semibatch reactor with pure A initially or a tubular reactor in which B is fed at different locations down the reactor. Other cases discussed in the text are $(\alpha_2 > \alpha_1, \beta_1 > \beta_2)$, $(\alpha_2 > \alpha_1, \beta_2 > \beta_1)$, and $(\alpha_1 > \alpha_2, \beta_1 > \beta_2)$.

The *overall selectivity*, based on molar flow rates leaving the reactor, for the reactions given by Equations (S8-1) and (S8-2) is

$$\tilde{S}_{D/U} = \frac{F_D}{F_U} \quad (\text{S8-4})$$

2. The *overall yield* is the ratio of the number of moles of a product at the end of a reaction to the number of moles of the key reactant that have been consumed

$$\tilde{Y}_D = \frac{F_D}{F_{A0} - F_A} \quad (\text{S8-5})$$

3. The algorithm for multiple reactions is shown in [Table S8-1](#). As noted earlier in this chapter, equations for the **Rates Step** are the major change in our CRE algorithm.

TABLE S8-1 ALGORITHM FOR MULTIPLE REACTIONS

Number all reactions (1), (2), and so on.	
Mole balances:	
Mole balance on each and every species	
PFR	$\frac{dF_j}{dV} = r_j \quad (\text{S8-6})$
CSTR	$F_{j0} - F_j = -r_j V \quad (\text{S8-7})$
Batch	$\frac{dN_j}{dt} = r_j V \quad (\text{S8-8})$
Membrane (“i” diffuses in)	$\frac{dF_i}{dV} = r_i + R_i \quad (\text{S8-9})$
Liquid-semibatch	$\frac{dC_i}{dt} = r_j + \frac{v_0(C_{j0} - C_j)}{V} \quad (\text{S8-10})$
$V = V_0 + v_0 t$	
Rates:	

Laws

$$r_{ij} = k_{ij} f_i (C_j, C_n) \quad (\text{S8-11})$$

Relative rates

$$\frac{r_{iA}}{-a_i} = \frac{r_{iB}}{-b_i} = \frac{r_{iC}}{c_i} = \frac{r_{iD}}{d_i} \quad (\text{S8-12})$$

Net rates

$$r_j = \sum_{i=1}^q r_{ij} \quad (\text{S8-13})$$

Stoichiometry:

Gas phase

$$C_j = C_{T0} \frac{F_j}{F_T} \frac{P}{P_0} \frac{T_0}{T} = C_{T0} \frac{F_j}{F_T} \frac{T_0}{T} p \quad (\text{S8-14})$$

$$p = \frac{P}{P_0}$$

$$F_T = \sum_{j=1}^n F_j \quad (\text{S8-15})$$

$$\frac{dp}{dW} = -\frac{\alpha}{2p} \left(\frac{F_T}{F_{T0}} \right) \frac{T}{T_0} \quad (\text{S8-16})$$

Liquid phase

$$v = v_0$$
$$C_A, C_B, \dots$$

Combine:

Polymath will combine all the equations for you. Thank you, Polymath!!

CRE WEB SITE MATERIALS

(<http://umich.edu/~elements/6e/08chap/obj.html#/>)

Useful Links

Living
Example
Problems

Extra Help

Additional
Materials

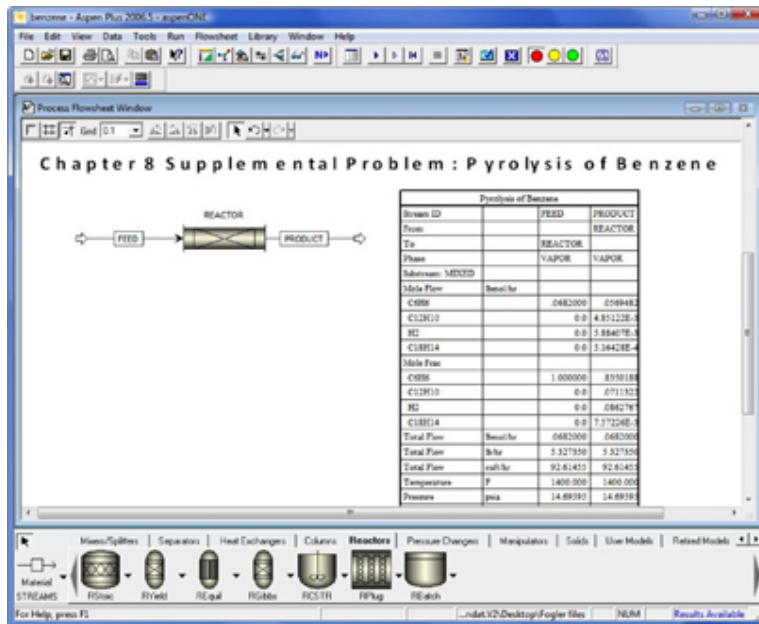
Professional
Reference
Shelf

Computer
Simulation
Problem
Statements

Evaluation

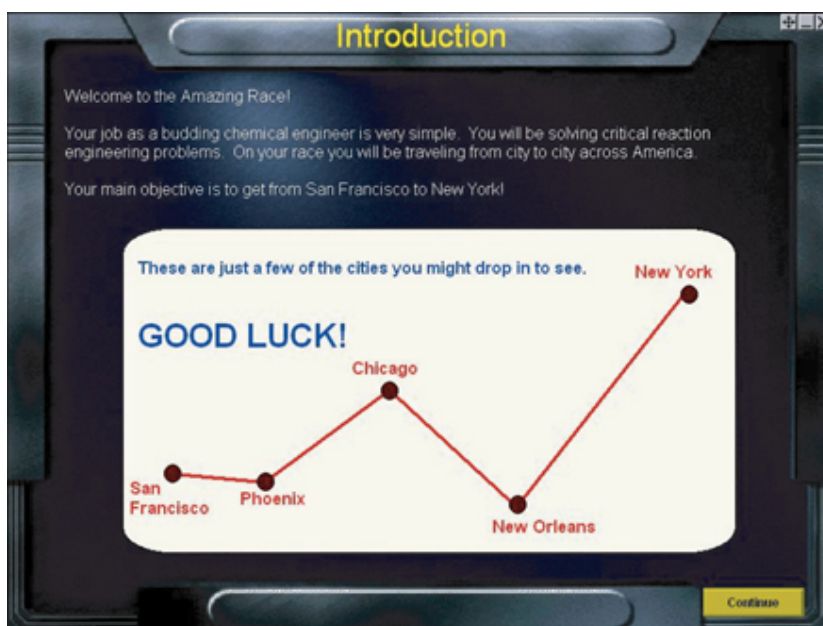
Self Tests

i>Clicker
Questions



AspenTech

(<http://umich.edu/~elements/6e/08chap/learn-aspen.html>)



The Great Race Computer Game
(<http://umich.edu/~elements/6e/icm/grace.html>)

QUESTIONS, SIMULATIONS, AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$A = \bullet \quad B = \blacksquare \quad C = \blacklozenge \quad D = \blacklozenge\blacklozenge$$

In each of the following questions and problems, rather than just drawing a box around your answer, write a sentence or two describing how you solved the problem, the assumptions you made, the reasonableness of your answer, what you learned, and any other facts that you want to include.



Questions

Q8-1_A QBR (*Question Before Reading*). Describe how the CRE algorithm will have to change when we have multiple and don't use conversion to solve problems.

Q8-2_A i>clicker. Go to the Web site (http://www.umich.edu/~elements/6e/08chap/iclicker_ch8_q1.html) and view at least five i>clicker questions. Choose one that could be used as is, or a variation thereof, to be included on the next exam. You also could consider the opposite case: explaining why the question should *not* be on the next exam. In either case, explain your reasoning.



Q8-3_A

1. Reactant A has been unsuccessful in courting/dating reactant B because of a completing reaction. The matchmaker advises that the only way A will succeed is to raise the temperature. Is this a *sure-fire* idea? Will that work?
2. Make up and solve an original problem to illustrate the principles of this chapter. See Problem P5-1_A for guidelines.
3. Write a question based on the material in this chapter that requires critical thinking. Explain why your question requires critical thinking.
Hint: See Preface Section G.

- Are the overall and instantaneous selectivities identical for a CSTR, that is, $S_{D/U} \equiv \tilde{S}_{D/U}$? Also, are the instantaneous and overall yields for a CSTR equal, that is, $Y_D \equiv \tilde{Y}_D$ for a CSTR?

Q8-3_C Read the cobra bite **Web Module**

(http://www.umich.edu/~elements/6e/web_mod/cobra/index.html).

- Determine how many cobra bites are necessary in order that no amount of antivenom will save the victim.
- Suppose the victim was bitten by a harmless snake and not bitten by a cobra and antivenom was injected. How much antivenom would need to be injected to cause death?
- What is the amount and latest possible time that antivenom can be injected after a bite, such that the victim would not die?
- Apply to this problem one or more of the six ideas discussed in Table P-4 in the Complete preface-Introduction on the Web site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>). *Hint:* The *Living Example* Polymath program is on the CRE Web site.



Q8-4_B AWFOS–S8 The Fire Triangle.

- What is ethylene oxide's relationship with oxidizing agents and how does this relate to the fire triangle?
- What makes stopping an ethylene oxide fire more difficult than normal?
- Explain how the Safety Triangle could help you minimize the hazard of a container of ethylene oxide. *Hint:* Try a Google search on ethylene oxide.
- It has been pointed out that the **Fire Triangle** is intuitively obvious and should be omitted from being included in the text. What counter arguments would you give to include it?

Q8-5_B Go to the LearnChemE page for Extra Help in Chapter 8 on the Web

(<http://www.umich.edu/~elements/6e/08chap/learn-cheme-videos.html>). Choose two or three of the screencasts.

1. List five points that expanded on the material in the text.
2. Write a two-sentence evaluation; for example, what was good, what should be changed?

Computer Simulations and Experiments

P8-1A

1. Example 8-1: Trambouze Reactions

Wolfram

1. Fix k_2 at 0.015 and then describe how the selectivity varies with k_1 and k_3 .
2. Write a conclusion about your experiments.

Polymath

3. What would have been the selectivity, $S_{B/XY}$, and conversion, X , if the reaction had been carried out in a single PFR with the same volume as the CSTR?
 4. Recalling $C_{A0} = P_0 RT$, how would your answers change if the pressure were increased by a factor of 100?
2. Example 8-2: Reactor Choice. Make a table/list for each reactor shown in Figure 8-2, identifying all the types of reactions that would be best carried out in this reactor. For example, Figure 8-2(d) Semibatch: used for (1) highly exothermic reactions and (2) increased selectivity.

3. Example 8-3: LEP Series Reactions in Batch Reactor

Wolfram and Polymath

1. Describe how the trajectories C_A , C_B , C_C , $S_{B/C}$, and $Y_{B/C}$ change by setting E_1 and E_2 equal to zero and then varying k_1 and k_2 from their maximum to minimum values.
 2. Fix T at 450 K and then vary E_1 and E_2 , and describe how selectivity and conversion vary.
 3. Write a set of conclusions about your experiment in (i)–(ii) above.
4. Example 8-4: LEP Series Reactions in a CSTR

Wolfram and Python

1. Use Wolfram to describe how the trajectories C_A , C_B , C_C , $S_{B/C}$, and $Y_{B/C}$ change by setting E_1 and E_2 equal to zero and then varying k_1

and k_2 from their maximum to minimum values.

- Write a set of conclusions about your experiment in (i) above.

Polymath

- What CSTR operating temperature (with $t = 0.5$ s) would you recommend to maximize B for $C_{A0} = 5 \text{ mol/dm}^3$, $k_1 = 0.4 \text{ s}^{-1}$ and $k_2 = 0.01 \text{ s}^{-1}$, with $E_1 = 10 \text{ kcal/mol}$ and $E_2 = 20 \text{ kcal/mol}$? *Hint:* Plot C_B versus T . Use either Wolfram or Polymath.

5. Example 8-5: LEP Multiple Gas-Phase Reactions in a PBR

Wolfram and Python

- Vary C_{T0} from its minimum value to its maximum value and then describe what happens to conversion, selectivity, and molar flow rates.
- Describe how varying k and C_{T0} affect the selectivity, $S_{C/D}$, and the yields, Y_C and Y_D .
- Write a set of conclusions about your experiment in (i) and (ii) above.

Polymath

- Make slight modifications in the Polymath program to explore the case when the first reaction is reversible



with $K_C = 0.002 (\text{dm}^3/\text{mol})^2$. Compare with the original problem and describe the difference you observe. Vary the ratio of entering flow rates of A to B to learn the effect on selectivity, and then do the same by varying the same for volumetric flow rate.

6. Example 8-6: LEP Complex Reactions in a Liquid-Phase CSTR

Wolfram and Python

- Explore the problem and describe what you find—that is, which parameters have the greatest effects on selectivity. (*One hint:* Repeat (e)—e.g., vary C_B .)

7. Example 8-7: LEP Complex Reactions in a Semibatch Reactor

Wolfram and Python

- Vary F_{A0} between its minimum and maximum values and then describe what happens to the profiles when compared to the base case.
- Which parameter has the greatest effect on selectivity?
- Write a set of conclusions about your experiments in (i) and (ii) above.

8. Example 8-8: LEP Membrane Reactor to Improve Selectivity

Wolfram and Python

A Stop and Smell the Roses Simulation. Play with this simulation to understand the interaction between maximum selectivity and conversion.

1. Vary C_{T0} , k_{1A} , and k_{2A} between their minimum and maximum values to describe what happens to the profiles of the molar flow rates and to the selectivity and conversion.
2. Write a set of conclusions about your experiment in (i) above.



Polymath

3. Describe how your answers would change for the base case if $F_{A0} = 2F_{A0}$. What if the reaction were $A + 2B \rightarrow D$ with the rate law remaining the same? Vary the parameters and describe what you find.
9. **AspenTech Benzene Pyrolysis Example.** (1) Change the activation energies to $E_1 = 28$ kcal/mol and $E_2 = 32$ kcal/mol, run the AspenTech program, and describe what you find. Compare with original data. (2) Repeat (1) by changing $E_1 = 32$ kcal/mol and $E_2 = 28$ kcal/mol, and describe what you find. (3) Double the reactor volume and compare the molar flow rate profiles. Describe what you find.
10. **Web Example. PFR Mesitylene Reaction.** Download the *Living Example Problem (LEP)* from the CRE Web site. (1) How would your answers change if the feed were equal molar in hydrogen and mesitylene? (2) What is the effect of Θ_H on τ_{opt} ? $\tilde{S}_{X/T}$?
11. **Web Example. CSTR Mesitylene Reaction.** Same question as P8-1(j).
12. **Web Example. Oxidation of Ammonia.** Consider the following set of reactions:

Rate Laws Determined from Totusimetry Data (11/2/2019)

Reaction 1: $4\text{NH}_3 + 6\text{NO} \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O}$ $-r_{1\text{NO}} = k_{1\text{NO}} C_{\text{NH}_3} C_{\text{NO}}^{1.5}$

Reaction 2: $2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$ $r_{2\text{N}_2} = k_{2\text{N}_2} C_{\text{NO}}^2$

Reaction 3: $\text{N}_2 + 2\text{O}_2 \rightarrow 2\text{NO}_2$ $-r_{3\text{O}_2} = k_{3\text{O}_2} C_{\text{N}_2} C_{\text{O}_2}^2$

Use **Wolfram** to investigate the set of reactions in a PFR. Describe what you find by writing a set of conclusions.
13. **Read Solved Blood-Coagulation Problem.** Download the *Living Example Problem*. (1) If blood was flowing out of a small wound at a

rate of $0.05 \text{ dm}^3/\text{minute}$, what is the value of k_1 below which would cause you to bleed to death? (2) Plot out some of the other concentrations, such as TF-VIIa and TF-VIIaX. (3) Why do the curves look the way they do? What reaction in the cascade is most likely to be inhibited causing one to bleed to death? (4) What reactions, if eliminated, could cause one to die of a blood clot? Hint: Look at ATIII and/or TFPI.

- 14. Web Module Living Example: Oscillating Reactions.** Use the *Living Example Polymath Program* for oscillating reactions on the CRE Web site. For the (IO⁻) and (I) reactions set $k_1 = 0.0001/\text{min}^{-1}$ and for reaction (1) $C_{P0} = 0.01 \text{ mol/dm}^3$. (1) What did you find? Look at the linearized stability analysis on the CRE Web site. (2) What factors affect the frequency and onset of the oscillations? (3) Explore and write a paragraph describing what you find. (4) Download the *Living Example Polymath Program* for the BZ reaction. Vary the parameters and write a paragraph describing what you find.

Interactive Computer Games

P8-2_A Download the *Interactive Computer Game (ICG) The Great Race* from the CRE Web site

(<http://www.umich.edu/~elements/6e/icm/index.html>).

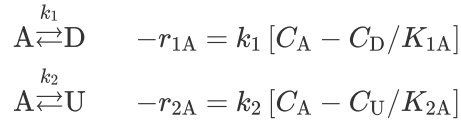
Play the game and then record your performance number for the module, which indicates your mastery of the material. Your professor has the key to decode your performance number. Performance #

Also check out the Web site

(https://www.cbs.com/shows/amazing_race/).

Problems

P8-3_B The following reactions



take place in a batch reactor.

Additional information:

$$k_1 = 1.0 \text{ min}^{-1}, K_{1A} = 10$$

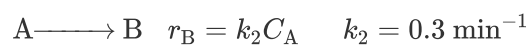
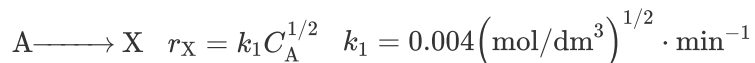
$$k_2 = 100 \text{ min}^{-1}, K_{2A} = 1.5$$

$$C_{A0} = 1 \text{ mol/dm}^3$$

(Adapted from a problem by Prof. John Falconer, University of Colorado.)

1. Plot and analyze conversion and the concentrations of A, D, and U as a function of time. When would you stop the reaction to maximize the concentration of D? Describe what you find.
2. When does the maximum concentration of U occur? (**Ans:** $t = 0.31 \text{ min}$)
3. What are the equilibrium concentrations of A, D, and U?
4. What would be the exit concentrations from a CSTR with a space time of 1.0 min? Of 10.0 min? Of 100 min?

P8-4_A Consider the following system of gas-phase reactions:



B is the desired product, and X and Y are foul pollutants that are expensive to get rid of. The specific reaction rates are at 27°C. The reaction system is to be operated at 27°C and 4 atm. Pure A enters the system at a volumetric flow rate of 10 dm³/min.

1. Sketch the instantaneous selectivities ($S_{B/X}$, $S_{B/XY} = r_B/(r_X + r_Y)$) as a function of the concentration of C_A .
2. Consider a series of reactors. What should be the volume of the first reactor?

3. What are the effluent concentrations of A, B, X, and Y from the first reactor?
4. What is the conversion of A in the first reactor?
5. If 99% conversion of A is desired, what reaction scheme and reactor sizes should you use to maximize $S_{B/XY}$?
6. Suppose that $E_1 = 20000$ cal/mol, $E_2 = 10000$ cal/mol, and $E_3 = 30000$ cal/mol. What temperature would you recommend for a single CSTR with a space time of 10 min and an entering concentration of A of 0.1 mol/dm^3 ?
7. If you could vary the pressure between 1 and 100 atm, what pressure would you choose?

P8-5_B OEQ (Old Exam Question). Pharmacokinetics

concerns the ingestion, distribution, reaction, and elimination reaction of drugs in the body. Consider the application of pharmacokinetics to one of the major problems we have in the United States, drinking and driving. Here, we shall model how long one must wait to drive after having a tall martini. In most states, the legal intoxication limit is 0.8 g of ethanol per liter of body fluid. (In Sweden it is 0.5 g/L, and in Eastern Europe and Russia it is any value above 0.0 g/L.)



The ingestion of ethanol into the bloodstream and its subsequent elimination can be modeled as a series reaction. The rate of absorption from the gastrointestinal tract into the bloodstream and body is a first-order reaction with a specific reaction-rate constant of 10 h^{-1} . The rate at which ethanol is broken down in the bloodstream is limited by

regeneration of a coenzyme. Consequently, the process may be modeled as a zero-order reaction with a specific reaction rate of $0.192 \text{ g/h} \cdot \text{L}$ of body fluid.



Suppose you immediately drank two tall martinis after arriving at a party. How long would you have to wait before your blood alcohol concentration is below the legal limit in order to drive **(a)** in the United States, **(b)** in Sweden, and **(c)** in Russia? How would your answer change if **(d)** the drinks were taken $\frac{1}{2}$ h apart and **(e)** if the two drinks were consumed at a uniform rate during the first hour? **(Ans: (b) $t = 7.8$ h)** **(f)** Suppose that one went to a party, had two tall martinis right away, and then received a phone call saying an emergency had come up and the person needed to drive home immediately. How many minutes would the individual have to reach home before he/she became legally intoxicated, assuming that the person had nothing further to drink? **(g)** How would a plot of blood alcohol concentration-time curve change in part **(e)** if you continuously drank Bud Light at a rate of one, 1 oz. swallow per minute for 2 h? **(h)** How would your answers be different for a thin person? A heavy person? *Hint:* Base all ethanol concentrations on the volume of body fluid. Plot the concentration of ethanol in the blood as a function of time. What generalizations can you make? **(i)** What is the major unspoken point of this problem?

Additional information:

Ethanol in a tall martini: 40 g

Volume of body fluid: 40 L (SADD-MADD problem)

For a more complete description of alcohol metabolism and pharmacokinetics, see PRS on the Web site for

Chapter 9

(http://www.umich.edu/~elements/6e/09chap/J_Alcohol_35_2005.pdf and

<http://www.umich.edu/~elements/6e/09chap/prof-pharmacokinetics.html>).

P8-6_B OEQ (Old Exam Question). Pharmacokinetics.

Tarzlon is a liquid antibiotic that is taken orally to treat infections of the spleen. It is effective only if it can maintain a concentration in the bloodstream (based on volume of body fluid) above 0.4 mg per dm^3 of body fluid. Ideally, a concentration of 1.0 mg/dm^3 in the blood should be realized. However, if the concentration in the blood exceeds 1.5 mg/dm^3 , harmful side effects can occur. Once the Tarzlon reaches the stomach, it can proceed in two pathways, both of which are first order: (1) It can be absorbed into the bloodstream through the stomach walls; (2) it can pass out through the gastrointestinal tract and not be absorbed into the blood. Both these processes are first order in Tarzlon's concentration in the stomach. Once in the bloodstream,

Tarzlon attacks bacterial cells and is subsequently degraded by a zero-order process. Tarzlon can also be removed from the blood and excreted in urine through a first-order process within the kidneys. In the stomach:



Absorption into blood

$$k_1 = 0.15 \text{ h}^{-1}$$

Elimination through gastrointestinal

$$k_2 = 0.6 \text{ h}^{-1}$$

In the bloodstream:

Degradation of Tarzlon

$$k_3 = 0.1 \text{ mg/dm}^3 \cdot \text{h}$$

Elimination through urine

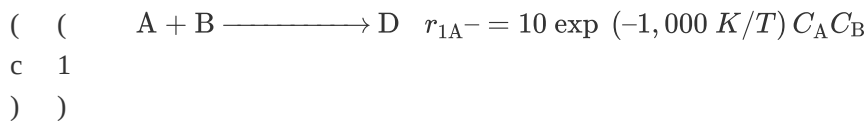
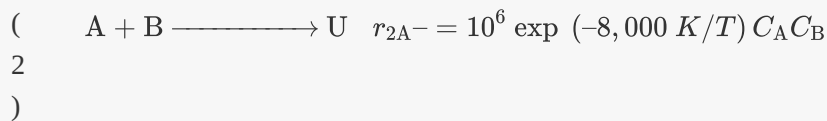
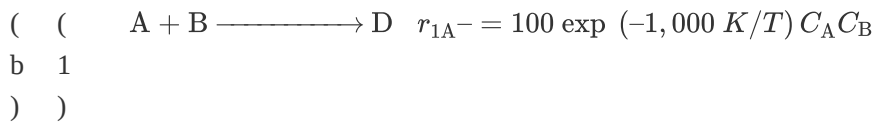
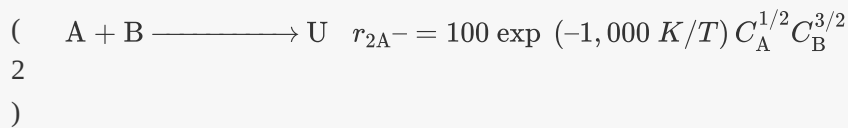
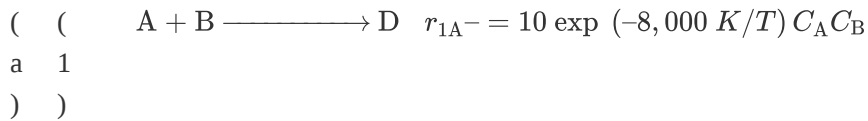
$$k_4 = 0.2 \text{ h}^{-1}$$

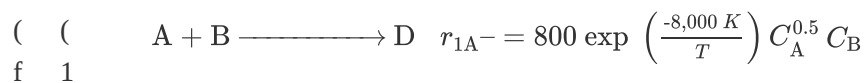
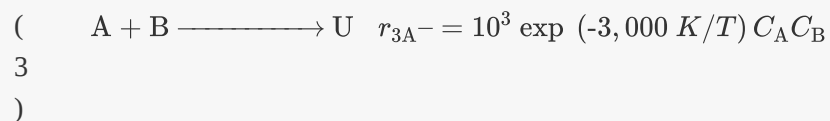
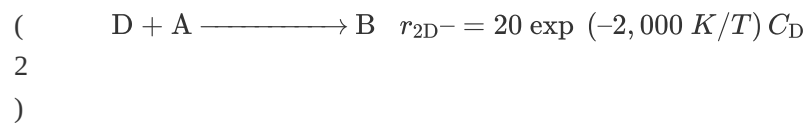
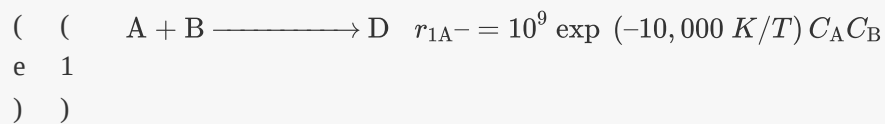
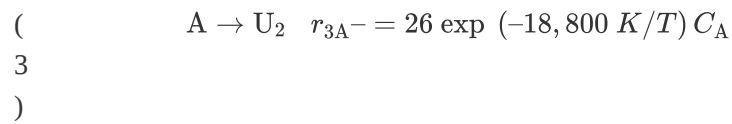
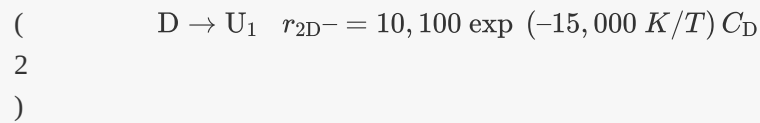
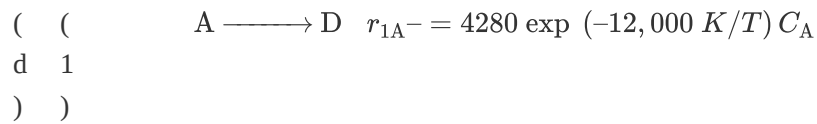
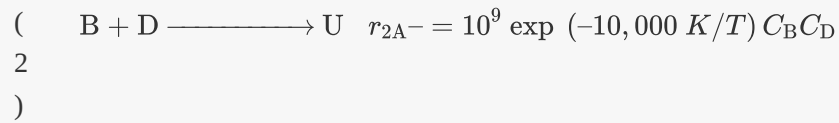
One dose of Tarzlon is 250 mg in liquid form: Volume of body fluid = 40 dm^3 .

1. Plot and analyze the concentration of Tarzlon in the blood as a function of time when 1 dose (i.e., one liquid capsule) of Tarzlon is taken.

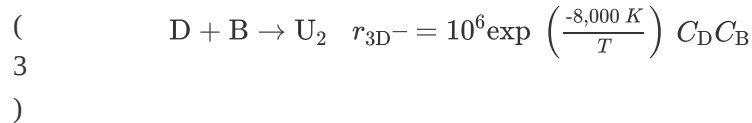
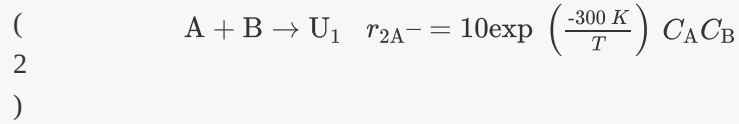
- How should the Tarzlon be administered (dosage and frequency) over a 48-h period to be most effective? *Hint:* Recall what it says on many antibiotic prescriptions regarding the first dose.
- Comment on the dose concentrations and potential hazards.
- How would your answers change if the drug were taken on a full or empty stomach?

P8-7C Reactor selection and operating conditions. For each of the following sets of reactions, describe your reactor system and conditions to maximize the selectivity to D. Make sketches where necessary to support your choices. The rates are in $(\text{mol}/\text{dm}^3 \cdot \text{s})$, and concentrations are in (mol/dm^3) .





))



P8-8B OEQ (Old Exam Question). Consider the reaction



Pure A is fed to a 1.0-dm³ CSTR where it reacts to form a desired product (D), which can then react further to produce an undesired product (U); both reactions are elementary and irreversible, and everything is liquid phase. The entering concentration of A is 1 mole/dm³ at a molar flow rate of 1 mol/min.

1. Sketch the conversion of A, X, the instantaneous selectivity of D to U, $S_{D/U}$, and the instantaneous yield of D, Y_D , as a function of space time (make sure to label them on the plot). You may want to write a sentence or two explaining your reasoning for partial credit purposes.
2. If at $\tau = 1.0$ minutes the instantaneous selectivity, $S_{D/U}$, is (1/2) and the conversion of A is (0.5), what are the specific reactions rates k_1 and k_2 ?

P8-9B OEQ (Old Exam Question). The elementary liquid-phase series reaction

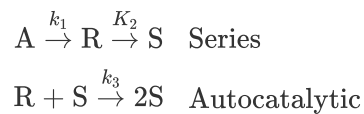


is carried out in a 500-dm³ batch reactor. The initial concentration of A is 1.6 mol/dm³. The desired product is B, and separation of the undesired product C is very difficult and costly. Because the reaction is carried out at a relatively high temperature, the reaction is easily quenched.

1. Plot and analyze the concentrations of A, B, and C as a function of time. Assume that each reaction is irreversible, with $k_1 = 0.4 \text{ h}^{-1}$ and $k_2 = 0.01 \text{ h}^{-1}$.
2. Plot and analyze the concentrations of A, B, and C as a function of time when the first reaction is reversible, with $k_{-1} = 0.3 \text{ h}^{-1}$.
3. Plot and analyze the concentrations of A, B, and C as a function of time for the case where both reactions are reversible, with $k_{-2} = 0.005 \text{ h}^{-1}$.
4. Compare (a), (b), and (c) and describe what you find.
5. Vary k_1 , k_2 , k_{-1} , and k_{-2} . Explain the consequence of $k_1 > 100$ and $k_2 < 0.1$ with $k_{-1} = k_{-2} = 0$ and with $k_{-2} = 1$, $k_{-1} = 0$, and $k_{-2} = 0.25$.
6. Apply to this problem one or more of the six ideas discussed in Table P-4 in the Complete preface-Introduction on the Web site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>).

P8-10_B Terephthalic acid (TPA) finds extensive use in the manufacture of synthetic fibers (e.g., Dacron) and as an intermediate for polyester films (e.g., Mylar). The formation of potassium terephthalate from potassium benzoate was studied using a tubular reactor (*Ind. Eng. Chem. Res.*, 26, 1691).

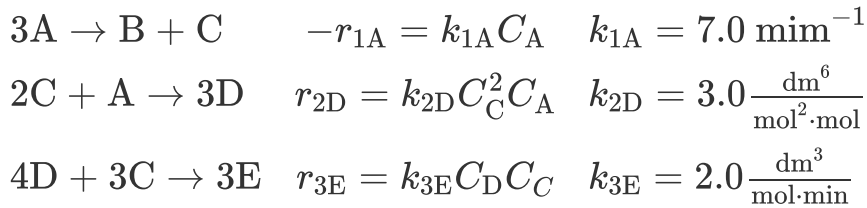
It was found that the intermediates (primarily K-phthalates) formed from the dissociation of K-benzoate over a CdCl₂ catalyst reacted with K-terephthalate in an autocatalytic reaction step



where A = K-benzoate, R = lumped intermediates (K-phthalates, K-isophthalates, and K-benzenecarboxylates), and S = K-terephthalate. Pure A is charged to the reactor at a pressure of 110 kPa. The specific reaction rates at 410°C are $k_1 = 1.08 \times 10^{-3} \text{ s}^{-1}$ with $E_1 = 42.6 \text{ kcal/mol}$, $k_2 = 1.19 \times 10^{-3} \text{ s}^{-1}$ with $E_2 = 48.6 \text{ kcal/mol}$, and $k_3 = 1.59 \times 10^{-3} \text{ dm}^3/\text{mol} \cdot \text{s}$ with $E_3 = 32 \text{ kcal/mol}$.

1. Plot and analyze the concentrations of A, R, and S as a function of time in a batch reactor at 410°C, noting when the maximum in R occurs.
2. Repeat (a) for temperatures of 430°C and 390°C.
3. What would be the exit concentrations from a CSTR operated at 410°C and a space time of 1200 s?

P8-11A The following liquid-phase reactions were carried out in a CSTR at 325 K:



Sketch the trends or results you expect before working out the details of the problem.

The concentrations measured inside the reactor were $C_{\text{A}} = 0.10$, $C_{\text{B}} = 0.93$, $C_{\text{C}} = 0.51$, and $C_{\text{D}} = 0.049$ all in mol/dm^3 .

1. What are the values of $r_{1\text{A}}$, $r_{2\text{A}}$, and $r_{3\text{A}}$? ($r_{1\text{A}} = -0.7 \text{ mol/dm}^3 \cdot \text{min}$)
2. What are the values of $r_{1\text{B}}$, $r_{2\text{B}}$, and $r_{3\text{B}}$?
3. What are the values of $r_{1\text{C}}$, $r_{2\text{C}}$, and $r_{3\text{C}}$? ($r_{1\text{C}} = 0.23 \text{ mol/dm}^3 \cdot \text{min}$)
4. What are the values of $r_{1\text{D}}$, $r_{2\text{D}}$, and $r_{3\text{D}}$?
5. What are the values of $r_{1\text{E}}$, $r_{2\text{E}}$, and $r_{3\text{E}}$?
6. What are the values of the net rates of formation of A, B, C, D, and E?
7. The entering volumetric flow rate is $100 \text{ dm}^3/\text{min}$ and the entering concentration of A is 3 M.

What is the CSTR reactor volume? (**Ans:** 400 dm^3 .)

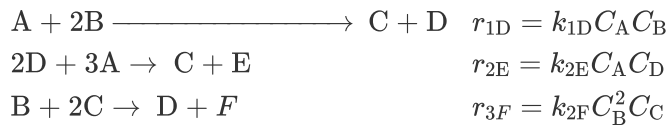
8. What are the exit molar flow rates from the 400 dm^3 CSTR?

Note: The following parts require an ODE solver and are of “B level” difficulty.

9. **PFR.** Now assume the reactions take place in the gas phase. Use the preceding data to plot the molar flow rate's selectivity and p as a function of PFR volume up to 400 dm^3 . The pressure-drop parameter is 0.001 dm^{-3} , the total concentration entering the reactor is 0.2 mol/dm^3 , and $v_0 = 100 \text{ dm}^3/\text{min}$. What are the values $\tilde{S}_{D/E}$ of and $\tilde{S}_{C/D}$?
10. **Membrane Reactor.** Repeat (i) when species C diffuses out of a membrane reactor and the transport coefficient, k_C , is 10 min^{-1} . Compare your results with part (i).

P8-12_B In this problem, the complex reactions described below will first be carried out in the liquid phase (parts (a) through (d)) and then in the gas phase (parts (e) through (g)). One need not solve the liquid phase to solve the gas-phase problems.

The following reactions are carried out isothermally.



Additional information:

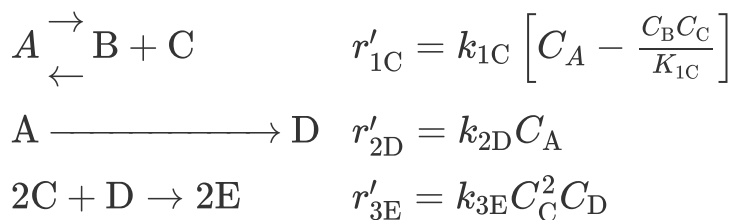
$$k_{1D} = 0.25 \text{ dm}^6/\text{mol}^2 \cdot \text{min} \quad v_0 = 10 \text{ dm}^3/\text{min}$$

$$k_{2E} = 0.1 \text{ dm}^3/\text{mol} \cdot \text{min} \quad C_{A0} = 1.5 \text{ mol/dm}^3$$

$$k_{3F} = 5.0 \text{ dm}^9/\text{mol}^2 \cdot \text{min} \quad C_{B0} = 2.0 \text{ mol/dm}^3$$

1. Consider the reactions to be liquid phase and plot the species concentrations and the conversion of A as a function of the distance (i.e., volume) down a 50-dm³ PFR. Note any maxima.
2. Consider the reactions to be liquid phase and determine the effluent concentrations and conversion from a 50-dm³ CSTR. (**Ans:** $C_A = 0.61$, $C_B = 0.79$, $C_F = 0.25$, and $C_D = 0.45$ mol/dm³.)
3. Plot and analyze the species concentrations and the conversion of A as a function of time when the reaction is carried out in a semibatch reactor initially containing 40 dm³ of liquid. Consider two cases: (1) A is fed to B, and (2) B is fed to A. What differences do you observe for these two cases? Describe what you find.
4. Vary the ratio of B to A ($1 < \Theta_B < 10$) in the feed to the PFR and describe what you find. What generalizations can you make from this problem?
5. Rework (a) for the case when the reaction is a gas-phase reaction. We will keep the constants the same so you won't have to make too many changes in your Polymath program, but we will make $v_0 = 100$ dm³/min, $C_{T0} = 0.4$ mol/dm³, $V = 500$ dm³, and an equimolar feed of A and B. Plot the molar flow rates and $S_{C/D}$ and $S_{E/F}$ down a PFR. Describe what you find.
6. Repeat (e) when D diffuses out through the sides of a membrane reactor where the mass transfer coefficient, k_{CD} , can be varied between 0.1 and 10 min⁻¹. What trends do you find?
7. Repeat (e) when B is fed through the sides of a membrane reactor. Describe what you find.

P8-13B The gas-phase reactions take place isothermally in a membrane reactor packed with catalyst. Pure A enters the reactor at 24.6 atm and 500 K, and a flow rate of A of 10 mol/min.



Sketch the trends or results you expect **before** working out the details of the problem.

Only species B diffuses out of the reactor through the membrane.

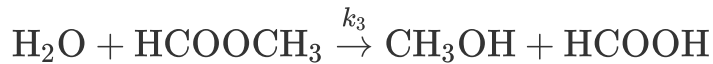
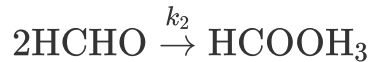
Additional information:

Overall mass transfer coefficient $k_C = 1.0 \text{ dm}^3 / \text{kg-cat} \cdot \text{min}$

$k_{1C} = 2$ $\text{dm}^3 / \text{kg-cat} \cdot \text{min}$	$k_{3E} = 5.0$ $\text{dm}^3 / \text{mol}^2 \cdot \text{kg-cat} \cdot \text{min}$
$K_{1C} = 0.2 \text{ mol} / \text{dm}^3$	$W_f = 100 \text{ kg}$
$k_{2D} = 0.4$ $\text{dm}^3 / \text{kg-cat} \cdot \text{min}$	$\alpha = 0.008$ kg^{-1}

1. Plot and analyze the concentrations down the length of the reactor.
2. Explain why your curves look the way they do.
3. Describe the major differences you observe when C diffuses out instead of B, with the same mass transfer coefficient.
4. Vary some of the parameters (e.g., k_B , k_{1C} , K_{1C}) and write a paragraph describing what you find.

P8-14_B The complex reactions involved in the oxidation of formaldehyde to formic acid over a Vanadium titanium oxide catalyst (*Ind. Eng. Chem. Res.*, 28, 387) are shown below. Each reaction follows an elementary rate law.



Sketch the trends or results you expect **before** working out the details of the problem.

Let A = HCHO, B = O₂, C = HCOOH, D = HCOOCH₃, E = CO, W = H₂O, and G = CH₃OH.

The entering flow rates are $F_{A0} = 10$ mol/s and $F_{B0} = 5$ mol/s, and $v_0 = 100$ dm³/s. At a total entering concentration $C_{T0} = 0.147$ mol/dm³, the suggested reactor volume is 1000 dm³.

Additional information:

At 300 K

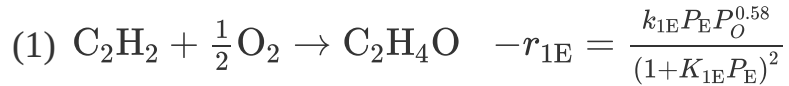
$$k_1 = 0.014 \left(\frac{\text{dm}^3}{\text{mol}} \right)^{1/2} / \text{s}, \quad k = 0.007 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}}$$

$$k_3 = 0.014 / \text{s}, \quad k_4 = 0.45 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}}$$

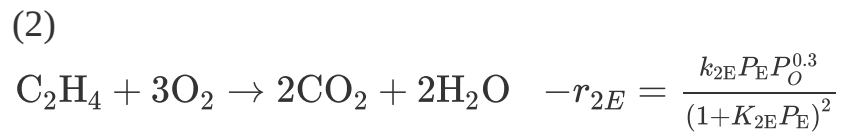
1. Plot the molar flow rates of each species along the volume (length) of the reactor on the same figure and then analyze why the profiles look the way they do.
2. Plot and analyze \tilde{Y}_C , $\tilde{S}_{A/E}$, $\tilde{S}_{C/D}$, and $\tilde{S}_{D/G}$ along the length of the reactor. Note and explain any maximums and the volume at which they occur.
3. Plot and analyze the overall HCOOH yield and overall selectivity of HCOH to CO, of HCOOCH₃ to CH₃OH, and of HCOOH to HCOOCH₃ as a function of the Θ_{O_2} . Suggest some conditions to best produce formic acid. Write a paragraph describing what you find.
4. Compare your plot in part (a) with a similar plot when pressure drop is taken into account with $\alpha = 0.002$ dm⁻³. Note any unusual differences between parts (a) and (d).

5. Suppose that $E_1 = 10000$ cal/mol, $E_2 = 30000$ cal/mol, $E_3 = 20000$ cal/mol, and $E_4 = 10000$ cal/mol, what temperature would you recommend for a 1000-dm^3 PFR?

P8-15C The ethylene epoxydation is to be carried out using a cesium-doped silver catalyst in a packed-bed reactor.



Along with the desired reaction, the complete combustion of ethylene also occurs



(M. Al-Juaied, D. Lafarga, and A. Varma, *Chem. Eng. Sci.* 56, 395 (2001)).

It is proposed to replace the conventional PBR with a membrane reactor in order to improve the selectivity. As a rule of thumb, a 1% increase in the selectivity to ethylene oxide translates to an increase in profit of about \$2 million/yr. The feed consists of 12% (mole) oxygen, 6% ethylene, and the remainder nitrogen at a temperature of 250°C and a pressure of 2 atm. The total molar flow rate is 0.0093 mol/s to a reactor containing 2 kg of catalyst.

Additional information:

$$k_{1E} = 0.15 \frac{\text{mol}}{\text{kg}\cdot\text{s}\cdot\text{atm}^{1.58}} \text{ at } 523 \text{ K with } E_1 = 60.7 \text{ kJ/mol}$$

$$k_{2E} = 0.0888 \frac{\text{mol}}{\text{kg}\cdot\text{s}\cdot\text{atm}^{1.3}} \text{ at } 523 \text{ K with } E_2 = 73.2 \text{ kJ/mol}$$

$$K_{1E} = 6.50 \text{ atm}^{-1}, K_{2E} = 4.33 \text{ atm}^{-1}$$

1. What conversion and selectivity of ethylene epoxide to CO_2 are expected in a conventional PBR?

2. What would be the conversion and selectivity if the total molar flow rate were divided and the 12% oxygen stream (no ethylene) were uniformly fed through the sides of the membrane reactor, and 6% ethylene (no oxygen) were fed at the entrance?
3. Repeat (b) for a case when ethylene is fed uniformly through the sides and oxygen is fed at the entrance. Compare with parts (a) and (b). Describe what you find.

P8-16_B OEQ (Old Exam Question). **Solar energy** capture has great potential to help meet the world's growing energy demand, which is 12 terawatts in 2010 and is expected to rise to 36 terawatts in 2050 (cf. Problem **P3-15_B**). Professor Al Weiner and his students at the University of Colorado are engaged in developing methods of utilizing solar thermal energy. In solar thermal reactors, mirrors are used to focus and concentrate the sun's energy on a flow-type cavity reactor where temperatures as high as 1200°C can be realized, as shown in Figure P8-16.1.

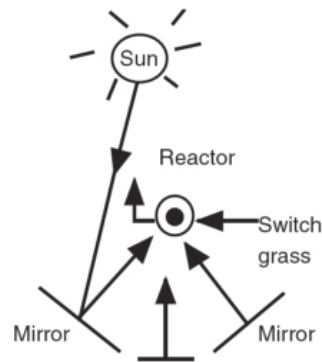
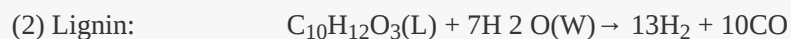


Figure P8-16_B Solar field design. Five 265-m-tall towers with three heliostat fields/tower, on 275 acres of land in Daggett, CA. Net concentration 3,868 suns and 295 MW delivered to each solar reactor. (Melinda M. Channel, Jonathan Scheffe, Allan Lewandowski, and Alan W. Weimer, November 11,

2009. Also see: *Chemical Engineering*, 116, p. 18, March
 2009. Photo by Glowimages/Getty.)
 (<http://www.sciencedirect.com/science/article/pii/S0009250907005878> and
<http://www.sciencedirect.com/science/article/pii/S0038092X03004663>)

The switch grass is fed to the 1200°C solar thermal reactor. At these temperatures, biomass can be converted to CO and H₂, that is, syn gas, which then can be used for liquid fuels. Switch grass, which is approximately $\frac{2}{3}$ cellulose (C₆H₁₀O₅) and $\frac{1}{3}$ lignin (C₁₀H₁₂O₃) will be fed with steam to produce CO, H₂, and a small amount of ash, which we will neglect. In order to simplify this process into a tractable home problem, we assume the switch grass is volatilized immediately upon entering the plug-flow reactor and that the reactions and postulated rate laws are



(*AIChE J.*, 55, 286 (2009)). Also see *Science*, 326, 1472 (2009).

The rate laws and constants are hypothesized to be

$$-r_{1C} = k_{1C} C_C C_W$$

$$-r_{2L} = k_{2L} C_L C_W^2$$

With $k_{1C} = 3 \times 10^4 \left(\frac{\text{dm}^3}{\text{mol}} \right) / \text{s}$ and $k_{2L} = 1.4 \times 10^7 \left(\frac{\text{dm}^3}{\text{mol}} \right) / \text{s}$

Total gas concentration in the feed and reactor with

$$C_{T0} = \frac{P_0}{RT_0} = \frac{1 \text{ atm}}{(0.082)(1473)} = 0.00828 \text{ mol/dm}^3 \text{ with the}$$

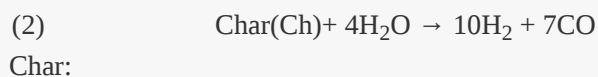
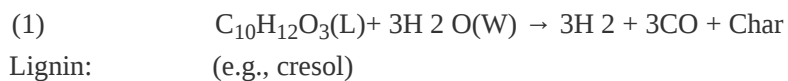
entering molar flow rates of cellulose, lignin, and water

are $F_{C0} = 0.00411 \text{ mol/s}$ and $F_{L0} = 0.00185 \text{ mol/s}$, $F_{W0} =$

0.02 mol/s , respectively.

1. Plot and analyze the molar flow rates as a function of PFR volume up to $V = 0.417 \text{ dm}^3$.
2. Plot and analyze Y_C , Y_W , Y_L , and $\tilde{S}_{\text{CO/H}_2}$ down the reactor. Describe what you find.
3. Repeat (a) for different molar flow rates of water.

P8-17_B Solar thermal biochar gasification has also been studied at the University of Colorado (see Problem **P8-16_B**). (*Chemical Engineering and Processing: Process Intensification* 48, 1279 (2009) and *AIChE J.*, 55, 286 (2009).) While this process follows a shrinking core model (see Chapter 14), for the purposes of this example, we will use the following sequence:



The rate laws at 1200°C are hypothesized to be

$$-r_{1L} = k_{1L} C_L C_W^2 \text{ with } k_{1L} = 3721 \left(\frac{\text{dm}^3}{\text{mol}} \right)^2 / \text{s}$$

$$-r_{2Ch} = k_{2Ch} C_{Ch} C_W^2 \text{ with } k_{2Ch} = 1000 \left(\frac{\text{dm}^3}{\text{mol}} \right)^2 / \text{s}$$

The entering molar flow rates are $F_{L0} = 0.0123 \text{ mol/s}$, $F_{W0} = 0.111 \text{ mol/s}$, the total entering concentration is $C_{T0} = 0.2 \text{ mol/dm}^3$, and the reactor volume is 0.417 dm^3 .

1. Plot and analyze F_{Ch} , F_L , F_W , F_{CO} , and F_{H_2} down the length of a plug-flow reactor.
2. Repeat **(a)** for the concentrations C_C , C_{Ch} , and so on.
3. and analyze the selectivity \tilde{S}_{C_0/H_2} and yields \tilde{Y}_W and Y_L down the PFR.
4. At what point is the char molar flow rate a maximum? How does it change with changing feed conditions, such as the ratio of (F_{W0}/F_{L0}) , C_{T0} , and so on? Describe what you found in parts **(a)** through **(d)**.

P8-18_A Go to Professor Herz's **Reactor Lab** on the CRE Web site at www.reactorlab.net.

1. Download Division 5, Lab 2 of the Reactor Lab from the CRE Web site for the selective oxidation of ethylene to ethylene oxide. Click the [i] info button to get information about the system. Perform experiments and develop rate equations for the reactions. Write a technical memo that reports your results and includes plots and statistical measurements of how well your kinetic model fits experimental data.
2. Download Division 5, Labs 3 and 4 of the Reactor Lab for batch reactors in which parallel and series reactions, respectively, can be carried out. Investigate how dilution with solvent affects the selectivity for different reaction orders and write a memo describing your findings.

• **Additional Homework Problems**

A number of homework problems that can be used for exams or supplementary problems or examples are found on the CRE Web site, <http://www.umich.edu/~elements/6e/index.html>.

SUPPLEMENTARY READING

1. Selectivity, reactor schemes, and staging for multiple reactions, together with evaluation of the corresponding design equations, may or may not be presented in

THORNTON W. BURGESS, *The Adventures of Chatterer the Red Squirrel*, New York: Dover Publications, Inc., 1915.

JOHN B. BUTT, *Reaction Kinetics and Reactor Design, Second Edition, Revised and Expanded*, New York: Marcel Dekker, Inc., 1999.

K. G. DENBIGH and J. C. R. TURNER, *Chemical Reactor Theory*, 2nd ed. Cambridge: Cambridge University Press, 1971, Chap. 6.

2. Many analytical solutions for parallel, series, and combination reactions are presented in

S. M. WALAS, *Chemical Reaction Engineering Handbook of Solved Problems*. Newark, NJ: Gordon and Breach, 1995.

9. Reaction Mechanisms, Pathways, Bioreactions, and Bioreactors

The next best thing to knowing something is knowing where to find it.

—Samuel Johnson (1709–1784)

Overview. This chapter applies chemical reaction engineering principles to nonelementary reactions and to bioreactions and bioreactors. The topics include the pseudo-steady-state hypothesis (PSSH), enzyme mechanisms and reaction kinetics, and the growth of microorganisms.

We start with **Section 9.1** where we discuss PSSH and the formation of active intermediate species, which disappear virtually as fast as they are formed. Next, we show how to propose a mechanism and then apply the PSSH to active intermediate species to develop rate laws for chemical reactions that do not follow elementary rate laws.

To develop rate laws for nonelementary reactions we

- Choose an active intermediate and a reaction mechanism
- Write the elementary rate law for each reaction in the mechanism
- Write the net rates of reaction for each species
- Invoke the PSSH for the active intermediates in order to arrive at a rate law that is consistent with experimental observation

In **Section 9.2** we apply the PSSH to biochemical reactions, with a focus on enzymatic reaction mechanisms and kinetics. Here, we study

- Michaelis–Menten kinetics
- Lineweaver–Burk plot and other plots to analyze data, and types of enzyme inhibition and the corresponding rate laws

In **Section 9.3**, we study the growth of microorganisms. Microorganism growth logically follows the discussion of enzyme kinetics because of the similarity of the Michaelis–Menten rate law and the Monod growth law. Here, we study

- Balances on the cell mass and the substrate
- Kinetics of cell growth
- Yield coefficients relating to cell growth to substrate consumption
- Bioreactors

We will use these principles to model both batch reactors and CSTRs, which are called chemostats. We should note that microorganism growth is becoming

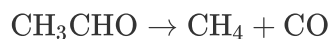
of increasing interest because of applications such as the use of algae as a biofuel.

9.1 ACTIVE INTERMEDIATES AND NONELEMENTARY RATE LAWS

In Chapter 3, a number of simple power-law models, for example,

$$-r_A = kC_A^n$$

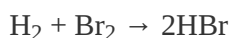
were presented, where n was an integer of 0, 1, or 2 corresponding to a zero-, first-, or second-order reaction. However, for a large number of reactions, the orders are noninteger, such as the decomposition of acetaldehyde at 500°C



where the rate law developed in Problem P9-5B(b) is

$$-r_{\text{CH}_3\text{CHO}} = kC_{\text{CH}_3\text{CHO}}^{3/2}$$

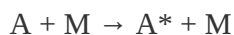
Many rate laws have concentration terms in both the numerator and denominator such as the formation of HBr from hydrogen and bromine



where the rate law developed in Problem P9-5B(c) is

$$r_{\text{HBr}} = \frac{k_1 C_{\text{H}_2} C_{\text{Br}_2}^{3/2}}{C_{\text{HBr}} + k_2 C_{\text{Br}_2}}$$

Rate laws of this form usually involve a number of elementary reactions and at least one active intermediate. An *active intermediate* is a high-energy molecule that reacts virtually as fast as it is formed. As a result, it is present in very small concentrations. Active intermediates (e.g., A^*) can be formed by collisions or interactions with other molecules.



Properties of an active intermediate A*

Here, the activation occurs when translational kinetic energy is transferred into internal energy, that is, vibrational and rotational energy.¹ An unstable molecule (i.e., active intermediate) is not formed solely as a consequence of the molecule moving at a high velocity (high translational kinetic energy). The energy must be absorbed into the chemical bonds, where high-amplitude oscillations will lead to bond ruptures, molecular rearrangement, and decomposition. In the absence of photochemical effects or similar phenomena, the transfer of translational energy to vibrational energy to produce an active intermediate can occur only as a consequence of molecular collision or interaction. Collision theory is discussed in the *Professional Reference Shelf* in Chapter 3

(<http://www.umich.edu/~elements/6e/03chap/prof.html>) on the CRE Web site. Other types of active intermediates that can be formed are *free radicals* (one or more unpaired electrons; e.g., $\text{CH}_3\cdot$), ionic intermediates (e.g., carbonium ion), and enzyme–substrate complexes, to mention a few (<http://www.umich.edu/~elements/6e/09chap/prof.html>).

¹W. J. Moore, *Physical Chemistry*, Reading, MA: Longman Publishing Group, 1998.

"Wild" oscillations

The idea of an active intermediate was first postulated in 1922 by F. A. Lindemann, who used it to explain changes in the reaction order with changes in reactant concentrations.² Because the active intermediates were so short-lived and present in such low concentrations, their existence was not really definitively confirmed until the work of Ahmed Zewail, who received the Nobel Prize in Chemistry in 1999 for femtosecond spectroscopy.³ His work on cyclobutane showed that the reaction to form two ethylene molecules did not proceed directly, as shown in Figure 9-1(a), but formed the active intermediate shown in the small trough at the top of the

energy barrier on the reaction coordinate diagram in Figure 9-1(b). As discussed in Chapter 3, an estimation of the barrier height, E , can be obtained using computational software packages such as Spartan, Cerius², or Gaussian as discussed in the *Molecular Modeling Web Module* in Chapter 3 on the CRE Web site, www.umich.edu/~elements/6e/index.html.

²F. A. Lindemann, *Trans. Faraday. Soc.*, 17, 598 (1922).

³J. Peterson, *Science News*, 156, 247 (1999).

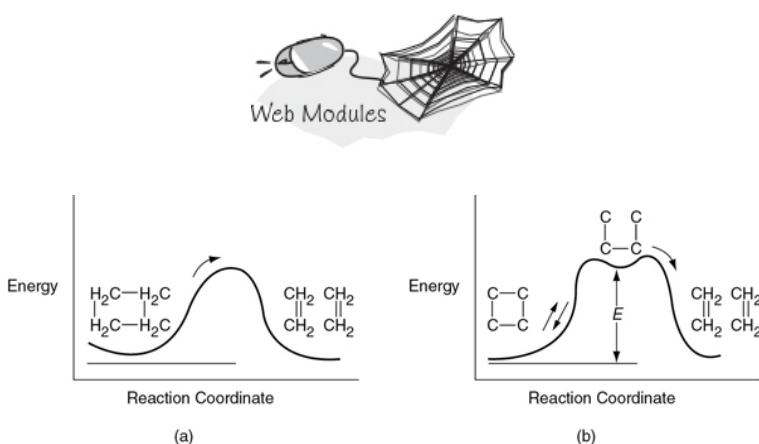


Figure 9-1 Reaction coordinate. Ivars Peterson, "Chemistry Nobel spotlights fast reactions," *Sci. News*, 156, 247 (1999).

9.1.1 Pseudo-Steady-State Hypothesis (PSSH)

In the theory of active intermediates, decomposition of the intermediate does not occur instantaneously after internal activation of the molecule; rather, there is a time lag, although infinitesimally small, during which the species remains activated. Zewail's work was the first definitive proof of a gas-phase active intermediate that exists for an infinitesimally short time. Because a reactive intermediate reacts virtually as fast as it is formed, the net rate of formation of an active intermediate (e.g., A^*) is zero, that is,

$$r_{A^*} \equiv 0 \quad (9-1)$$

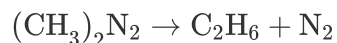
This condition is also referred to as the *Pseudo-Steady-State Hypothesis* (PSSH). If the active intermediate appears in n

reactions, then

$$r_{A^*} = \sum_{i=1}^n r_{iA^*} = 0 \quad (9-2)$$

PSSH

To illustrate how noninteger power rate laws are formed, we shall first consider the gas-phase decomposition of azomethane, AZO, to give ethane and nitrogen



Experimental observations show that the rate of formation of ethane is first order with respect to AZO at pressures greater than 1 atm (relatively high concentrations)⁴

$$r_{\text{C}_2\text{H}_6} \propto C_{\text{AZO}}$$

⁴ H. C. Ramsperger, *J. Am. Chem. Soc.*, 49, 912.

and second order at pressures below 50 mmHg (low concentrations):

$$r_{\text{C}_2\text{H}_6} \propto C_{\text{AZO}}^2$$

Why the reaction order changes

We could combine these two observations to postulate a rate law of the form

$$-r_{\text{AZO}} = \frac{k_1 C_{\text{AZO}}^2}{1 + k_2 C_{\text{AZO}}}$$

To find a mechanism that is consistent with the experimental observations, we use the steps shown in [Table 9-1](#).

TABLE 9-1 STEPS TO DEDUCE A RATE LAW

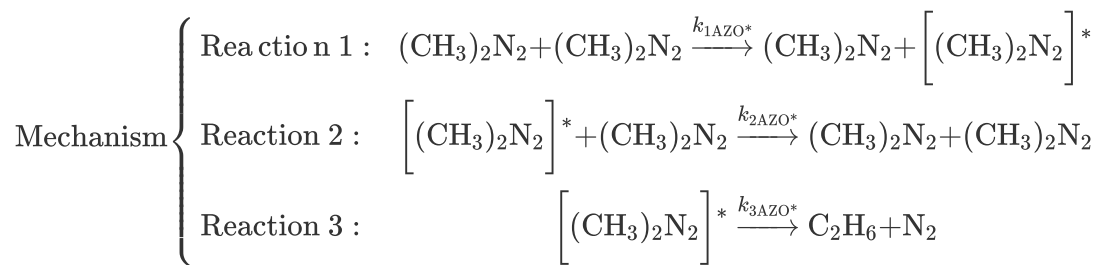
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1. Propose an active intermediate(s).
2. Propose a mechanism, utilizing the rate law obtained from experimental data, if possible.
3. Model each reaction in the mechanism sequence as an elementary reaction.
4. After writing rate laws for the rate of formation of desired product, write the rate laws for each of the active intermediates.
5. Write the net rate of formation for the active intermediate and use the PSSH.
6. Eliminate the concentrations of the intermediate species in the rate laws by solving the simultaneous equations developed in Steps 4 and 5.
7. If the derived rate law does not agree with experimental observation, assume a new mechanism and/or intermediates and go to Step 3. A strong background in organic and inorganic chemistry is helpful in predicting the activated intermediates for the reaction under consideration.

We will now follow the steps in Table 9-1 to develop the rate law for azomethane (AZO) decomposition, $-r_{\text{AZO}}$.

Step 1. **Propose an active intermediate.** We will choose as an active intermediate an azomethane molecule that has been excited through molecular collisions, to form AZO^* , that is, $[(\text{CH}_3)_2\text{N}_2]^*$.

Step 2. **Propose a mechanism.**



In *reaction 1*, two AZO molecules collide and the kinetic energy of one AZO molecule is transferred to the internal rotational and vibrational energies of the other AZO molecule, and it becomes activated and highly reactive (i.e., AZO*). In *reaction 2*, the activated molecule (AZO*) is deactivated through collision with another AZO by transferring its internal energy to increase the kinetic energy of the molecules with which AZO* collides. In *reaction 3*, this highly activated AZO* molecule, which is *wildly* vibrating, spontaneously decomposes into ethane and nitrogen.

Step 3. Write rate laws.

Because each of the reaction steps is elementary, the corresponding rate laws for the active intermediate AZO* in reactions (1), (2), and (3) are

$$(1) \quad r_{1\text{AZO}^*} = k_{1\text{AZO}^*} C_{\text{AZO}}^2 \quad (9-3)$$

$$(2) \quad r_{2\text{AZO}^*} = -k_{2\text{AZO}^*} C_{2\text{AZO}^*} C_{\text{AZO}} \quad (9-4)$$

$$(3) \quad r_{3\text{AZO}^*} = -k_{3\text{AZO}^*} C_{\text{AZO}^*} \quad (9-5)$$

Note: The specific reaction rates, k , are all defined wrt the active intermediate AZO*.

(Let $k_1 = k_{1\text{AZO}^*}$, $k_2 = k_{2\text{AZO}^*}$, and $k_3 = k_{3\text{AZO}^*}$)

The rate laws shown in Equations (9-3)–(9-5) are pretty much useless in the design of any reaction system because the concentration of the active intermediate AZO* is not readily measurable.

Consequently, we will use the Pseudo-Steady-State

Hypothesis (PSSH) to obtain a rate law in terms of measurable concentrations.

Step 4. Write rate of formation of product.

We first write the rate of formation of product

$$r_{C_2H_6} = k_3 C_{AZO^*} \quad (9-6)$$

Step 5. Write net rate of formation of the active intermediate and use the PSSH.

To find the concentration of the active intermediate AZO^* , we set the net rate of formation of AZO^* equal to zero,⁵ $r_{AZO^*} \equiv 0$.

⁵ For further elaboration on this section, see R. Aris, *Am. Sci.*, 58, 419 (1970).

$$\begin{aligned} r_{AZO^*} &= r_{1AZO^*} + r_{2AZO^*} + r_{3AZO^*} = 0 \\ &= k_1 C_{AZO}^2 - k_2 C_{AZO^*} C_{AZO} - k_3 C_{AZO^*} = 0 \quad (9-7) \end{aligned}$$

Solving for C_{AZO^*}

$$C_{AZO^*} = \frac{k_1 C_{AZO}^2}{k_2 C_{AZO} + k_3} \quad (9-8)$$

Step 6. Eliminate the concentration of the active intermediate species in the rate laws by solving the simultaneous equations developed in Steps 4 and 5. Substituting Equation (9-8) into Equation (9-6)

$$r_{C_2H_6} = \frac{k_1 k_3 C_{AZO}^2}{k_2 C_{AZO} + k_3} \quad (9-9)$$

Step 7. Compare with experimental data.

At low AZO concentrations,

$$k_2 C_{AZO} \ll k_3$$

for which case we obtain the following second-order rate law:

$$r_{C_2H_6} = k_1 C_{AZO}^2$$

At high concentrations

$$k_2 C_{AZO} \gg k_3$$

in which case the rate expression follows first-order kinetics

$$r_{\text{C}_2\text{H}_6} = \frac{k_1 k_3}{k_2} C_{\text{AZO}} = k C_{\text{AZO}}$$

In describing reaction orders for this equation, one would say that the reaction is *apparent first order* at high azomethane concentrations and *apparent second order* at low azomethane concentrations.

Apparent reaction orders

9.1.2 If Two Molecules Must Collide, How Can the Rate Law Be First Order?

The PSSH can also explain why one observes so many first-order reactions such as



Symbolically, this reaction will be represented as A going to product P; that is,

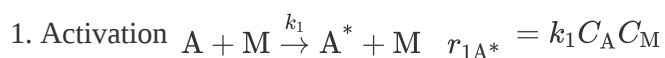


with

$$-r_{\text{A}} = k C_{\text{A}}$$

The reaction is first order *but* the reaction is not elementary. The reaction proceeds by first forming an active intermediate, A*, from the collision of the reactant molecule A and an inert molecule of M. Either this *wildly* oscillating active intermediate, A*, is deactivated by collision with inert M, or it decomposes to form product. See [Figure 9-2](#).

The mechanism consists of the three elementary reactions:



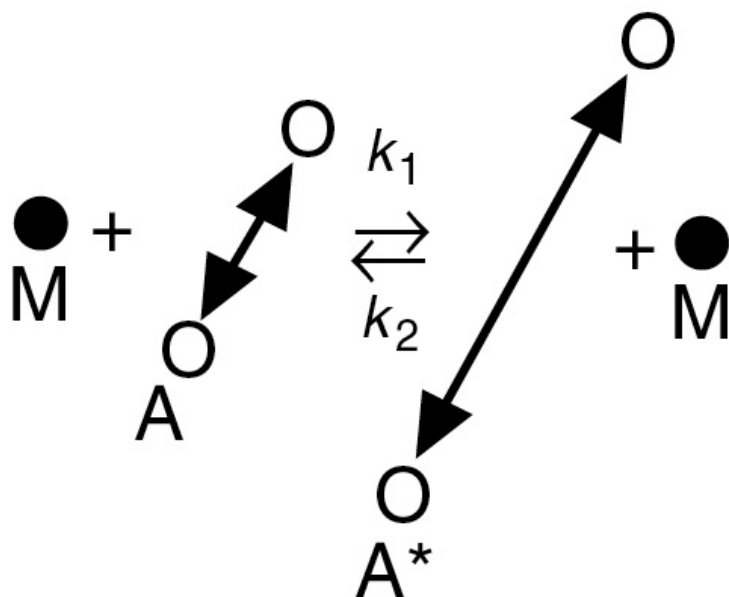
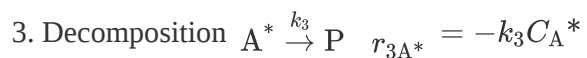


Figure 9-2 Collision and activation of a vibrating A molecule.⁶

⁶ The reaction pathway for the reaction in Figure 9-2 is shown in the margin. We start at the top of the pathway with A and M, and move down to show the pathway of A and M touching k_1 (collision) where the curved lines come together and then separate to form A^* and M. The reverse of this reaction is shown starting with A^* and M and moving upward along the pathway where arrows A^* and M touch, k_2 , and then separate to form A and M. At the bottom, we see the arrow from A^* to form P with k_3 .

Writing the rate of formation of product

$$r_P = k_3 C_{A^*}$$

and using the PSSH to find the concentrations of A^* in a manner similar to the azomethane decomposition described earlier, the rate law can be shown to be

$$r_P = -r_A = \frac{k_3 k_1 C_A C_M}{k_2 C_M + k_3} \quad (9-10)$$

Because the concentration of the inert M is constant, we let

$$k = \frac{k_1 k_3 C_M}{k_2 C_M + k_3} \quad (9-11)$$

Reaction pathways⁶

to obtain the first-order rate law

$$-r_A = kC_A$$

Consequently, we see the reaction



follows an elementary rate law but is not an elementary reaction. Reactions similar to the AZO decomposition mechanism would also be apparent first order *if* the corresponding to the term $(k_2 C_{AZO})$ in the denominator of Equation (9-9) were larger than the other term k_3 (i.e., $(k_2 C_{AZO}) \gg k_3$). The reaction pathway for this reaction is shown in the margin here. Reaction pathways for other reactions are given on the Web site (<http://www.umich.edu/~elements/6e/09chap/prof-rxnpath.html>).

First-order rate law for a nonelementary reaction

9.1.3 Searching for a Mechanism

In many instances the rate data are correlated before a mechanism is found. It is a normal procedure to reduce the additive constant in the denominator to 1.

We therefore divide the numerator and denominator of Equation (9-9) by k_3 to obtain

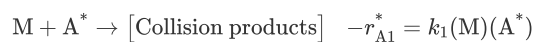
$$r_{C_2H_6} = \frac{k_1 C_{AZO}^2}{1 + k' C_{AZO}} \quad (9-12)$$

General Considerations. Developing a mechanism is a difficult and time-consuming task. The rules of thumb listed in Table 9-2 are by no means inclusive but may be of some help in the development of a simple mechanism that is consistent with the experimental rate law.



TABLE 9-2 RULES OF THUMB FOR DEVELOPMENT OF A MECHANISM

1. Species having the concentration(s) appearing in the *denominator* of the rate law probably collide with the active intermediate; for example,



2. If a constant appears in the *denominator*, one of the reaction steps is probably the spontaneous decomposition of the active intermediate; for example,



3. Species having the concentration(s) appearing in the *numerator* of the rate law probably produce the active intermediate in one of the reaction steps; for example,



Upon application of Table 9-2 to the azomethane example just discussed, we observe the following from rate equation (9-12):

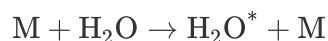
1. The active intermediate, AZO^* , collides with azomethane, AZO [Reaction 2], resulting in the concentration of AZO in the denominator.
2. AZO^* decomposes spontaneously [Reaction 3], resulting in a constant in the denominator of the rate expression.
3. The appearance of AZO in the numerator suggests that the active intermediate AZO^* is formed from AZO . Referring to [Reaction 1], we see that this case is indeed true.

Example 9-1 The Stern–Volmer Equation

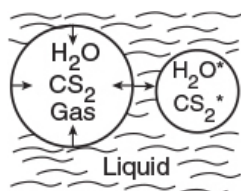
Light is given off when a high-intensity ultrasonic wave is applied to water.⁷ You should be able to see the glow if you turn out the lights and irradiate water with a *focused* ultrasonic tip. This light results from microsize gas bubbles (0.1 mm) being formed by the ultrasonic wave and then being compressed by it. During the compression stage of the wave, the contents of the bubble (e.g., water and whatever else is dissolved in the water, CS₂, O₂, N₂) are compressed adiabatically.

⁷ P. K. Chendke and H. S. Fogler, *J. Phys. Chem.*, 87, 1362.

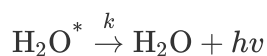
This compression gives rise to high temperatures and kinetic energies of the gas molecules, which through molecular collisions generate active intermediates and cause chemical reactions to occur in the bubble.



Collapsing cavitation microbubble



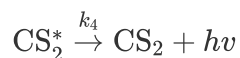
The intensity of the light given off, I , is proportional to the rate of deactivation of an activated water molecule that has been formed in the microbubble.



$$\text{Light intensity (I)} \propto (-r_{H_2O^*}) = k C_{H_2O^*}$$

An order-of-magnitude increase in the intensity of sonoluminescence is observed when either carbon disulfide or carbon tetrachloride is added to the water.

The intensity of luminescence, I , for the reaction



is

$$I \propto (-r_{\text{CS}_2^*}) = k_4 C_{\text{CS}_2^*}$$

A similar result exists for CCl_4 .

However, when an aliphatic alcohol, X, is added to the solution, the intensity decreases with increasing concentration of alcohol. The data are usually reported in terms of a Stern–Volmer plot in which relative intensity is given as a function of alcohol concentration, C_X . (See Figure E9-1.1, where I_0 is the sonoluminescence intensity in the absence of alcohol and I is the sonoluminescence intensity in the presence of alcohol.)

1. Suggest a mechanism consistent with experimental observation.
2. Derive a rate law consistent with Figure E9-1.1.

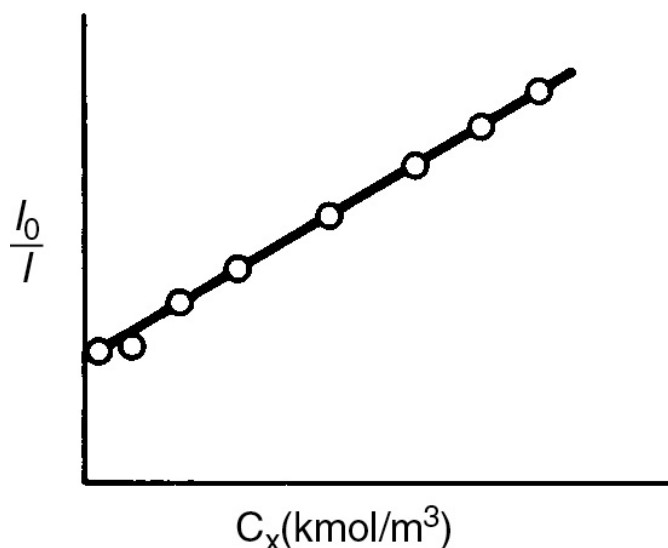


Figure E9-1.1 Ratio of luminescence intensities as a function of scavenger concentration.

Stern–Volmer plot

*Solution***(a) Mechanism**

From the linear plot in [Figure E9-1.1](#) we know that

$$\frac{I_0}{I} = A + BC_X \equiv A + B(X) \quad (\text{E9-1.1})$$

where $C_X \equiv (X)$ and A and B are numerical constants.

Inverting Equation (E9-1.1) yields

$$\frac{I}{I_0} = \frac{1}{A+B(X)} \quad (\text{E9-1.2})$$

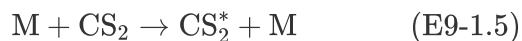
From **Rule 1** of [Table 9-2](#), the denominator suggests that alcohol (X) collides with the active intermediate:



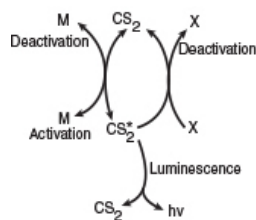
The alcohol acts as what is called a *scavenger* to deactivate the active intermediate. The fact that the addition of CCl_4 or CS_2 increases the intensity of the luminescence

$$I \propto (\text{CS}_2) \quad (\text{E9-1.4})$$

leads us to postulate (**Rule 3** of [Table 9-2](#)) that the active intermediate CS_2^* was probably formed from the collision of either CS_2 or another gas M or both in the collapsing bubble

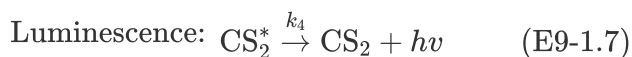
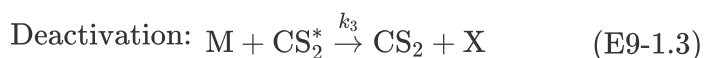
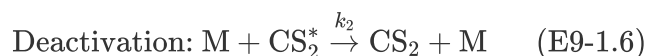
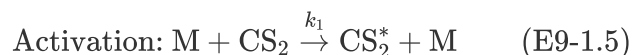


Reaction pathways



where M is a third body (CS_2 , H_2O , N_2 , etc.).

We also know that deactivation can occur by the reverse of reaction (E9-1.5). Combining this information, we have as our mechanism:



$$I = k_4(\text{CS}_2^*) \quad (\text{E9-1.8})$$

The mechanism

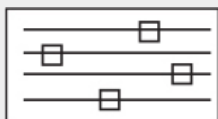
(b) Rate Law

Using the PSSH on CS_2^* in each of the above elementary reactions yields

$$r_{\text{CS}_2^*} = 0 = k_1(\text{CS}_2)(\text{M}) - k_2(\text{CS}_2^*)(\text{M}) - k_3(\text{X})(\text{CS}_2^*) - k_4(\text{CS}_2^*)$$

Solving for (CS_2^*) and substituting into Equation (E9-1.8) gives us

$$I = \frac{k_4 k_1 (\text{CS}_2)(\text{M})}{k_2(\text{M}) + k_3(\text{X}) + k_4} \quad (\text{E9-1.9})$$



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In the absence of alcohol

$$I_0 = \frac{k_4 k_1 (\text{CS}_2)(\text{M})}{k_2(\text{M}) + k_4} \quad (\text{E9-1.10})$$

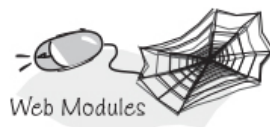
For constant concentrations of CS_2 and the third body, M, we take a ratio of Equation (E9-1.10) to (E9-1.9)

$$\frac{I_0}{I} = 1 + \frac{k_3}{k_2(\text{M}) + k_4} (\text{X}) = 1 + k' (\text{X}) \quad (\text{E9-1.11})$$

which is of the same form as that suggested by Figure E9-1.1. Equation (E9-1.11) and similar equations involving scavengers are called *Stern–Volmer equations*.

Analysis: This example showed how to use the Rules of Thumb (Table 9-2) to develop a mechanism. Each step in the mechanism is assumed to follow an elementary rate law. The PSSH was applied to the net rate of reaction for the *active intermediate* in order to find the concentration of the *active intermediate*. This concentration was then substituted into the rate law for the rate of formation of product to give the rate law. The rate law from the mechanism was found to be consistent with experimental data.

A discussion of luminescence is given in the **Web Module, Glow Sticks** on the CRE Web site (www.umich.edu/~elements/6e/09chap/web.html). Here, the PSSH is applied to glow sticks. First, a mechanism for the reactions and luminescence is developed. Next, mole balance equations are written on each species and coupled with the rate law obtained using the PSSH; the resulting equations are solved and compared with experimental data. See Problem P9-1A.



9.1.4 Chain Reactions

A chain reaction consists of the following sequence:

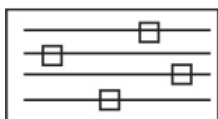
1. *Initiation*: formation of an active intermediate
2. *Propagation or chain transfer*: interaction of an active intermediate with the reactant or product to produce another active intermediate
3. *Termination*: deactivation of the active intermediate to form products



Glow sticks Web Module

Steps in a chain reaction

An example comparing the application of the PSSH with the Polymath solution to the full set of equations is given in the Professional Reference Shelf R9.1, *Chain Reactions* (<http://www.umich.edu/~elements/6e/09chap/prof-chain.html>). Also included in Professional Reference Shelf R9.2 is a discussion of *Reaction Pathways* and the chemistry of smog formation (<http://www.umich.edu/~elements/6e/09chap/prof-rxnpath.html>).



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9.2 ENZYMATIC REACTION FUNDAMENTALS

We now extend our discussion on active intermediates to enzymatic reactions. An *enzyme*[†] is a high-molecular-weight protein or protein-like substance that acts on a substrate (reactant molecule) to transform it chemically at a greatly accelerated rate, usually 10^3 – 10^{17} times faster than the

uncatalyzed rate. The pharmaceutical business that will synthesize therapeutic proteins using CHO has been estimated to reach \$200 billion by 2020. A colleague, Prof. Greg Thurber, and his students are doing exciting research in drug development using enzyme kinetics. The group applies the principles of enzyme kinetics to describe where drugs distribute and degrade in the body to design new therapeutics and diagnostic imaging agents for diseases such as breast cancer.^{8,9} Without enzymes, essential biological reactions would not take place at a rate necessary to sustain life. Enzymes are usually present in small quantities and are not consumed during the course of the reaction, nor do they affect the chemical reaction equilibrium. Enzymes provide an alternate pathway for the reaction to occur, thereby requiring a lower activation energy. Figure 9-3 shows the reaction coordinate for the uncatalyzed reaction of a reactant molecule, called a *substrate* (S), to form a product (P)

[†] See <http://www.rsc.org/Education/Teachers/Resources/cfb/enzymes.htm> and <https://en.wikipedia.org/wiki/Enzyme>.

⁸ S. Bhatnagar, et. al., "Oral administration and detection of a near-infrared molecular imaging agent in an orthotopic mouse model for breast cancer screening," *Mol. Pharm.*, 15, 1746–1754 (2018).

⁹ C. Cilliers, B. Menezes, I. Nessler, J. Linderman, and G. M. Thurber, "Improved tumor penetration and single-cell targeting of antibody-drug conjugates increases anticancer efficacy and host survival.," *Cancer Res.*, 78, 758–768 (2018).

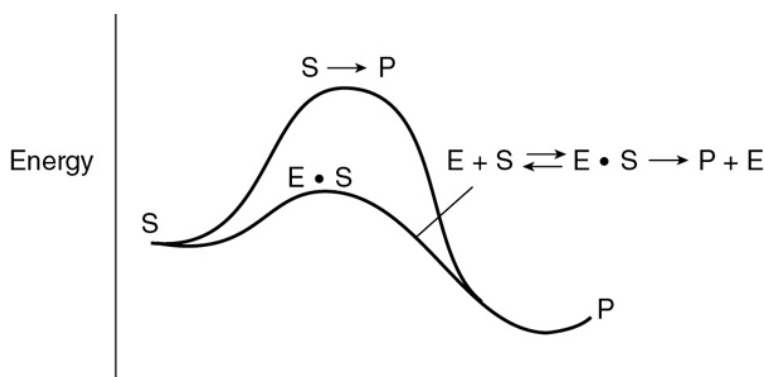


Figure 9-3 Reaction coordinate for enzyme catalysis.



This figure also shows the catalyzed reaction pathway that proceeds through an *active intermediate* ($E \cdot S$), called the *enzyme–substrate complex*, that is,



Because enzymatic pathways have lower activation energies, enhancements in reaction rates can be enormous, as in the degradation of urea by urease, where the degradation rate is on the order of 10^{14} faster than would be without the enzyme urease.

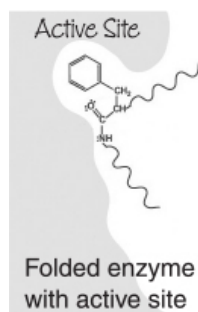
#You'reTheOnlyOne ForMe!

An important property of enzymes is that they are specific; that is, **one** enzyme can usually catalyze only **one** type of reaction. For example, a protease hydrolyzes *only* bonds between specific amino acids in proteins, an amylase works on bonds between glucose molecules in starch, and lipase attacks fats, degrading them to fatty acids and glycerol. Consequently, unwanted products are easily controlled in enzyme-catalyzed reactions. Enzymes are produced only by living organisms, and commercial enzymes are generally produced by bacteria. Enzymes usually work (i.e., catalyze reactions) under mild conditions: pH 4–9 and temperatures 75°F–160°F. Most enzymes are named in terms of the reactions they catalyze. It is a customary practice to add the suffix *-ase* to a major part of the name of the substrate on which the enzyme acts. For example, the enzyme that catalyzes the decomposition of urea is urease and the enzyme that attacks tyrosine is tyrosinase. However, there are a few exceptions to the naming convention, such as α -amylase. The enzyme α -amylase catalyzes the transformation of starch in the first step in the production of the controversial soft drink (e.g., Red Pop) sweetener high-fructose corn syrup (HFCS) from corn starch, which is a \$4 billion per year business.



9.2.1 Enzyme–Substrate Complex

The key factor that sets enzymatic reactions apart from other catalyzed reactions is the formation of an enzyme–substrate complex, ($E \cdot S$). Here, substrate, (S), binds with a specific *active site* of the enzyme, (E), to form this complex.¹⁰ Figure 9-4 shows a schematic of the enzyme chymotrypsin (MW = 25,000 Daltons), which catalyzes the hydrolytic cleavage of polypeptide bonds. In many cases, the enzyme's active catalytic sites are found where the various folds or loops interact. For chymotrypsin, the catalytic sites are noted by the amino acid numbers 57, 102, and 195 in Figure 9-4. Much of the catalytic power is attributed to the binding energy of the substrate to the enzyme through multiple bonds with the specific functional groups on the enzyme (amino side chains, metal ions). The type of interactions that stabilize the enzyme–substrate complex include hydrogen bonding and hydrophobic, ionic, and London van der Waals forces. If the enzyme is exposed to extreme temperatures or pH environments (i.e., both high and low pH values), it may unfold, losing its active sites. When this occurs, the enzyme is said to be *denatured* (see Figure 9.8 and Problem P9-13_B).



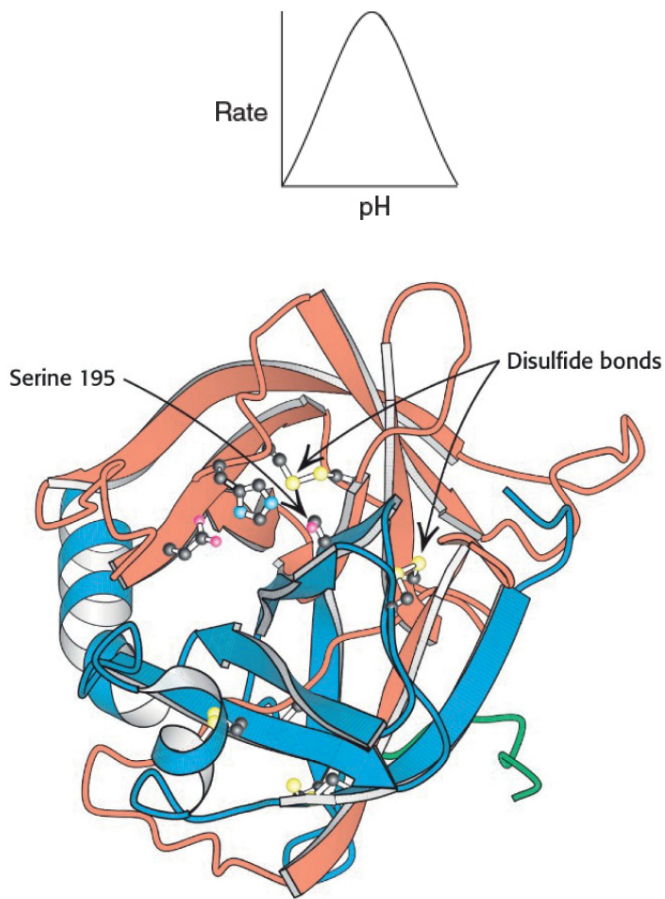


Figure 9-4 Enzyme chymotrypsin from *Biochemistry*, 7th ed., 2010 by Lubert Stryer, p. 258. Used with permission of W. H. Freeman and Company.

¹⁰ M. L. Shuler and F. Kargi, *Bioprocess Engineering Basic Concepts*, 2nd ed. Upper Saddle River, NJ: Prentice Hall, 2002.

Schematic showing the loops and folds

Two often used models for enzyme–substrate interactions are the *lock-and-key model* and the *induced fit model*, both of which are shown in [Figure 9-5](#). For many years, the lock-and-key model was preferred because of the stereospecific effects of one enzyme acting on one substrate. However, the induced fit model is the more useful model. In the induced fit model, both the enzyme molecule and the substrate molecules are distorted. These changes in conformation distort one or more of the substrate bonds, thereby stressing and weakening the bond to

make the molecule more susceptible to rearrangement or attachment.

Two models for the enzyme–substrate complex

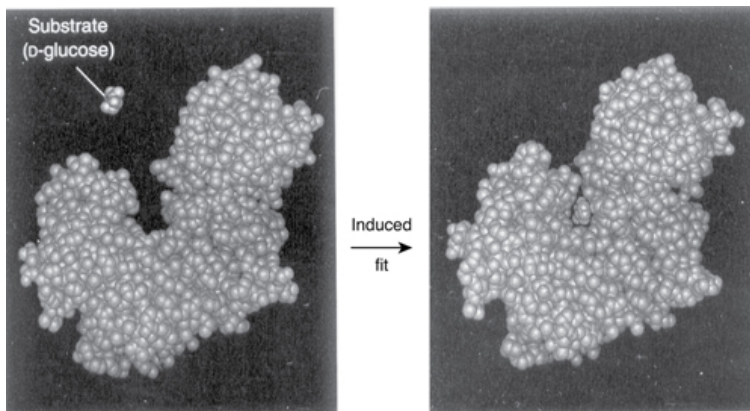
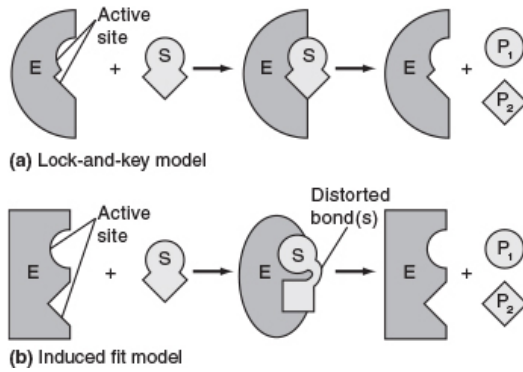


Figure 9-5 Two models for enzyme–substrate interaction.

There are six classes of enzymes and only six:

1. Oxidoreductases $AH_2 + B + E \rightarrow A + BH_2 + E$

2. Transferases $AB + C + E \rightarrow AC + B + E$

3. Hydrolases $AB + H_2O + E \rightarrow AH + BOH + E$

4. Isomerases $A + E \rightarrow \text{iso}A + E$

5. Lyases $AB + E \rightarrow A + B + E$

6. Ligases $A + B + E \rightarrow AB + E$

More information about enzymes can be found on the following two Web sites: <http://us.expasy.org/enzyme/> and www.chem.qmw.ac.uk/iubmb/enzyme. These sites also give information about enzymatic reactions in general.



9.2.2 Mechanisms

In developing some of the elementary principles of the kinetics of enzyme reactions, we shall discuss an enzymatic reaction that has been suggested by Levine and LaCourse as part of a system that would reduce the size of an artificial kidney.¹¹ The desired result is a prototype of an artificial kidney that could be worn by the patient and would incorporate a replaceable unit for the elimination of the body's nitrogenous waste products, such as uric acid and creatinine. A schematic of this device is shown on the CRE Web site (<http://www.umich.edu/~elements/6e/09chap/summary.html#sec2>). In the microencapsulation scheme proposed by Levine and LaCourse, the enzyme urease would be used in the removal of urea from the bloodstream. Here, the catalytic action of urease would cause urea to decompose into ammonia and carbon dioxide. The mechanism of the reaction is believed to proceed by the following sequence of elementary reactions:

¹¹ N. Levine and W. C. LaCourse, *J. Biomed. Mater. Res.*, 1, 275.

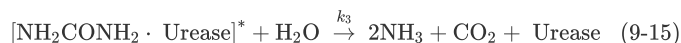
1. The unbound enzyme urease (E) reacts with the substrate urea (S) to form an enzyme-substrate complex (E · S):



2. This complex (E · S) can decompose back to urea (S) and urease (E):



3. Or, it can react with water (W) to give the products (P) ammonia and carbon dioxide, and recover the enzyme urease (E):



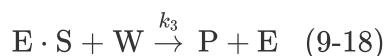
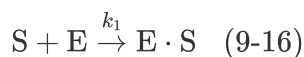
The reaction mechanism

Symbolically, the overall reaction is written as



We see that *some* of the enzyme added to the solution binds to the urea, and *some* of the enzyme remains unbound. Although we can easily measure the total concentration of enzyme, (E_t), it is difficult to measure either the concentration of free enzyme, (E), or the concentration of the bound enzyme ($E \cdot S$).

Letting E , S , W , $E \cdot S$, and P represent the enzyme, substrate, water, the enzyme–substrate complex, which is the *active intermediate*, and the reaction products, respectively, we can write Reactions (9-13)–(9-15) symbolically in the forms



Here, $P = 2\text{NH}_3 = \text{CO}_2$.

The corresponding rate laws for Reactions (9-16)–(9-18) are

$$r_{1\text{E}\cdot\text{S}} = k_1(E)(S) \quad (9-16\text{A})$$

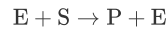
$$r_{2\text{E}\cdot\text{S}} = -k_2(E \cdot S) \quad (9-17\text{A})$$

$$r_{3\text{E}\cdot\text{S}} = -k_3(E \cdot S)(W) \quad (9-18\text{A})$$

where all the specific reaction rates are *defined with respect to* ($E \cdot S$). The net rate of formation of product, r_P , is

$$\boxed{r_P = k_3(W)(E \cdot S)} \quad (9-19)$$

For the overall reaction



we know that the rate of consumption of the urea substrate equals the rate of formation of product CO_2 , that is, $-r_S = r_P$.

This rate law, Equation (9-19), is of not much use to us in making reaction engineering calculations because we cannot measure the concentration of the *active intermediate*, which is the enzyme–substrate complex ($E \cdot S$). We will use the PSSH to express ($E \cdot S$) in terms of measured variables.

$$-r_S = r_P, \text{ that is,}$$

$$-r_{\text{NH}_2\text{CONH}_2}$$

$$= r_{\text{CO}_2}$$

The net rate of formation of the enzyme–substrate complex is

$$r_{E \cdot S} = r_{1E \cdot S} + r_{2E \cdot S} + r_{3E \cdot S}$$

Substituting the rate laws, we obtain

$$r_{E \cdot S} = k_1(E)(S) - k_2(E \cdot S) - k_3(W)(E \cdot S) \quad (9-20)$$

Using the PSSH, $r_{E \cdot S} = 0$, we can now solve Equation (9-20) for ($E \cdot S$)

$$(E \cdot S) = \frac{k_1(E)(S)}{k_2 + k_3(W)} \quad (9-21)$$

and substitute for ($E \cdot S$) into Equation (9-19)

$$-r_S = r_P = \frac{k_1 k_3 (E)(S)(W)}{k_2 + k_3(W)} \quad (9-22)$$

We *still cannot* use this rate law because we cannot measure the unbound enzyme concentration (E); however, we *can* measure the total enzyme concentration, E_t .

We need to replace unbound enzyme concentration (E) in the rate law.

In the absence of enzyme denaturation, the total concentration of the enzyme in the system, (E_t) , is constant and equal to the sum of the concentrations of the free or unbounded enzyme, (E) , and the enzyme–substrate complex, $(E \cdot S)$:

$$(E_t) = (E) + (E \cdot S) \quad (9-23)$$

Total enzyme concentration = Bound + Free enzyme concentration.

Substituting for $(E \cdot S)$

$$(E_t) = (E) + \frac{k_1(E)(S)}{k_2 + k_3(W)}$$

solving for (E)

$$(E) = \frac{(E_t)(k_2 + k_3(W))}{k_2 + k_3(W) + k_1(S)}$$

and substituting for (E) in Equation (9-22), the rate law for substrate consumption is

$$-r_S = \frac{k_1 k_3 (W) (E_t) (S)}{k_1 (S) + k_2 + k_3 (W)} \quad (9-24)$$

Note: Throughout the following text, $E_t \equiv (E_t)$ = total concentration of enzyme with typical units such as (kmol/m^3) or (g/dm^3) .

9.2.3 Michaelis–Menten Equation

Because the reaction of urea and urease is carried out in an aqueous solution, water is, of course, in excess, and the concentration of water (W) is therefore considered constant, ca. $55 \text{ mol}/\text{dm}^3$. Let

$$k_{\text{cat}} = k_3(W) \text{ and let } K_M = \frac{k_2 + k_3(W)}{k_1}$$

After dividing the numerator and denominator of Equation (9-24) by k_1 , we obtain a form of the *Michaelis–Menten equation*:

$$-r_S = \frac{k_{\text{cat}}(E_t)(S)}{(S) + K_M} \quad (9-25)$$

The final form of the rate law

Turnover number k_{cat}

The parameter k_{cat} is also referred to as the **turnover number**. It is the number of substrate molecules converted to product in a given time on a single-enzyme molecule when the enzyme is saturated with substrate (i.e., all the active sites on the single-enzyme molecule are occupied, $(S) \gg K_M$). For example, the turnover number for the decomposition of hydrogen peroxide, H_2O_2 , by the enzyme catalase is $40 \times 10^6 \text{ s}^{-1}$. That is, 40 million molecules of H_2O_2 are decomposed every second on a single-enzyme molecule saturated with H_2O_2 . The constant K_M (mol/dm^3) is called the *Michaelis constant* and for simple systems is a measure of the attraction of the enzyme for its substrate, so it's also called the *affinity constant*. The Michaelis constant, K_M , for the decomposition of H_2O_2 discussed earlier is 1.1 M, while that for chymotrypsin is 0.1 M.¹²

¹² D. L. Nelson and M. M. Cox, *Lehninger Principles of Biochemistry*, 3rd ed. New York: Worth Publishers, 2000.

Michaelis constant K_M

If, in addition, we let V_{max} represent the maximum rate of reaction for a given total enzyme concentration

$$V_{\text{max}} = k_{\text{cat}} (E_t)$$

the Michaelis–Menten equation takes the familiar form

$$-r_S = \frac{V_{\text{max}}(S)}{K_M + (S)} \quad (9-26)$$

Michaelis–Menten equation

A sketch of the rate of disappearance of the substrate, $-r_s$, at a given concentration of total enzyme, E_T , is shown as a function of the substrate concentration, S , in Figure 9-6.

A plot of this type is sometimes called a *Michaelis–Menten* plot.

At low substrate concentrations, $K_M \gg (S)$, Equation (9-26) reduces to

$$-r_s \cong \frac{V_{\max}(S)}{K_M}$$

and the reaction is apparent first order in the substrate concentration.

At high substrate concentrations,

$$(S) \gg K_M$$

Michaelis–Menten plot

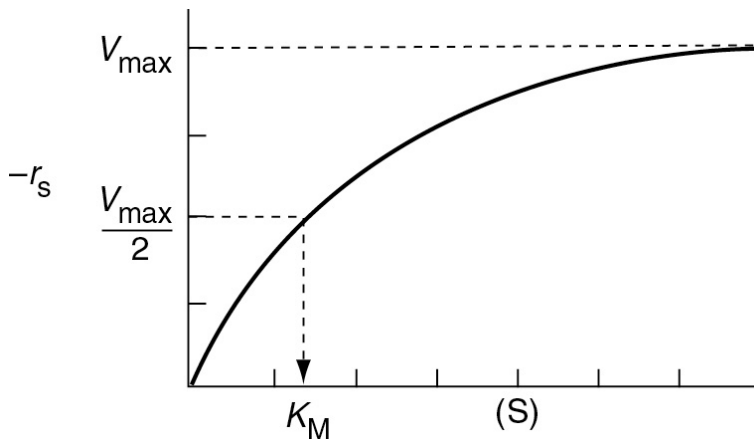


Figure 9-6 Michaelis–Menten plot identifying the parameters V_{\max} and K_M .

Equation (9-26) reduces to

$$-r_s \cong V_{\max}$$

and we see the reaction is apparent zero order.

Interpretation of Michaelis constant

What does K_M represent? Consider the case when the substrate concentration is such that the reaction rate is equal to one-half the maximum rate

$$-r_s = \frac{V_{\max}}{2}$$

then

$$\frac{V_{\max}}{2} = \frac{V_{\max}(S_{1/2})}{K_M + (S_{1/2})} \quad (9-27)$$

Solving Equation (9-27) for the Michaelis constant yields

$$K_M = (S_{1/2}) \quad (9-28)$$

The Michaelis constant is equal to the substrate concentration at which the rate of reaction is equal to one-half the maximum rate, that is, $-r_s = V_{\max}/2$. The larger the value of K_M , the higher the substrate concentration(s) necessary for the reaction rate to reach half of its maximum value.

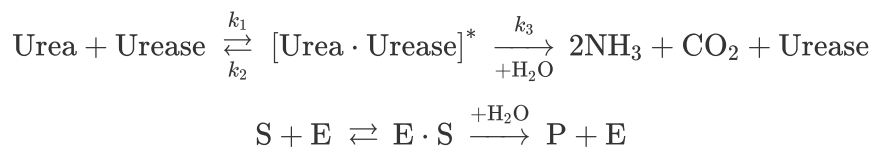
$$K_M = (S_{1/2})$$

The parameters V_{\max} and K_M characterize the enzymatic reactions that are described by Michaelis–Menten kinetics. V_{\max} is dependent on total enzyme concentration, whereas K_M is not.

Two enzymes may have the same values for k_{cat} but have different reaction rates because of different values of K_M . One way to compare the catalytic efficiencies of different enzymes is to compare their ratios k_{cat}/K_M . When this ratio approaches 10^8 – 10^9 (dm³/mol/s), the reaction rate approaches becoming diffusion limited. That is, it takes a long time for the enzyme and substrate to diffuse around in the fluid and find each other, but once they do they react immediately. We will discuss diffusion-limited reactions in Chapters 14 and 15.

**Example 9–2 Evaluation of Michaelis–Menten
Parameters V_{\max} and K_M**

In this example, we illustrate how to determine the enzymatic reaction-rate parameters V_{\max} and K_M for the reaction rate.



The rate of reaction is given as a function of urea concentration in Table E9-2.1, where $(S) \equiv C_{\text{urea}}$.

TABLE E9-2.1 RATE DATA[†]

C_{urea} (kmol/m ³)	0.2	0.02	0.01	0.005	0.002
$-r_{\text{urea}}$ (kmol/m ³ ·s)	1.08	0.55	0.38	0.2	0.09

[†] Unfiltered real data.

1. Determine the Michaelis–Menten parameters V_{\max} and K_M for the reaction.
2. In addition to forming a Lineweaver–Burk Plot, form Hanes–Woolf and Eadie–Hofstee plots, and discuss the attributes of each type of plot.
3. Use non-linear regression to find V_{\max} and K_M .

Solution

Part (a)

Inverting Equation (9-26) gives us the Lineweaver–Burk equation

$$\frac{1}{-r_s} = \frac{(S) + K_M}{V_{\max}(S)} = \frac{1}{V_{\max}} + \frac{K_M}{V_{\max}} \frac{1}{(S)} \quad (\text{E9-2.1})$$

or in terms of urea

$$\frac{1}{-r_{\text{urea}}} = \frac{1}{V_{\text{max}}} + \frac{K_M}{V_{\text{max}}} \left(\frac{1}{C_{\text{urea}}} \right) \quad (\text{E9-2.2})$$

Lineweaver–Burk equation

A plot of the reciprocal reaction rate versus the reciprocal urea concentration should be a straight line with an intercept $(1/V_{\text{max}})$ and slope (K_M/V_{max}) . This type of plot is called a *Lineweaver–Burk plot*. We shall use the data in Table E9-2.2 to make two plots: a plot of $-r_{\text{urea}}$ as a function of C_{urea} using Equation (9-26), which is called a *Michaelis–Menten plot* and is shown in Figure E9-2.1(a); and a plot of $(1/-r_{\text{urea}})$ as a function $(1/C_{\text{urea}})$, which is called a *Lineweaver–Burk plot* and is shown in Figure 9-2.1(b).

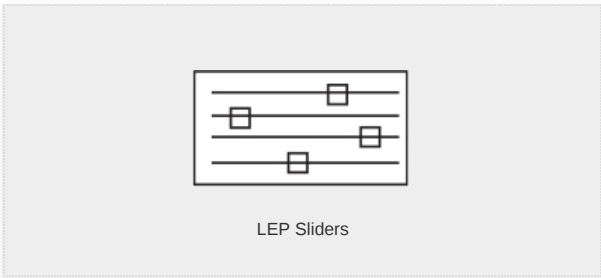
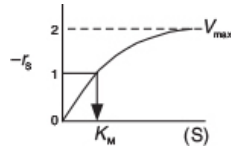


TABLE E9-2.2 RAW AND PROCESSED DATA

C_{urea} (kmol/m ³)	$-r_{\text{urea}}$ (kmol/m ³ ·s)	$1/C_{\text{urea}}$ (m ³ /kmol)	$1/-r_{\text{urea}}$ (m ³ ·s/kmol)
0.20	1.08	5.0	0.93
0.02	0.55	50.0	1.82
0.01	0.38	100.0	2.63
0.005	0.20	200.0	5.00
0.002	0.09	500.0	11.11



Michaelis–Menten Plot

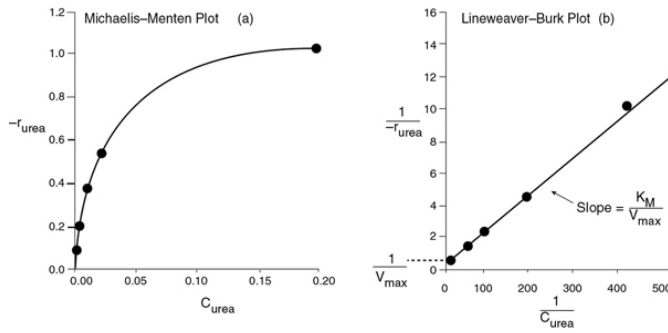
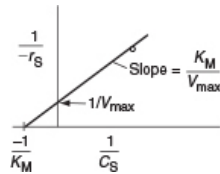


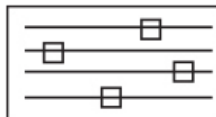
Figure E9-2.1 (a) Michaelis–Menten plot; (b) Lineweaver–Burk plot.



Lineweaver–Burk Plot

The intercept on Figure E9-2.1(b) is 0.75, so

$$\frac{1}{V_{\max}} = 0.75 \text{ m}^3 \cdot \text{s/kmol}$$



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Therefore, the maximum rate of reaction is

$$V_{\max} = 1.33 \text{ kmol/m}^3 \cdot \text{s} = 1.33 \text{ mol/dm}^3 \cdot \text{s}$$

From the slope, which is 0.02 s, we can calculate the Michaelis constant, K_M

$$\frac{K_M}{V_{\max}} = \text{slope} = 0.02\text{s}$$

For enzymatic reactions, the two key rate-law parameters are V_{\max} and K_M .

Solving for K_M :

$$K_M = 0.0266 \text{ kmol/m}^3.$$

Substituting K_M and V_{\max} into Equation (9-26) gives us

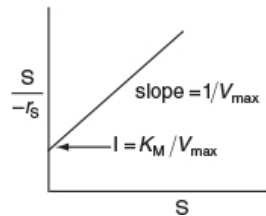
$$-r_{\text{urea}} = \frac{1.33 C_{\text{urea}}}{0.0266 + C_{\text{urea}}} \quad (\text{E9-2.3})$$

where C_{urea} has units of (kmol/m^3) and $-r_{\text{urea}}$ has units of ($\text{kmol/m}^3 \cdot \text{s}$). Levine and LaCourse suggest that the total concentration of urease, (E_t), corresponding to the value of V_{\max} above is approximately 5 g/dm^3 .

Part (b)

In addition to the *Lineweaver–Burk plot*, one can also use a *Hanes–Wolf plot* or an *Eadie–Hofstee plot*. Here, $S \equiv C_{\text{urea}}$, and $-r_S \equiv -r_{\text{urea}}$.

$$-r_S = \frac{V_{\max}(S)}{K_M + (S)} \quad (9-26)$$



Hanes–Wolf Plot

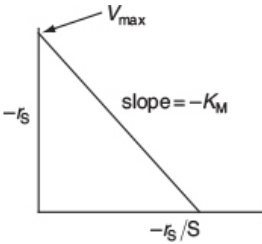
For the *Hanes–Wolf* form, we can rearrange Equation (9-26) to

$$\frac{(S)}{-r_S} = \frac{K_M}{V_{\max}} + \frac{1}{V_{\max}}(S) \quad (E9-2.4)$$

Equation (9-26) can be rearranged in the following forms. For the *Eadie–Hofstee* form

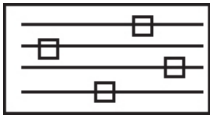
$$-r_S = V_{\max} - K_M \left(\frac{-r_S}{(S)} \right) \quad (E9-2.5)$$

and for the *Hanes–Wolf* model, we plot [(S)/−r_S] as a function of (S) and for the *Eadie–Hofstee* model, we plot −r_S as a function of [−r_S/(S)].



Eadie–Hofstee Plot

When to use the different models? The *Eadie–Hofstee* plot does not bias the data points at low substrate concentrations, while the *Hanes–Wolf* plot gives a more accurate evaluation of V_{max}. In Table E9-2.3, we add two columns to Table E9-2.2 to generate these plots (C_{urea} ≡ S).



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TABLE E9-2.3 RAW AND PROCESSED DATA

S	$-r_S$ (kmol/m ³ · s)	$1/-r_S$ (m ³ · s/kmol)	$S/-r_S$ (1/s)
(kmol/m ³ · s)		(m ³ /kmol)	r_S (1/s)
)			
0.20	1.08	5.0	0.93
			0.185
			5.4

0.02	0.55	50.0	1.82	0.0364	27.5
0.01	0.38	100.0	2.63	0.0263	38
0.005	0.20	200.0	5.00	0.0250	40
0.002	0.09	500.0	11.11	0.0222	45

The slope of the *Hanes–Woolf* plot in Figure E9-2.2 (i.e., $(1/V_{\max}) = 0.826 \text{ s} \cdot \text{m}^3/\text{kmol}$), gives $V_{\max} = 1.2 \text{ kmol/m}^3 \cdot \text{s}$ and from the intercept, $K_M/V_{\max} = 0.02 \text{ s}$, we obtain K_M to be 0.024 kmol/m^3 .

Best plot to evaluate V_{\max}

$$\frac{(S)}{-r_S} = \frac{K_M}{V_{\max}} + \frac{1(S)}{V_{\max}}$$

Hanes–Woolf plot

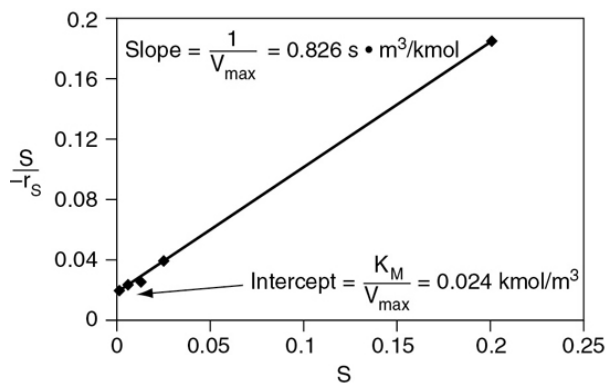


Figure E9-2.2 Hanes–Woolf plot.

We next generate an Eadie–Hofstee plot from the data in Table E9-2.3. From the slope (-0.0244 kmol/m^3) in the *Eadie-Hofstee* plot in Figure E9-2.3, we find $K_M = 0.024 \text{ kmol/m}^3$. Next, extrapolating the line ($-r_S/S$) to zero, we find the intercept to be 1.22, therefore $V_{\max} = 1.22 \text{ kmol/m}^3 \cdot \text{s}$.

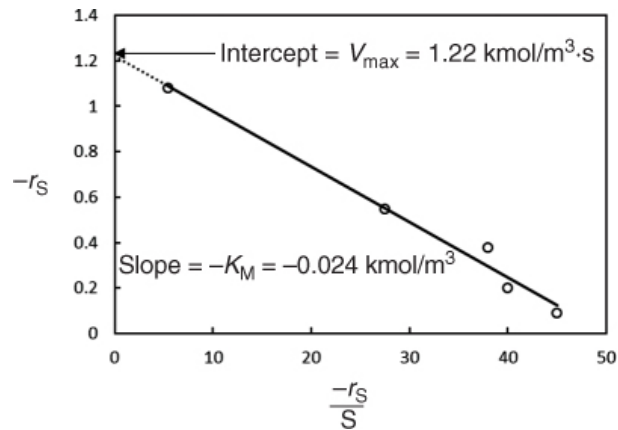


Figure E9-2.3 Eadie–Hofstee plot.

$$-r_S = V_{\max} - K_M \left(\frac{-r_S}{S} \right)$$

Eadie–Hofstee plot

Part (c) Regression

Equation (9-26) and Table E9-2.2 were used in the regression program of Polymath with the following results for V_{\max} and K_M , as shown in Table E9-2.4.

TABLE E9-2.4 REGRESSION RESULTS

Nonlinear regression (L-M)			
Model: rate = Vmax*Curea/(Km+Curea)			
Variable	Ini guess	Value	95% confidence
Vmax	1	1.2057502	0.0598303
Km	0.02	0.0233322	0.003295
Nonlinear regression settings			
Max # iterations = 64			
Precision			
R ²	= 0.9990611		
R ² adj	= 0.9987481		
Rmsd	= 0.0047604		
Variance	= 1.888E-04		

A comparison of the values V_{\max} and K_M is shown in Table E9-2.5.

TABLE E9-2.5 COMPARISON OF MICHAELIS–MENTON
PARAMETER CALCULATIONS

<i>Lineweaver–Burk Eadie–Hofstee Hanes–Woolf Regression</i>				
V_{\max} (kmol/m ³ • s)	1.33	1.22	1.21	1.2
K_M (kmol/m ³)	0.027	0.024	0.024	0.023

These values are within experimental error of those values of V_{\max} and K_M determined graphically.

Analysis: This example demonstrated how to evaluate the parameters V_{\max} and K_M in the Michaelis–Menten rate law from enzymatic reaction data. Four techniques were used to evaluate V_{\max} and K_M from experimental data: Lineweaver–Burk plot, Hanes–Woolf plot, Eadie–Hofstee plot, and non-linear regression. The advantage of each type of plot was discussed for evaluating the parameters V_{\max} and K_M .

9.2.4 Batch Reactor Calculations for Enzyme Reactions

A mole balance on urea in a batch reactor gives

$$-\frac{dN_{\text{urea}}}{dt} = -r_{\text{urea}} V \quad (9-29)$$

Mole balance

Because this reaction is liquid phase, $V = V_0$, the mole balance can be put in the following form:

$$-\frac{dC_{\text{urea}}}{dt} = -r_{\text{urea}} \quad (9-30)$$

The rate law for urea decomposition is

$$-r_{\text{urea}} = \frac{V_{\max} C_{\text{urea}}}{K_M + C_{\text{urea}}} \quad (9-31)$$

Rate law

Substituting Equation (9-31) into Equation (9-30) and then rearranging and integrating, we get

$$t = \int_{C_{\text{urea}}}^{C_{\text{urea0}}} \frac{dC_{\text{urea}}}{-r_{\text{urea}}} = \int_{C_{\text{urea}}}^{C_{\text{urea0}}} \frac{K_M + C_{\text{urea}}}{V_{\text{max}} C_{\text{urea}}} dC_{\text{urea}}$$

Combine

$$t = \frac{K_M}{V_{\text{max}}} \ln \frac{C_{\text{urea0}}}{C_{\text{urea}}} + \frac{C_{\text{urea0}} - C_{\text{urea}}}{V_{\text{max}}} \quad (9-32)$$

Integrate

We can write Equation (9-32) in terms of conversion as

$$C_{\text{urea}} = C_{\text{urea0}} (1 - X)$$

Time to achieve a conversion X in a batch enzymatic reaction

$$t = \frac{K_M}{V_{\text{max}}} \ln \frac{1}{1-X} + \frac{C_{\text{urea0}} X}{V_{\text{max}}} \quad (9-32a)$$

The parameters K_M and V_{max} can readily be determined from batch reactor data by using the integral method of analysis. Here, as shown in Chapter 7 Figures 7-1, 7-2, and 7-3, we want to arrange our equation so that we can obtain a linear plot of our data. Letting $S = C_{\text{urea}}$ and $S_0 = C_{\text{urea0}}$, we arrange Equation (9-32) in the form

$$\frac{1}{t} \ln \frac{S_0}{S} = \frac{V_{\text{max}}}{K_M} - \frac{S_0 - S}{K_M t} \quad (9-33)$$

The corresponding plot in terms of substrate concentration is shown in Figure 9-7.

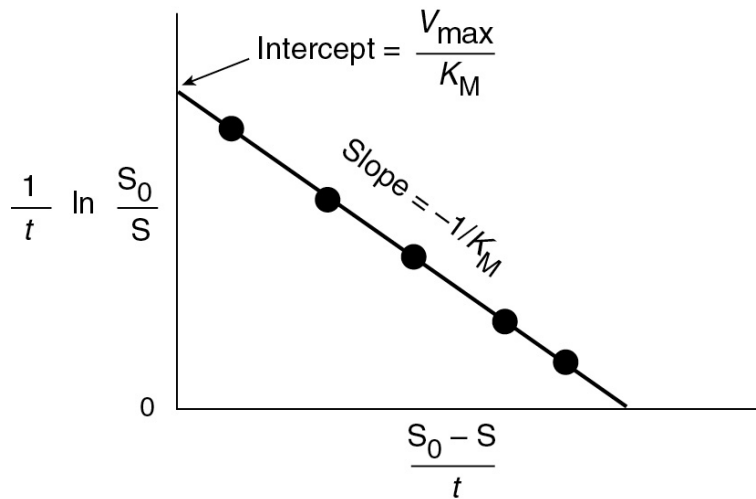
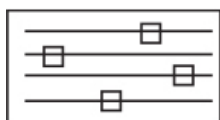


Figure 9-7 Evaluating V_{\max} and K_M from batch reactor data.

From Equation (9-33), we see that the slope of a plot of $\left[\frac{1}{t} \ln \frac{S_0}{S}\right]$ as a function of $\left[\frac{S_0 - S}{t}\right]$ will be $\left(-\frac{1}{K_m}\right)$ and the y intercept will be $\left(\frac{V_{\max}}{K_m}\right)$. In cases similar to Equation (9-33) where there is no possibility of confusion, we shall not bother to enclose the substrate or other species in parentheses to represent concentration (i.e., $C_S \equiv (S) \equiv S$). You will note you cannot use the substrate concentration at $t = 0$ to construct this plot.

Example 9–3 Batch Enzymatic Reactors

Calculate the time needed to convert 99% of the urea to ammonia and carbon dioxide in a 0.5-dm³ batch reactor. The initial concentration of urea is 0.1 mol/dm³, and the urease concentration is 0.001 g/dm³. The reaction is to be carried out isothermally at the same temperature at which the data in Table E9-2.2 were obtained.



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Solution

We can use Equation (9-32a)

$$t = \frac{K_M}{V_{\max}} \ln \frac{1}{1-X} + \frac{C_{\text{urea}0} X}{V_{\max}} \quad (9-32a)$$

From Table E9-2.4 we know $K_M = 0.0233 \text{ mol/dm}^3$, $V_{\max} = 1.2 \text{ mol/dm}^3 \cdot \text{s}$. The conditions given are $X = 0.99$ and $C_{\text{urea}0} = 0.1 \text{ mol / dm}^3$ (i.e., 0.1 kmol/m^3). However, for the conditions in the batch reactor, the enzyme concentration is only 0.001 g/dm^3 , compared with 5 g/dm^3 in Example 9-2. Because $V_{\max} = E_t \cdot k_3$, V_{\max} for the second enzyme concentration is

$$V_{\max 2} = \frac{E_{t2}}{E_{t1}} V_{\max 1} = \frac{0.001}{5} \times 1.2 = 2.4 \times 10^{-4} \text{ mol/s} \cdot \text{dm}^3$$

$$K_M = 0.0233 \text{ mol/dm}^3 \text{ and } X = 0.99$$

Substituting into Equation (9-32)

$$\begin{aligned}
 t &= \frac{2.33 \times 10^{-2} \text{ mol/dm}^3}{2.4 \times 10^{-4} \text{ mol/dm}^3/\text{s}} \ln\left(\frac{1}{0.01}\right) + \frac{(0.1 \text{ mol/dm}^3)(0.99)}{2.4 \times 10^{-4} \text{ mol/dm}^3/\text{s}} \\
 &= 447 \text{ s} + 412 \text{ s} \\
 &= 859 \text{ s (14.325 min)} \quad \underline{\text{Answer}}
 \end{aligned}$$

Analysis: This example shows a straightforward Chapter 5-type calculation of the batch reactor time to achieve a certain conversion X for an enzymatic reaction with a Michaelis–Menten rate law. This batch reaction time is very short; consequently, a continuous-flow reactor might be better suited for this reaction.

Effect of Temperature

The effect of temperature on enzymatic reactions is very complex. If the enzyme structure would remain unchanged as the temperature is increased, the rate would probably follow the Arrhenius temperature dependence. However, as the temperature increases, the enzyme can unfold and/or become denatured and lose its catalytic activity. Consequently, as the temperature increases, the reaction rate, $-r_S$, increases up to a maximum and then decreases as the temperature is increased further. The descending part of this curve is called *temperature inactivation* or *thermal denaturizing*.¹³

¹³ M. L. Shuler and F. Kargi, *Bioprocess Engineering Basic Concepts*, 2nd ed. Upper Saddle River, NJ: Prentice Hall, 2002, p. 77.

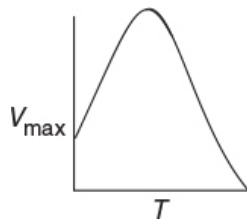


Figure 9-8 shows an example of this optimum in enzyme activity.¹⁴

¹⁴ S. Aiba, A. E. Humphrey, and N. F. Mills, *Biochemical Engineering*, New York: Academic Press, 1973, p. 47.

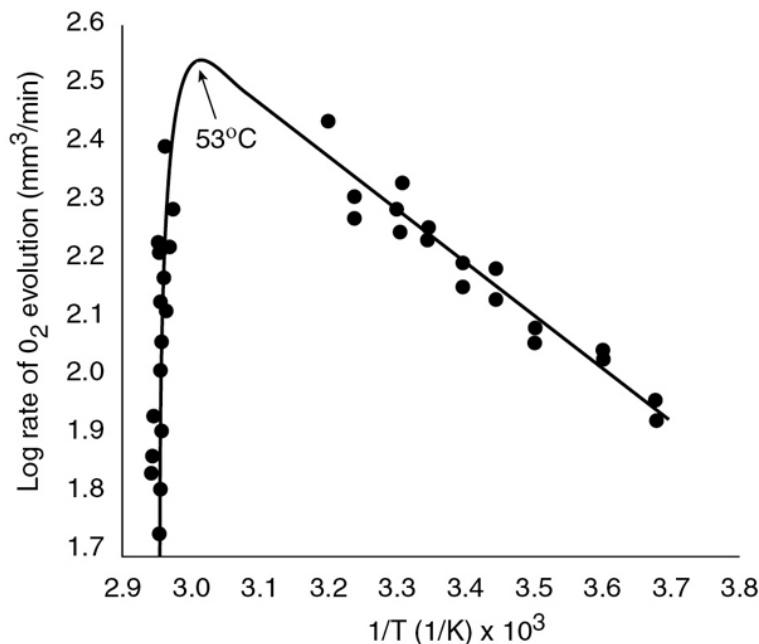


Figure 9-8 Catalytic breakdown rate of H_2O_2 depending on temperature. Courtesy of S. Aiba, A. E. Humphrey, and N. F. Mills, *Biochemical Engineering*, Academic Press (1973).

9.3 INHIBITION OF ENZYME REACTIONS

In addition to temperature and solution pH, another factor that greatly influences the rates of enzyme-catalyzed reactions is the presence of an inhibitor. Inhibitors are species that interact with enzymes and render the enzyme either partially or totally ineffective to catalyze its specific reaction. The most dramatic consequences of enzyme inhibition are found in living organisms, where the inhibition of any particular enzyme involved in a primary metabolic pathway will render the entire pathway inoperative, resulting in either serious damage to or death of the organism. For example, the inhibition of a single enzyme, cytochrome oxidase, by cyanide will cause the aerobic oxidation process to stop; death occurs in a very few minutes. There are also beneficial inhibitors, such as the ones used in the treatment of leukemia and other neo-plastic diseases. Aspirin inhibits the enzyme that catalyzes the synthesis of the molecule prostaglandin, which is involved in the pain-producing process. Aspirin and other covalent drugs

with enzyme inhibitors are discussed in *Nature Reviews*, 10, 307 (2011) “The resurgence of covalent drugs,” by Professor Adrian Whitty. Data for an inhibitor discussed in this article is given in Problem P9-15. As shown in TV advertisements, the recent discovery of DDP-4 enzyme inhibitor Januvia has been approved for the treatment of Type 2 diabetes, a disease affecting 240 million people worldwide. Work Problem P9-20_C and then as the TV ad said, “Ask your doctor if Januvia is right for you.”

The three most common types of reversible inhibition occurring in enzymatic reactions are *competitive*, *uncompetitive*, and *noncompetitive*. The enzyme molecule is analogous to a heterogeneous catalytic surface in that it contains active sites. When *competitive* inhibition occurs, the substrate and inhibitor are usually similar molecules that compete for the same site on the enzyme. *Uncompetitive* inhibition occurs when the inhibitor deactivates the enzyme–substrate complex, sometimes by attaching itself to both the substrate and enzyme molecules of the complex. *Noncompetitive* inhibition occurs with enzymes containing at least two different types of sites. The substrate attaches only to one type of site, and the inhibitor attaches only to the other to render the enzyme inactive.

9.3.1 Competitive Inhibition

Competitive inhibition is of particular importance in pharmacokinetics (drug therapy). If a patient were administered two or more drugs that react simultaneously within the body with a common enzyme, cofactor, or active species, this interaction could lead to competitive inhibition in the formation of the respective metabolites and produce serious consequences. An example of competitive inhibition that is important in blood pressure regulation is the inhibition of the enzyme angiotensin by Mercapto-propanal-L-praline.[†]

[†] *Biochemistry*, 16 (25), 5481.

In competitive inhibition, another substance, that is, I, competes with the substrate for the enzyme molecules to form

an inhibitor–enzyme complex, as shown in [Figure 9-9](#). That is, in addition to the three Michaelis–Menten reaction steps, there are two additional steps as the inhibitor (I) reversely ties up the enzyme, as shown in Reaction Steps 4 and 5.

The rate law for the formation of product in Reaction Step 3 is the same (cf. Equations (9-18A) and (9-19)) as it was before, that is, in the absence of inhibitor

$$r_P = k_3(E \cdot S) \quad (9-34)$$

Applying the PSSH, the net rate of reaction of the enzyme–substrate complex is

$$r_{E \cdot S} = 0 = k_1(E)(S) - k_2(E \cdot S) - k_3(E \cdot S) \quad (9-35)$$

In a similar fashion, apply the PSSH to the net rate of formation of the inhibitor–substrate complex ($E \cdot I$) is also zero

$$r_{E \cdot I} = 0 = k_4(E)(I) - k_5(E \cdot I) \quad (9-36)$$

Reaction Steps

- (1) $E + S \xrightarrow{k_1} E \cdot S$
- (2) $E \cdot S \xrightarrow{k_2} E + S$
- (3) $E \cdot S \xrightarrow{k_3} P + E$
- (4) $I + E \xrightarrow{k_4} E \cdot I \text{ (inactive)}$
- (5) $E \cdot I \xrightarrow{k_5} E + I$

Competitive Inhibition Pathway

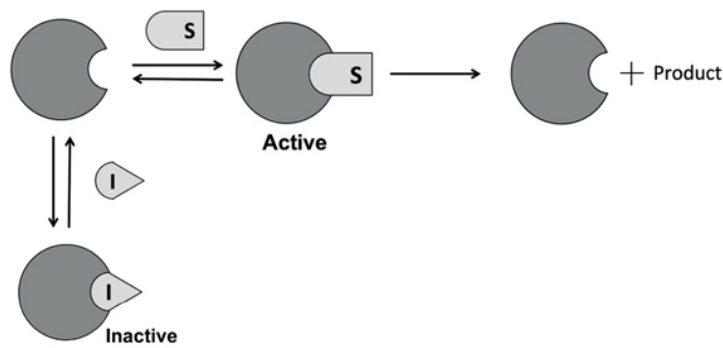
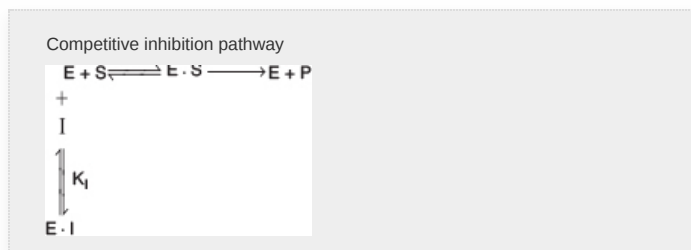


Figure 9-9 Competitive inhibition. Schematic drawing courtesy of Jofostan National Library, Lunčo, Jofostan, established 2019. New building completion expected in fall 2022.



The total enzyme concentration is the sum of the bound and unbound enzyme concentrations

$$E_t = (E) + (E \cdot S) + (E \cdot I) \quad (9-37)$$

Combining Equations (9-35), (9-36), and (9-37), solving for $(E \cdot S)$ then substituting in Equation (9-34) and simplifying

$$r_P = -r_S = \frac{V_{\max}(S)}{(S) + K_M \left(1 + \frac{(I)}{K_i}\right)} \quad (9-38)$$

Rate law for competitive inhibition

V_{\max} and K_M are the same as before when no inhibitor is present; that is,

$$V_{\max} = k_3 E_t \text{ and } K_M = \frac{k_2 + k_3}{k_1}$$

and the competitive inhibition constant K_I (mol/dm³) is defined as

$$K_I = \frac{k_5}{k_4}$$

By letting $K'_M = K_M(1 + (I)/K_I)$, we can see that the effect of adding a competitive inhibitor is to increase the “apparent” Michaelis constant, K'_M . A consequence of the larger “apparent” Michaelis constant is K'_M that a larger substrate concentration is needed for the rate of substrate decomposition, $-r_S$, to reach half its maximum rate.

Rearranging Equation (9-38) in order to generate a Lineweaver–Burk plot

$$\frac{1}{-r_S} = \frac{1}{V_{\max}} + \frac{1}{(S)} \left[\frac{K_M}{V_{\max}} \left(1 + \frac{(I)}{K_I} \right) \right] \quad (9-39)$$

From the Lineweaver–Burk plot (Figure 9-10), we see that as the inhibitor (I) concentration is increased, the slope increases (i.e., the rate decreases), while the intercept remains fixed.

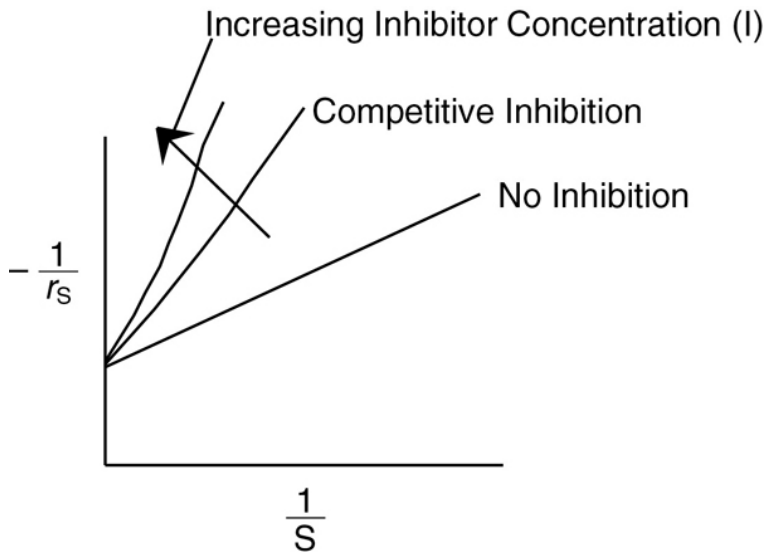
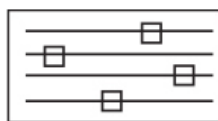


Figure 9-10 Lineweaver–Burk plot for competitive inhibition.

(<http://www.umich.edu/~elements/6e/09chap/live.html>)



LEP Sliders

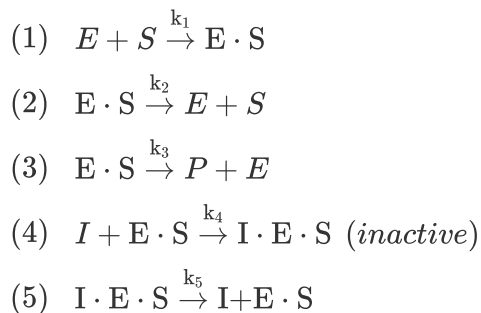
Side Note: Methanol Poisoning. An interesting and important example of *competitive substrate inhibition* is the enzyme alcohol dehydrogenase (ADH) in the presence of ethanol and methanol. If a person ingests methanol, ADH will convert it to formaldehyde and then formate, which can cause blindness and even death. Consequently, one treatment involves intravenously injecting ethanol (which is metabolized at a slower rate than methanol) at a controlled rate to tie up ADH to slow the metabolism of methanol to formaldehyde to formate so that the kidneys have time to filter out the methanol, which is then excreted in the urine. With this treatment, blindness and death may be avoided.

9.3.2 Uncompetitive Inhibition

An example of uncompetitive inhibition is the inhibitor epristeride that affects androgen testosterone, as enzyme that stimulates growth. In uncompetitive inhibition, the inhibitor has no affinity for the enzyme by itself and thus does not compete with the substrate for the enzyme; instead, it ties up the enzyme–substrate complex by forming an inhibitor–enzyme–substrate complex, ($I \cdot E \cdot S$), which is inactive. In uncompetitive inhibition, the inhibitor reversibly ties up enzyme–substrate complex *after* it has been formed.

As with competitive inhibition, two additional reaction steps are added to the Michaelis–Menten kinetics for uncompetitive inhibition, as shown in Reaction Steps 4 and 5 in [Figure 9-11](#).

Reaction Steps



Uncompetitive Pathway

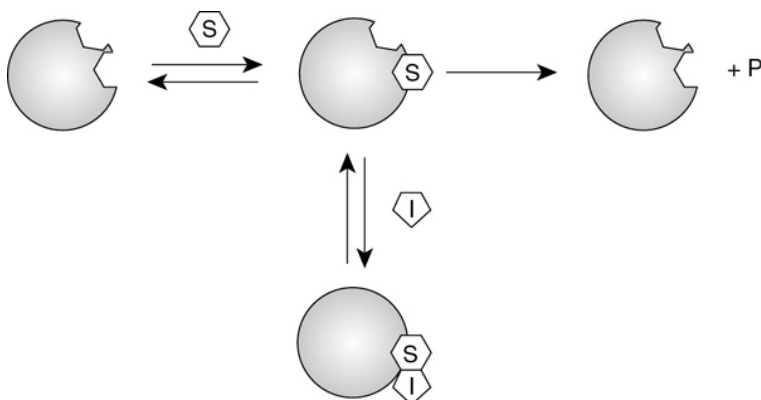
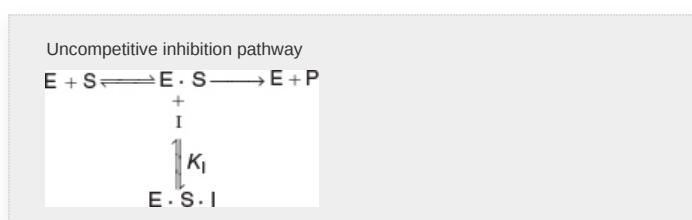


Figure 9-11 Steps in uncompetitive enzyme inhibition.



Starting with the equation for the rate of formation of product, Equation (9-34), and then applying the pseudo-steady-state hypothesis to the intermediate ($\text{I} \cdot \text{E} \cdot \text{S}$), we arrive at the rate law for uncompetitive inhibition

$$-r_s = r_p = \frac{V_{\max}(\text{S})}{K_M + (\text{S}) \left(1 + \frac{(\text{I})}{K_I}\right)} \quad \text{where } K_I = \frac{k_5}{k_4} \quad (9-40)$$

Rate law for uncompetitive inhibition

The intermediate steps are shown in the [Chapter 9 Summary Notes](http://www.umich.edu/~elements/6e/09chap/summary-example4.html) in Learning Resources on the CRE Web site (<http://www.umich.edu/~elements/6e/09chap/summary-example4.html>).

Rearranging Equation (9-40)

$$\frac{1}{-r_s} = \frac{1}{(\text{S})} \frac{K_M}{V_{\max}} + \frac{1}{V_{\max}} \left(1 + \frac{(\text{I})}{K_I}\right) \quad (9-41)$$

The Lineweaver–Burk plot for uncompetitive enzyme inhibition is shown in [Figure 9-12](#) for different inhibitor concentrations. The slope (K_M/V_{\max}) remains the same as the

inhibitor (I) concentration is increased, while the intercept $[(1/V_{\max})(1 + (I)/K_I)]$ increases.

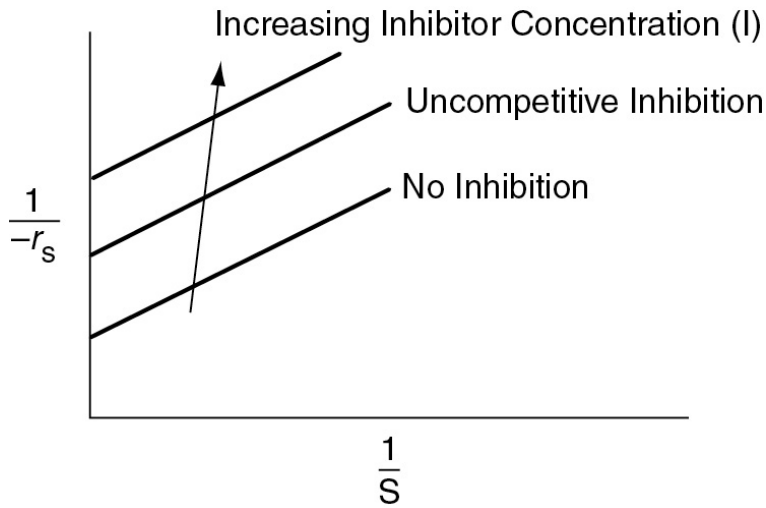


Figure 9-12 Lineweaver–Burk plot for uncompetitive inhibition.

9.3.3 Noncompetitive Inhibition (Mixed Inhibition)¹⁵

¹⁵ In some literature, mixed inhibition is a combination of competitive and uncompetitive inhibition.

In noncompetitive inhibition, also sometimes called *mixed inhibition*, the substrate and inhibitor molecules react with different types of sites on the enzyme molecule. Examples of noncompetitive inhibitors include heavy metal ions such as Pb^{2+} , Ag^+ , and Hg^{2+} and the inhibitor FK866, which affects the enzyme nicotinamide phosphoribosyltransferase.[†] Whenever the inhibitor is attached to the enzyme, it is inactive and cannot form products. Consequently, the deactivating complex ($\text{I} \cdot \text{E} \cdot \text{S}$) can be formed by two reversible reaction paths.

[†] *Cancer Res.*, 63 (21), 7436.

1. After a substrate molecule (S) attaches to the enzyme molecule (E) at the substrate site, then the inhibitor molecule attaches to the enzyme at the inhibitor site. ($\text{E} \cdot \text{S} + \text{I} \rightleftharpoons \text{I} \cdot \text{E} \cdot \text{S}$)
2. After an inhibitor molecule (I) attaches to the enzyme molecule (E) at the inhibitor site, then the substrate molecule attaches to the enzyme at the substrate site. ($\text{E} \cdot \text{I} + \text{S} \rightleftharpoons \text{I} \cdot \text{E} \cdot \text{S}$)

These paths, along with the formation of the product, P, are shown in [Figure 9-13](#). In noncompetitive inhibition, the enzyme can be tied up in its inactive form either *before or after* forming the enzyme–substrate complex as shown in Steps 2, 3, and 4.

Again, starting with the rate law for the rate of formation of product and then applying the PSSH to the complexes (I · E) and (I · E · S), we arrive at the rate law for the noncompetitive inhibition

$$-r_s = \frac{V_{\max}(S)}{((S) + K_M) \left(1 + \frac{(I)}{K_I}\right)} \quad (9-42)$$



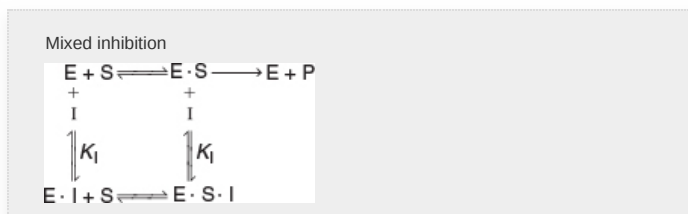
Rate law for noncompetitive inhibition

The derivation of the rate law is given in the *Summary Notes* on the CRE Web site

(<http://www.umich.edu/~elements/6e/09chap/summary-derive3.html>). Equation (9-42) is in the form of the rate law that is given for an enzymatic reaction exhibiting noncompetitive inhibition.

Reaction Steps

- (1) $E + S \rightleftharpoons E \cdot S$
- (2) $E + I \rightleftharpoons I \cdot E$ (inactive)
- (3) $I + E \cdot S \rightleftharpoons I \cdot E \cdot S$ (inactive)
- (4) $S + I \cdot E \rightleftharpoons I \cdot E \cdot S$ (inactive)
- (5) $E \cdot S \rightarrow P + E$



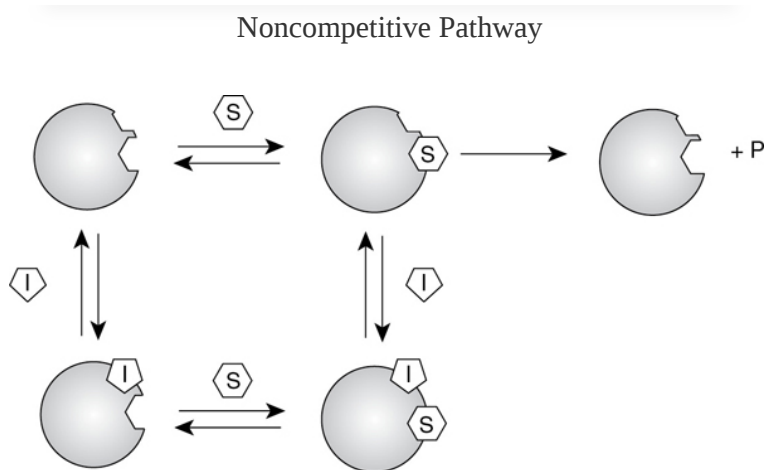


Figure 9-13 Steps in noncompetitive enzyme inhibition.

$$\frac{1}{-r_s} = \frac{1}{V_{\max}} \left(1 + \frac{(I)}{K_I} \right) \frac{1}{(S)} \frac{K_M}{V_{\max}} \left(1 + \frac{(I)}{K_I} \right) \quad (9-43)$$

For noncompetitive inhibition, we see on the Lineweaver–Burk plot in Figure 9-14 both the slope $\left(\frac{K_M}{V_{\max}} \left[1 + \frac{(I)}{K_I} \right] \right)$ and intercept $\left(\frac{1}{V_{\max}} \left[1 + \frac{(I)}{K_I} \right] \right)$ increase with increasing inhibitor concentration. In practice, *uncompetitive inhibition* and *mixed inhibition* are generally observed only for enzymes with two or more substrates, S_1 and S_2 .

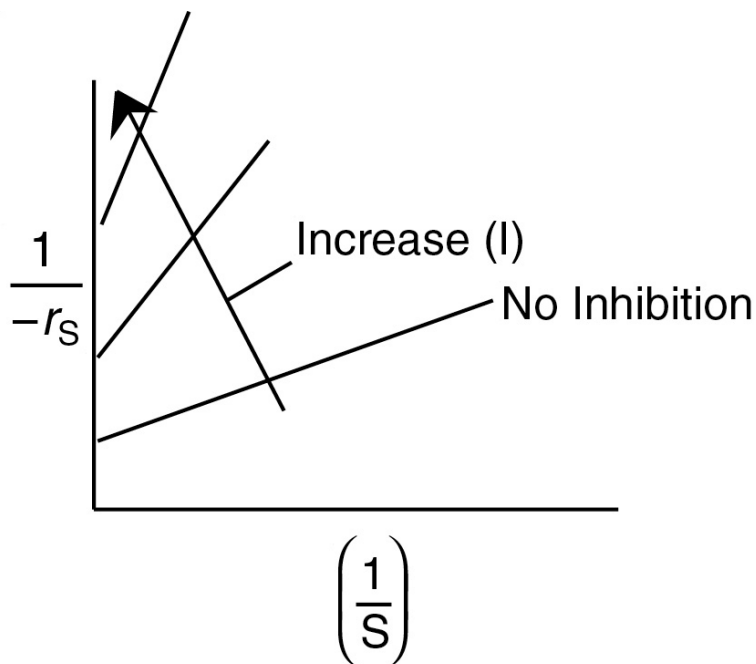


Figure 9-14 Lineweaver–Burk plot for noncompetitive enzyme inhibition.

The three types of inhibition are compared with a reaction without inhibitors and are summarized on the Lineweaver–Burk plot shown in Figure 9-15.

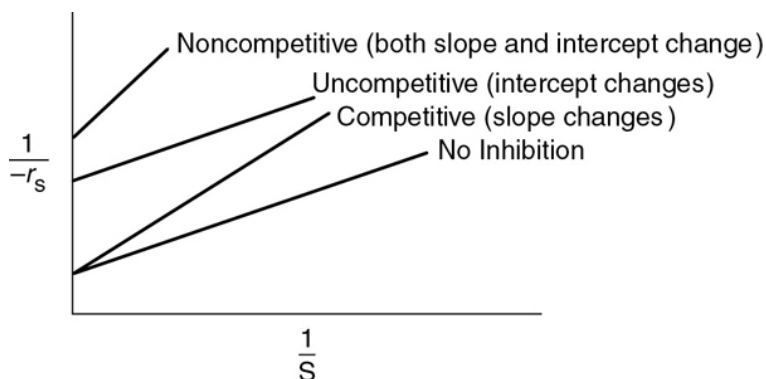
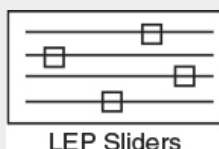


Figure 9-15 Summary: Lineweaver–Burk plots for three types of enzyme inhibition.

(<http://www.umich.edu/~elements/6e/09chap/live.html>)

Summary plot of types of inhibition



In summary, we observe the following trends and relationships:

1. In *competitive inhibition*, the slope increases with increasing inhibitor concentration, while the intercept remains fixed.
2. In *uncompetitive inhibition*, the y-intercept increases with increasing inhibitor concentration, while the slope remains fixed.
3. In *noncompetitive inhibition (mixed inhibition)*, both the y-intercept and slope will increase with increasing inhibitor concentration.

Problem P9-12_B asks you to use the experimental data to identify the type of inhibition for the enzyme catalyzed

reaction of starch.

Differences on Lineweaver–Burk Plot

9.3.4 Substrate Inhibition

In a number of cases, the substrate itself can act as an inhibitor, especially at high substrate concentrations. In the case of uncompetitive inhibition, the inactive molecule ($S \cdot E \cdot S$) is formed by the reaction



Consequently, we see that by replacing (I) by (S) in Equation (9-40), the rate law for $-r_s$ is

$$-r_s = \frac{V_{\max}(S)}{K_M + (S) + \frac{(S)^2}{K_I}} \quad (9-44)$$

We see that at low substrate concentrations

$$K_M \gg \left((S) + \frac{(S)^2}{K_I} \right) \quad (9-45)$$

then

$$-r_s \sim \frac{V_{\max}(S)}{K_M} \quad (9-46)$$

and the rate increases linearly with increasing substrate concentration.

At high substrate concentrations $((S)^2 / K_I) \gg (K_M + (S))$, then

$$-r_s = \frac{V_{\max}K_I}{S} \quad (9-47)$$

Substrate inhibition

and we see that the rate decreases as the substrate concentration increases. Consequently, the rate of reaction goes through a maximum in the substrate concentration, as shown in Figure 9-16. We also see that there is an optimum

substrate concentration at which to operate. This maximum is found by setting the derivative of $-r_S$ wrt S in Equation (9-44) equal to 0, to obtain

$$S_{\max} = \sqrt{K_M K_I} \quad (9-48)$$

When substrate inhibition is possible, the substrate is fed to a semibatch reactor called a *fed batch* to maximize the reaction rate and conversion.

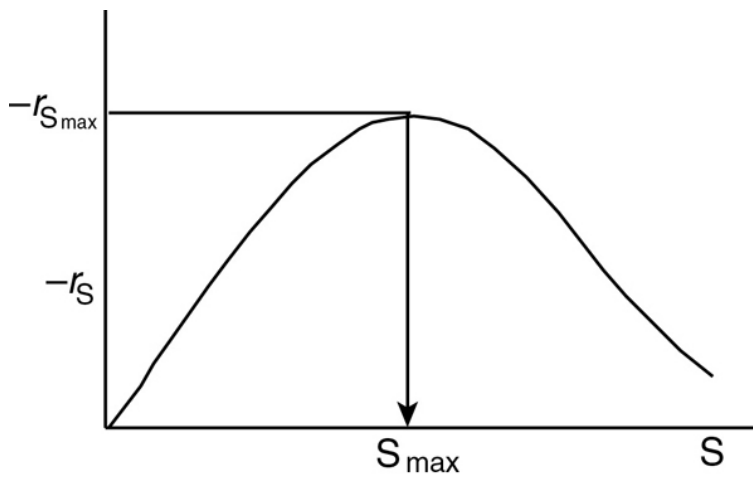
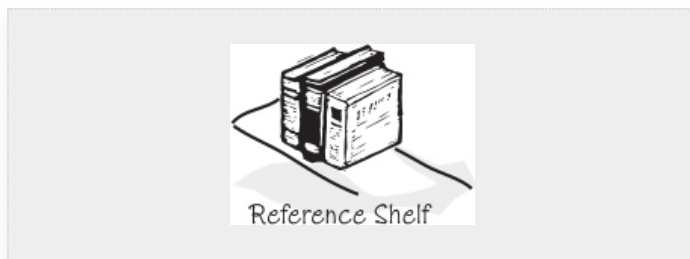


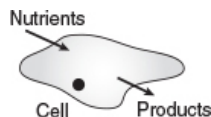
Figure 9-16 Substrate reaction rate as a function of substrate concentration for substrate inhibition.

Our discussion of enzymes is continued in the *Professional Reference Shelf* on the CRE Web site where we describe multiple enzyme and substrate systems, enzyme regeneration, and enzyme cofactors (see R9.6;

<http://www.umich.edu/~elements/6e/09chap/prof-07prof2.html>).



9.4 BIOREACTORS AND BIOSYNTHESIS



Because of the increased interest in chemical engineering of faculty and students in biochemical engineering, many chemical engineering departments have changed their names to chemical and biochemical engineering. Biochemical engineering can encompass biomedical applications involving enzymatic reactions as well as cellular dynamics. A *bioreactor* is a reactor that sustains and supports life for cells and tissue cultures. Virtually all cellular reactions necessary to maintain life are mediated by enzymes as they catalyze various aspects of cell metabolism such as the transformation of chemical energy and the construction, breakdown, and digestion of cellular components. Because enzymatic reactions are involved in the growth of microorganisms (biomass), we now proceed to study microbial growth and bioreactors. Not surprisingly, the Monod equation, which describes the growth law for a number of bacteria and microorganisms, is similar to the Michaelis–Menten equation. Consequently, even though bioreactors are not truly homogeneous because of the presence of living cells, we include them in this chapter as a logical progression from enzymatic reactions. This discussion is far from being even slightly inclusive on bioreactions, but is meant to at least introduce a vocabulary for bioreactions and bioreactors.

Current Trends

The use of living cells to produce marketable chemical products is becoming increasingly important. The number of chemicals, agricultural products, and food products produced by biosynthesis has risen dramatically. Both microorganisms and mammalian cells are being used to produce a variety of products, such as insulin, most antibiotics, and polymers. The January 2019 issue of Cell Press indicated that the monoclonal antibodies (mAb) market is expected to grow to \$130–\$200

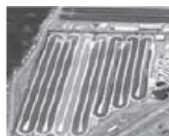
billion by 2020. mAb have been successful in fighting a number of cancers such as lymphoma, melanoma, along with breast, lung, and ovarian cancers. Mammalia cells are typically used in the production of mAb and the fundamentals of cell growth presented in this chapter may be used to model their growth. The reactors used for the grow mAb are batch, batch fed (semibatch), and perfusion

(<https://cellculturedish.com/perfusion-bioreactors-with-so-much-to-offer-they-deserve-a-closer-look/>). Additionally, it is expected that in the future a number of organic chemicals currently derived from petroleum will be produced by living cells. The advantages of bioconversions are mild reaction conditions; high yields (e.g., 100% conversion of glucose to gluconic acid with *Aspergillus niger*); and the fact that organisms contain several enzymes that can catalyze successive steps in a reaction and, most importantly, act as *stereospecific catalysts*. A common example of specificity in bioconversion is the production of a *single* desired isomer that, when produced chemically, yields a *mixture* of isomers.

The growth of biotechnology

C&E News

In the fifth edition, I focused on Sapphire Energy and its initiative to grow and use live algae to produce biomass as an alternative energy source. Because I visited the New Mexico plant and was privy to the process, two homework problems were created (cf. Homework Problem P9-20_C and P9-21_B). Unfortunately, on April 19, 2017, the Algae World News reported that Sapphire Energy no longer exists and was bought by a local farmer for pennies on the dollar (<https://news.algaeworld.org/2017/04/happened-sapphire-energy/>).



Pennies!

The Cell as a Chemical Reaction “Plant”

In biosynthesis, the cells, also referred to as the *biomass*, consume nutrients to grow and produce more cells and important products. Internally, a cell uses its nutrients to produce energy and more cells. This transformation of nutrients to energy and bioproducts is accomplished through a cell's use of a number of different enzymes in a series of reactions to produce metabolic products. These products can either remain in the cell (intracellular) or be secreted from the cells (extracellular). In the former case, the cells must be lysed (ruptured) and the product filtered and purified from the whole broth (reaction mixture). A schematic of a cell is shown in Figure 9-17 along with a photo showing cell division, which is also shown in Figure 9-19.

The Algorithm

- Cell Balance
- Substrate Balance
- Rate Law
- Stoichiometry

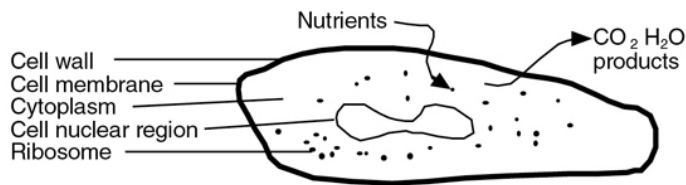


Figure 9-17 (a) Schematic of cell; (b) division of *E. Coli*.

Adapted from “Indole prevents *Escherichia coli* cell division by modulating membrane potential.” Catalin Chimirel, Christopher M. Field, Silvia Piñera-Fernandez, Ulrich F. Keyser, David K. Summers. *Biochimica et Biophysica Acta–Biomembranes*, vol. 1818, issue 7, July 2012.

The cell consists of a cell wall and an outer membrane that encloses the cytoplasm containing a nuclear region and ribosomes. The cell wall protects the cell from external influences. The cell membrane provides for selective transport of materials into and out of the cell. Other substances can attach to the cell membrane to carry out important cell functions. The cytoplasm contains the ribosomes that contain ribonucleic acid (RNA), which are important in the synthesis of proteins. The nuclear region contains deoxyribonucleic acid (DNA), which provides the genetic information for the production of proteins and other cellular substances and structures.¹⁶

¹⁶ M. L. Shuler and F. Kargi, *Bioprocess Engineering Basic Concepts*, 2nd ed. Upper Saddle River, NJ: Prentice Hall, 2002.

The reactions in the cell all take place simultaneously and are classified as either class (I) nutrient degradation (fueling reactions), class (II) synthesis of small molecules (amino acids), or class (III) synthesis of large molecules (polymerization, e.g., RNA, DNA). A rough overview with only a fraction of the reactions and metabolic pathways is shown in Figure 9-18. A more detailed model is given in Figures 5.1 and 6.14 of Shuler and Kargi.¹⁷ In the Class I reactions, adenosine triphosphate (ATP) participates in the degradation of nutrients to form products to be used in the biosynthesis reactions (Class II) of small molecules (e.g., amino acids), which are then polymerized to form RNA and DNA (Class III). ATP also transfers the energy it releases when it loses a phosphonate group to form adenosine diphosphate (ADP).

¹⁷ Ibid., pp. 135, 185.

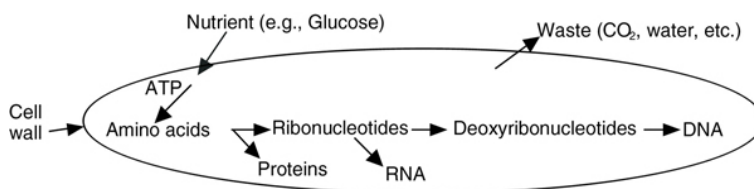


Figure 9-18 Examples of reactions occurring in the cell.

Cell Growth and Division

The cell growth and division typical of mammalian cells is shown schematically in [Figure 9-19](#). The four phases of cell division are called G₁, S, G₂, and M, and are also described in [Figure 9-19](#).

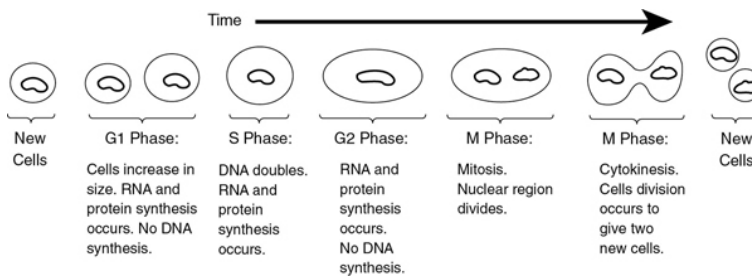
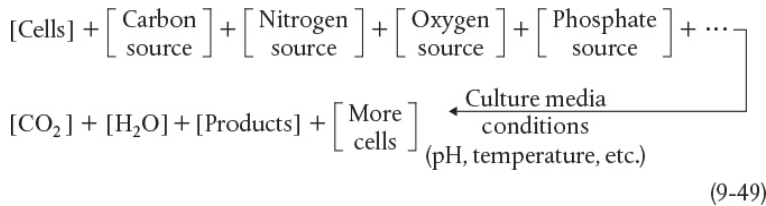


Figure 9-19 Phases of cell division.

In general, the growth of an aerobic organism follows the equation



Cell multiplication

A more abbreviated form of Equation (9-49) generally used is that a substrate in the presence of cells produces more cells plus product, that is,



The products in Equation (9-50) include carbon dioxide, water, proteins, and other species specific to the particular reaction. An excellent discussion of the stoichiometry (atom and mole balances) of Equation (9-49) can be found in texts by Shuler and Kargi,¹⁸ Bailey and Ollis,¹⁹ and Blanch and Clark.²⁰ The

substrate culture medium contains all the nutrients (carbon, nitrogen, etc.) along with other chemicals necessary for growth. Because, as we will soon see, the rate of this reaction is proportional to the cell concentration, the reaction is *autocatalytic*. A rough schematic of a simple batch biochemical reactor and the growth of two types of microorganisms, cocci (i.e., spherical) bacteria and yeast, is shown in Figure 9-20.

¹⁸ M. L. Shuler and F. Kargi, *Bioprocess Engineering Basic Concepts*, 2nd ed. Upper Saddle River, NJ: Prentice Hall, 2002.

¹⁹ J. E. Bailey and D. F. Ollis, *Biochemical Engineering*, 2nd ed. New York: McGraw-Hill, 1987.

²⁰ H. W. Blanch and D. S. Clark, *Biochemical Engineering*, New York: Marcel Dekker, Inc., 1996.

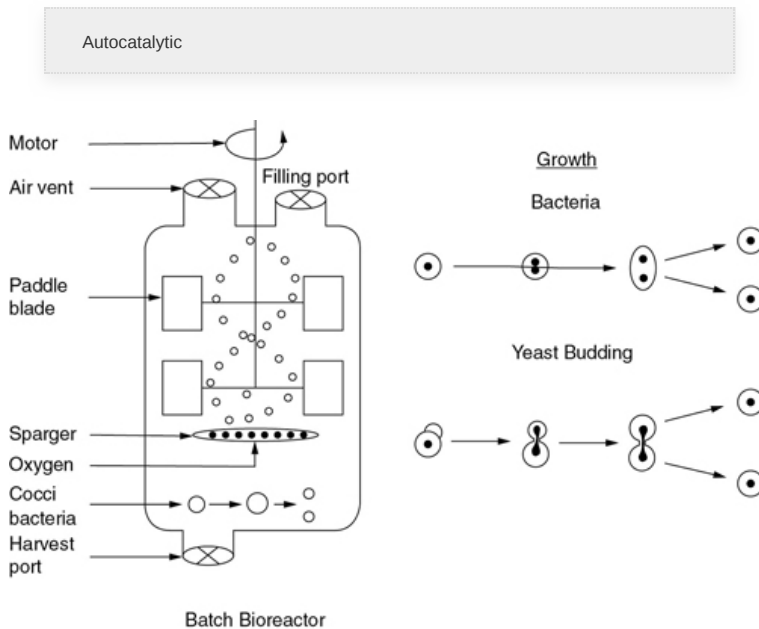


Figure 9-20 Batch bioreactor.

9.4.1 Cell Growth

Stages of cell growth in a batch reactor are shown schematically in Figures 9-21 and 9-22. Initially, a small number of cells is inoculated into (i.e., added to) the batch reactor containing the nutrients and the growth process begins, as shown in Figure 9-21. In Figure 9-22, the number of living cells is shown as a function of time. Actual cell concentration

time data taken in the author's research laboratory by PhD student Barry Wolf is shown on the CRE Web site²¹ (<http://www.umich.edu/~elements/6e/09chap/summary.html#sec3>).

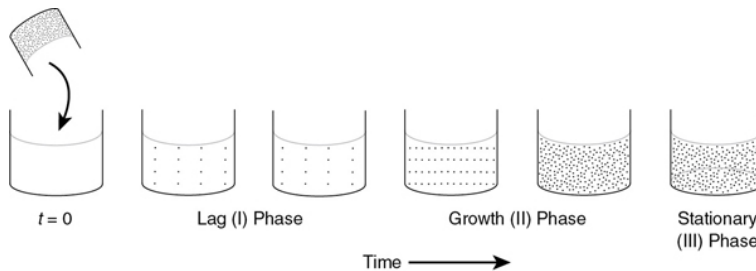


Figure 9-21 Increase in cell concentration.

Lag phase

Phase I, shown in Figure 9-22, is called the *lag phase*. There is little increase in cell concentration in this phase. In the lag phase, the cells are adjusting to their new environment, carrying out such functions as synthesizing transport proteins for moving the substrate into the cell, synthesizing enzymes for utilizing the new substrate, and beginning the work for replicating the cells' genetic material. The duration of the lag phase depends upon many things, one of which is the growth medium from which the inoculum was taken relative to the reaction medium in which it is placed. If the inoculum is similar to the medium of the batch reactor, the lag phase can be almost nonexistent. If, however, the inoculum were placed in a medium with a different nutrient or other contents, or if the inoculum culture were in the stationary or death phase, the cells would have to readjust their metabolic path to allow them to consume the nutrients in their new environment.²¹

²¹ B. Wolf and H. S. Fogler, "Alteration of the growth rate and lag time of *Leuconostoc mesenteroides* NRRL-B523," *Biotechnol. Bioeng.*, 72 (6), 603 (2001). B. Wolf and H. S. Fogler, "Growth of *Leuconostoc mesenteroides* NRRL-B523, in alkaline medium," *Biotechnol. Bioeng.*, 89 (1), 96 (2005).

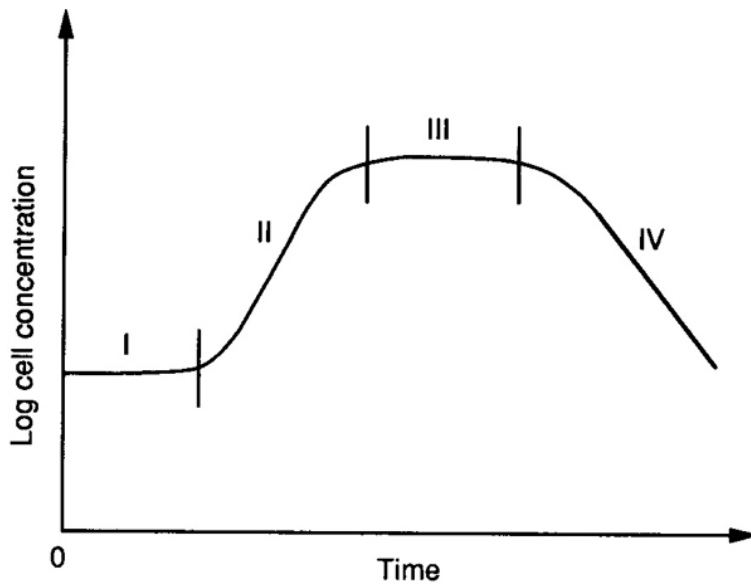


Figure 9-22 Phases of bacteria cell growth.

Phase II is called the *exponential growth phase*, owing to the fact that the cells' growth rate is proportional to the cell concentration. In this phase, the cells are dividing at the maximum rate because all of the enzyme's pathways for metabolizing the substrate are now in place (as a result of the lag phase) and the cells are able to use the nutrients most efficiently.

Exponential growth phase

Phase III is the *stationary phase*, during which the cells reach a minimum biological space where the lack of one or more nutrients limits cell growth. During the stationary phase the cells are functioning but the *net* cell growth rate is zero as a result of the depletion of nutrients and essential metabolites. Many important fermentation products, including many antibiotics, are produced in the stationary phase. For example, penicillin produced commercially using the fungus *Penicillium chrysogenum* is formed only after cell growth has ceased. Cell growth is also slowed by the build-up of organic acids and toxic materials generated during the growth phase.

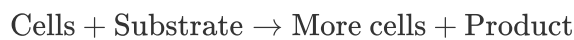
Antibiotics produced during the stationary phase

Phase IV the final phase, is the *death phase*, where a decrease in live cell concentration occurs. This decline is a result of the toxic by-products, harsh environments, and/or depletion of nutrient supply.

Death phase

9.4.2 Rate Laws

While many laws exist for the cell growth rate of new cells, that is,



the most commonly used expression is the *Monod* equation for exponential growth:

$$r_g = \mu C_c \quad (9-51)$$

where

r_g = cell growth rate, $\text{g/dm}^3 \cdot \text{s}$

C_c = cell concentration, g/dm^3

μ = specific growth rate, s^{-1}

The cell concentration is often given in terms of weight (g) of dry cells per liquid volume and is specified “grams dry weight per dm^3 ,” that is, (gdw/dm^3).

The specific cell growth rate can be expressed as

$$\mu = \mu_{\max} \frac{C_s}{K_s + C_s} \quad \text{S}^{-1} \quad (9-52)$$

where

μ_{\max} = maximum specific growth reaction rate, s^{-1}

K_s = *Monod* constant, g/dm^3

C_s = substrate (i.e., nutrient) concentration, g/dm^3

Representative values $\mu_{\max} = 1.3 \text{ h}^{-1}$ $K_S = 2.2 \times 10^{-5} \text{ (g/dm}^3\text{)}$

and is also shown in Figure 9-23. Representative values of μ_{\max} and K_S are 1.3 h^{-1} and $2.2 \times 10^{-5} \text{ g/dm}^3$, respectively, which are the parameter values for the *E. coli* growth on glucose. Combining Equations (9-51) and (9-52), we arrive at the Monod equation for bacterial cell growth rate

$$r_g = \frac{\mu_{\max} C_s C_c}{K_s + C_s} \quad (9-53)$$

Monod equation

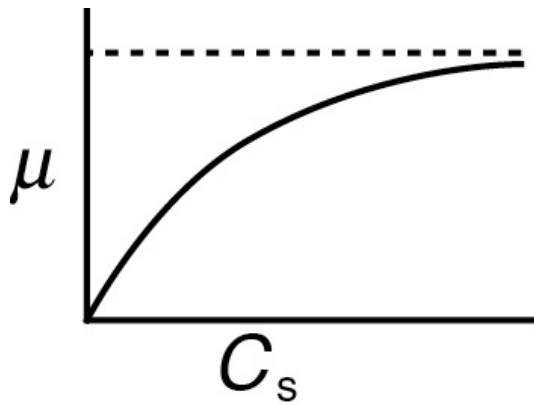


Figure 9-23 Specific cell growth rate, μ , as a function of substrate concentration C_s .

For a number of different bacteria, the constant K_S is very small, with regard to typical substrate concentrations, in which case the rate law reduces to

$$r_g = \mu_{\max} C_c \quad (9-54)$$

The growth rate, r_g , often depends on more than one nutrient concentration; however, the nutrient that is limiting is usually the one used in Equation (9-53).

In many systems the product inhibits the rate of growth. A classic example of this inhibition is in winemaking, where the

fermentation of glucose to produce ethanol is inhibited by the product ethanol. There are a number of different equations to account for inhibition; one such rate law takes the empirical form

$$r_g = k_{\text{obs}} = \frac{\mu_{\text{max}} C_s C_c}{K_s + C_s} \quad (9-55)$$

where

$$k_{\text{obs}} = \left(1 - \frac{C_p}{C_p^*}\right)^n \quad (9-56)$$

Empirical form of Monod equation for product inhibition

with

C_p = product concentration (g/dm³)

C_p^* = product concentration at which all metabolism ceases, g/dm³

n = empirical constant

For the glucose-to-ethanol fermentation, typical inhibition parameters are

$$n = 0.5 \quad \text{and} \quad C_p^* = 93 \text{ g/dm}^3$$

In addition to the *Monod* equation, two other equations are also commonly used to describe the cell growth rate; they are the *Tessier* equation

$$r_g = \mu_{\text{max}} \left[1 - \exp\left(-\frac{C_s}{k}\right)\right] C_c \quad (9-57)$$

Tessier Equation

and the *Moser* equation,

$$r_g = \frac{\mu_{\text{max}} C_c}{(1 + k C_s^{-\lambda})} \quad (9-58)$$

Moser Equation

where λ and k are empirical constants determined by a best fit of the data. The Moser and Tessier growth laws are often used because they have been found to better fit experimental data at the beginning or end of fermentation. Other growth equations can be found in Dean.²²

²² A. R. C. Dean, *Growth, Function, and Regulation in Bacterial Cells*, London: Oxford University Press, 1964.

The cell death rate is a result of harsh environments, mixing shear forces, local depletion of nutrients, and the presence of toxic substances. The rate law is

$$r_d = (k_d + k_t C_t) C_c \quad (9-59)$$

where C_t is the concentration of a substance toxic to the cell. The specific death rate constants k_d and k_t refer to the natural death and death due to a toxic substance, respectively. Representative values of k_d range from 0.1 h^{-1} to less than 0.0005 h^{-1} . The value of k_t depends on the nature of the toxin.

Microbial growth rates are measured in terms of *doubling times*. Doubling time is the time required for a mass of an organism to double. Typical doubling times for bacteria range from 45 minutes to 1 hour but can be as fast as 15 minutes. Doubling times for simple eukaryotes, such as yeast, range from 1.5 to 2 hours but may be as fast as 45 minutes.

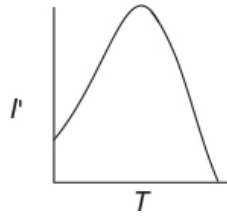
Doubling times

Effect of Temperature. As with enzymes (cf. Figure 9-8), there is an optimum in growth rate with temperature, owing to the competition of increased rates with increasing temperature and enzyme denaturation at high temperatures. An empirical law that describes this functionality is given in Aiba et al.²³ and is of the form

²³ S. Aiba, A. E. Humphrey, and N. F. Millis, *Biochemical Engineering*, New York: Academic Press, 1973, p. 407.

$$\mu(T) = \mu(T_m) I'$$

$$I' = \frac{aTe^{-E_1/RT}}{1+be^{-E_2/RT}} \quad (9-60)$$



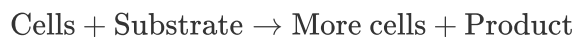
where I' is the fraction of the maximum growth rate, T_m is the temperature at which the maximum growth occurs, and $\mu(T_m)$ is the growth rate at this temperature. For the rate of oxygen uptake of *Rhizobium trifolii*, the equation takes the form

$$I' = \frac{0.0038Te^{[21.6-6700/T]}}{1 + e^{[153-48,000/T]}} \quad (9-61)$$

The maximum growth of *Rhizobium trifolii* was thought to occur at 310°K. However, experiments by Prof. Dr. Sven Köttlov and his students at Jofostan University in Riça, Jofostan, show that this temperature should be 312°K, not 310°K. A major turn of events in the *Rhizobium trifolii* scientific community!!

9.4.3 Stoichiometry

The stoichiometry for cell growth is very complex and varies with the micro-organism/nutrient system and environmental conditions such as pH, temperature, and redox potential. This complexity is especially true when more than one nutrient contributes to cell growth, as is usually the case. We shall focus our discussion on a simplified version for cell growth, one that is limited by only one nutrient in the medium. In general, we have



Tells us how much substrate is needed to produce new cells.

In order to relate the substrate consumed, new cells formed, and product generated, we introduce the *yield* coefficients. The yield coefficient for cells and substrate is

$$Y_{c/s} = \frac{\text{Mass of new cells formed}}{\text{Mass of substrate consumed}} = -\frac{\Delta C_c}{\Delta C_s} \quad (9-62)$$

The yield coefficient $Y_{c/s}$ is the ratio of the increase in the mass concentration of cells, ΔC_c , to the decrease in the substrate concentration ($-\Delta C_s$), ($-\Delta C_s = C_{s0} - C_s$), to bring about this increase in cell mass concentration. A representative value of $Y_{c/s}$ might be 0.4 (g/g).

The reciprocal of $Y_{c/s}$, that is, $Y_{s/c}$

$$Y_{s/c} = \frac{1}{Y_{c/s}}$$

gives the ratio of ($-\Delta C_s$), the substrate that must be consumed, to the increase in cell mass concentration ΔC_c with a representative value of 2.5 (g/g).

Product formation can take place during different phases of the cell growth cycle. When product formation only occurs during the exponential growth phase, the rate of product formation is

$$r_p = Y_{p/c} r_g = Y_{p/c} \mu C_c = Y_{p/c} \frac{\mu_{\max} C_c C_s}{K_s + C_s} \quad (9-63)$$

Growth associated product formation

where

$$Y_{p/c} = \frac{\text{Mass of product formed}}{\text{Mass of new cells formed}} = \frac{\Delta C_p}{\Delta C_c} \quad (9-64)$$

The product of $Y_{p/c}$ and μ , that is, ($q_p = Y_{p/c} \mu$), is often called the *specific rate of product formation*, q_p , (mass product/volume/time). When the product is formed during the stationary phase where no cell growth occurs, we can relate the rate of product formation to substrate consumption by

$$r_p = Y_{p/s} (-r_s) \quad (9-65)$$

Nongrowth-associated product formation

The substrate in this case is usually a secondary nutrient, which we discuss in more detail later when the stationary phase is discussed.

The stoichiometric yield coefficient that relates the amount of product formed per mass of substrate consumed is

$$Y_{p/s} = \frac{\text{Mass of product formed}}{\text{Mass of substrate consumed}} = \frac{\Delta C_p}{\Delta C_s} \quad (9-66)$$

Cell yield

In addition to consuming substrate to produce new cells, part of the substrate must be used just to maintain a cell's daily activities. The corresponding maintenance utilization term is

$$m = \frac{\text{Mass of substrate consumed for maintenance}}{\text{Mass of cells} \cdot \text{Time}}$$

Cell maintenance

A typical value is

$$m = 0.05 \frac{\text{g substrate}}{\text{g dry weight}} \frac{1}{\text{h}} = 0.05 \text{ h}^{-1}$$

The rate of substrate consumption for maintenance, r_{sm} , whether or not the cells are growing is

$$r_{sm} = mC_c \quad (9-67)$$

When maintenance *can be neglected*, we can relate the concentration of new cells formed to the amount of substrate consumed by the equation

$$C_c = Y_{c/s} [C_{s0} - C_s] \quad (9-68)$$

Neglecting cell maintenance

This equation is often used for both batch and continuous-flow reactors.

If it were possible to sort out the substrate (S) that is consumed in the presence of cells to form new cells (C) from the substrate that is consumed to form product (P), that is



the yield coefficients would be written as

$$Y'_{s/c} = \frac{\text{Mass of substrate consumed to form new cells}}{\text{Mass of new cells formed}} \quad (9-69A)$$

$$Y'_{s/p} = \frac{\text{Mass of substrate consumed to form product}}{\text{Mass of product formed}} \quad (9-69B)$$

These yield coefficients will be discussed further in the substrate utilization section.

Substrate Utilization. We now come to the task of relating the rate of nutrient (i.e., substrate) consumption, $-r_s$, to the rates of cell growth, product generation, and cell maintenance. In general, we can write

$$\begin{aligned} \left[\begin{array}{c} \text{Net rate of} \\ \text{substrate} \\ \text{consumption} \end{array} \right] &= \left[\begin{array}{c} \text{Rate of} \\ \text{substrate} \\ \text{consumed} \\ \text{by cells} \end{array} \right] + \left[\begin{array}{c} \text{Rate of} \\ \text{substrate} \\ \text{consumed to} \\ \text{from product} \end{array} \right] + \left[\begin{array}{c} \text{Rate of} \\ \text{substrate} \\ \text{consumed for} \\ \text{maintenance} \end{array} \right] \\ -r_s &= Y'_{s/c}r_g + Y'_{s/p}r_p + mC_c \end{aligned}$$

Substrate accounting

In a number of cases, extra attention must be paid to the substrate balance. If product is produced during the growth phase, it may not be possible to separate out the amount of substrate consumed for cell growth (i.e., produce more cells) from that consumed to produce the product. Under these circumstances, all the substrate consumed for growth and for

product formation is lumped into a single stoichiometric yield coefficient, $Y_{s/c}$, and the rate of substrate disappearance is

$$-r_s = Y_{s/c}r_g + mC_c \quad (9-70)$$

Equation (9-70) will be the rate law for the substrate consumption that we will use in our analyses of cell growth. The corresponding rate of product formation is

$$r_p = r_g Y_{p/c} \quad (9-63)$$

Growth-associated product formation in the growth phase

The Stationary Phase. Because there is no growth during the stationary phase, it is clear that Equation (9-70) cannot be used to account for substrate consumption, nor can the rate of product formation be related to the growth rate (e.g., Equation (9-63)). Many antibiotics, such as penicillin, are produced in the stationary phase. In this phase, the nutrient required for growth becomes virtually exhausted, and a different nutrient, called the *secondary nutrient*, is used for cell maintenance and to produce the desired product. Usually, the rate law for product formation during the stationary phase is similar in form to the Monod equation, that is

$$r_{pm} = \frac{k_p C_{sn} C_c}{K_{sn} + C_{sn}} \quad (9-71)$$

Nongrowth-associated product formation in the stationary phase

where

k_p = specific rate constant with respect to product,
($\text{dm}^3/\text{g} \cdot \text{s}$)

C_{sn} = concentration of the secondary nutrient,
(g/dm^3)

C_c = cell concentration, g/dm^3 ($\text{g} \equiv \text{gdw} = \text{gram dry weight}$)

K_{sn} = Monod constant for secondary nutrient,
(g/dm^3)

$$r_{pn} = Y_{p/sn}(=r_{sn}), (\text{g/dm}^3 \cdot \text{s})$$

The net rate of secondary nutrient consumption, r_{sn} , during the stationary phase is related to the rate of product formation, r_p

$$-r_{sn} = mC_c + Y_{sn/p}r_p$$

$$-r_{sn} = mC_c + \frac{Y_{sn/p}k_p C_{sn} C_c}{K_{sn} + C_{sn}} \quad (9-72)$$

In the stationary phase, the concentration of live cells is constant.

Because the desired product can be produced when there is no cell growth, it is always best to relate the product concentration to the change in secondary nutrient concentration. For a batch system, the concentration of product, C_p , formed after a time t in the stationary phase can be related to the change in the secondary nutrient concentration, C_{sn} , at that time, from the secondary nutrient's initial concentration, at time $t = 0$ C_{sn0} , that is,

$$C_p = Y_{p/sn} (C_{sn0} - C_{sn}) \quad (9-73)$$

Neglects cell maintenance

We have considered two limiting situations for relating substrate consumption to cell growth and product formation: product formation only during the growth phase and product formation only during the stationary phase. An example where neither of these situations applies is fermentation using *lactobacillus*, where lactic acid is produced during both the logarithmic growth and stationary phase.

The specific rate of product formation is often given in terms of the Luedeking–Piret equation, which has two parameters, α (growth) and β (nongrowth)

$$q_p = \alpha\mu_g + \beta \quad (9-74)$$

such that the rate of product formation is

$$r_p = q_p C_c$$

Luedeking–Piret equation for the rate of product formation

The assumption here in using the q_p -parameter is that the secondary nutrient is in excess.

Example 9–4 Estimate the Yield Coefficients

The following data (Table E9-4.1) was obtained from batch reactor experiments for the yeast *Saccharomyces cerevisiae*

TABLE E9-4.1 RAW DATA

Glucose $\xrightarrow{\text{cells}}$ More cells + Ethanol				
Time, t (hr)		Cells, C_c (g/dm ³)	Glucose, C_s (g/dm ³)	Ethanol, C_p (g/dm ³)
0	1	250	0	
1	1.5	244	2.14	
2	2.2	231	5.03	
3	3.29	218	8.96	

Add another data point?

1. Determine the yield coefficients $Y_{s/c}$, $Y_{c/s}$, $Y_{s/p}$, $Y_{p/s}$, and $Y_{p/c}$. Assume no lag and neglect maintenance at the start of the growth phase when there are just a few cells.
2. Find the rate-law parameters μ_{\max} and K_s .

Solution

1. Yield coefficients

Calculate the substrate and cell *yield coefficients*, $Y_{s/c}$ and $Y_{c/s}$.
Between $t = 0$ and $t = 1$ h

$$Y_{s/c} = \frac{-\Delta C_s}{\Delta C_c} = -\frac{244-250}{1.5-1} = 12 \text{ g/g} \quad (\text{E9-4.1})$$

Between $t = 2$ and $t = 3$ h

$$Y_{s/c} = -\frac{218-231}{3.29-2.2} = \frac{13}{1.09} = 11.93 \text{ g/g} \quad (\text{E9-4.2})$$

Taking an average

$Y_{s/c} = 11.96\text{g/g}$

(E9 – 4.3)

Equation (E9-4.3) tells us that 11.96 grams of substrate are consumed to produce 1.0 grams of cells. We could also have used Polymath regression to obtain

$$Y_{s/c} = \frac{1}{Y_{s/c}} = \frac{1}{11.96 \text{ g/g}} = 0.084 \text{ g/g} \quad (\text{E9-4.4})$$

that is 0.084 grams of cell are produced per gram of substrate consumed. Similarly, using the data at 1 and 2 hours, the substrate/product *yield coefficient* is

$$Y_{s/p} = -\frac{\Delta C_s}{\Delta C_p} = -\frac{231-244}{5.03-2.14} = \frac{13}{2.89} = 4.5 \text{ g/g} \quad (\text{E9-4.5})$$

$$Y_{p/s} = \frac{1}{Y_{s/p}} = \frac{1}{4.5 \text{ g/g}} = 0.22 \text{ g/g} \quad (\text{E9-4.6})$$

Here, approximately 0.22 grams of product are generated when 1.0 grams of substrate are consumed and the product/cell *yield coefficient* is

$$Y_{p/c} = -\frac{\Delta C_p}{\Delta C_c} = \frac{-5.03-2.14}{2.2-1.5} = 4.13 \text{ g/g} \quad (\text{E9-4.7})$$

We see 4.13 grams of product are generated with every gram of cells grown

$$Y_{c/p} = \frac{1}{Y_{p/c}} = \frac{1}{4.13 \text{ g/g}} = 0.242 \text{ g/g} \quad (\text{E9-4.8})$$

2. Rate-law parameters

We now need to determine the rate-law parameters μ_{\max} and K_s in the Monod equation

$$r_g = \frac{\mu_{\max} C_c C_s}{K_s + C_s} \quad (9-53)$$

For a batch system

$$r_g = \frac{dC_c}{dt} \quad (\text{E9-4.9})$$

To find the rate-law parameters μ_{\max} and K_s , we first apply the differential formulas in Chapter 7 to columns 1 and 2 of Table E9-4.1 to find r_g and add another column to Table E9-4.1. We will apply the differentiation formulas in Table 7-3 to the data in Table E9-4.1 in order to find r_g in Equation E9-4.9.

$$r_{g0} = \frac{-3C_{C0} + 4C_{C1} - C_{C2}}{2\Delta t} = \frac{-3(1) + 4(1.5) - 2.2}{2(1)} = 0.4 \quad (\text{E9-4.10})$$

$$r_{g1} = \frac{C_{C2} - C_{C0}}{2\Delta t} = \frac{2.2 - 1}{2(1)} = 0.6 \quad (\text{E9-4.11})$$

$$r_{g1} = \frac{C_{C3} - C_{C1}}{2\Delta t} = \frac{3.29 - 1.5}{2(1)} = 0.9 \quad (\text{E9-4.12})$$

$$r_{g3} = \frac{C_{C1} - 4C_{C2} + 3C_{C3}}{2\Delta t} = \frac{1.5 - 4(2.2) + 3(3.29)}{2(1)} = 1.29 \quad (\text{E9-4.13})$$

We now form the processed data Table E9-4.2.

TABLE E9-4.2 RATE DATA

t	C_C	C_S	r_g
0	1	250	0.4
1	1.5	244	0.6
2	2.2	231	0.9
3	3.29	218	1.29

Because $C_S \gg K_s$ initially, it is best to regress the data using the Hanes–Woolf form of the Monod equation

$$\frac{C_C C_S}{r_g} = \frac{K_s}{\mu_{\max}} + \frac{C_S}{\mu_{\max}} \quad (\text{E9-4.14})$$

How to regress the Monod equation for μ_{\max} and K_s

We will use nonlinear least squares to find μ_{\max} and K_s from the data in Table E9-4.2. We now use the newly calculated r_g along with C_C and C_S in Table E9-4.2 to prepare Table E9-4.3 given of $\left[\frac{C_C C_S}{r_g}\right]$ as a function of (C_S) to use in Polymath regression.

TABLE E9-4.3 PROCESSED DATA

t	0	1	2	3
$C_C C_S / r_g$	625	610	568	558
C_S	250	244	231	218

POLYMATH Report
Nonlinear Regression (L-M)

Model: C01 = Ks/umax+C02/umax

Variable	Initial guess	value	95% confidence
Ks	20.	33.50084	217.559
umax	0.3	0.4561703	0.3681699

Precision

R ²	0.9342517
R ² adj	0.9013775
Rmsd	3.587096
Variance	102.938

From the output of Polymath's nonlinear regression of Equation (E9-4.14), we find $\mu_{\max} = 0.46 \text{ h}^{-1}$ and $K_s = 33.5$

g/dm³.

$$r_g = \frac{0.46(\text{h}^{-1})C_c C_s}{33.5(\text{g/dm}^3) + C_s}$$

Analysis: In this example we showed how to use the concentrations of cells, substrate and product given in Table E9-4.1 to calculate the yield coefficients $Y_{s/c}$, $Y_{c/s}$, $Y_{s/p}$, $Y_{p/s}$, $Y_{c/p}$, and $Y_{p/c}$. We used simplified calculations in this example in order to gain a quick understanding of how to obtain the parameters. In practice, we would most likely collect many more data points and use nonlinear regression to evaluate all the parameters. Next, we differentiated the cell concentration times data and then used nonlinear regression to find the Monod rate-law parameters μ_{\max} and K_s .

9.4.4 Mass Balances

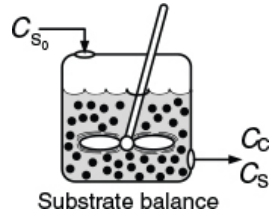
There are two ways that we could account for the growth of microorganisms. One is to account for the number of living cells, and the other is to account for the mass of the living cells. We shall use the latter, grams of cells. A mass balance on the microorganisms in a CSTR (chemostat; e.g., margin figure that follows and Figure 9-24) of constant volume is (9-75)

$$\begin{aligned} \left[\begin{array}{l} \text{Rate of} \\ \text{accumulation} \\ \text{of cells,} \\ g/s \end{array} \right] &= \left[\begin{array}{l} \text{Rate of} \\ \text{cells} \\ \text{entering,} \\ g/s \end{array} \right] - \left[\begin{array}{l} \text{Rate of} \\ \text{cells} \\ \text{leaving,} \\ g/s \end{array} \right] + \left[\begin{array}{l} \text{Net rate of} \\ \text{generation} \\ \text{of live cells,} \\ g/s \end{array} \right] \quad (9-75) \\ V \frac{dC_c}{dt} &= v_0 C_{c0} - v_0 C_c + (r_g - r_d) v \end{aligned}$$

Cell mass balance

The corresponding substrate balance is

$$\begin{aligned} \left[\begin{array}{c} \text{Rate of} \\ \text{accumulation} \\ \text{of substrate,} \\ g/s \\ V \frac{dC_s}{dt} \end{array} \right] &= \left[\begin{array}{c} \text{Rate of} \\ \text{substrate} \\ \text{entering,} \\ g/s \\ v_0 C_{s0} \end{array} \right] - \left[\begin{array}{c} \text{Rate of} \\ \text{substrate} \\ \text{leaving,} \\ g/s \\ v_0 C_s \end{array} \right] + \left[\begin{array}{c} \text{Rate of} \\ \text{substrate} \\ \text{generation,} \\ g/s \\ r_g V \end{array} \right] \quad (9-76) \end{aligned}$$



In most systems, the entering microorganism concentration, C_{c0} , is zero for a flow reactor.

Batch Operation

For a batch system $v = v_0 = 0$, the mass balances are as follows:

Cell Mass Balance

$$V \frac{dC_c}{dt} = r_g V - r_d V$$

The mass balances

Dividing by the reactor volume V gives

$$\boxed{\frac{dC_c}{dt} = r_g - r_d} \quad (9-77)$$

Substrate Mass Balance

The rate of disappearance of substrate, $=r_s$, results from substrate used for cell growth and substrate used for cell maintenance

$$\boxed{V \frac{dC_c}{dt} = r_s V = Y_{s/c} (-r_g) V - m C_c V} \quad (9-78)$$

Dividing by V yields the substrate balance for the growth phase

$$\frac{dC_s}{dt} = Y_{s/c} (-r_g) - mC_c \quad (9-79)$$

Growth phase

For cells in the *stationary phase*, where there is no growth in cell concentration, cell maintenance and product formation are the only reactions to consume the secondary substrate. Under these conditions the substrate balance, Equation (9-76), reduces to

$$V \frac{dC_{sn}}{dt} = -mC_c V + Y_{sn/p} (-r_{pn}) V \quad (9-80)$$

Stationary phase

Typically, the growth rate utilizing the secondary nutrients, r_{pn} , will have the same Monod form of the rate law as r_g (e.g., Equation (9-71)). Of course, Equation (9-79) only applies for substrate concentrations greater than zero.

Product Mass Balance

The rate of product formation, r_p , can be related to the rate of substrate consumption, $-r_s$, through the following balance when maintenance is neglected, that is, $m = 0$:

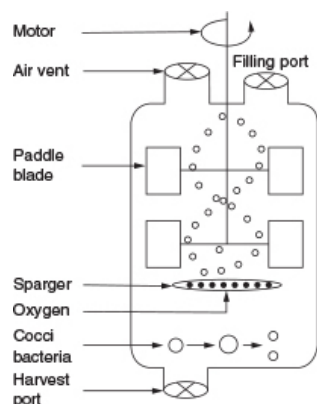
$$V \frac{dC_p}{dt} = r_p V = Y_{p/s} (-r_s) V \quad (9-81)$$

Batch stationary growth phase

During the growth phase, we could also relate the rate of formation of product, r_p , to the cell growth rate, r_g , Equation (9-63), that is, $r_p = Y_{p/c} r_g$. The coupled first-order ordinary differential equations above can be solved by a variety of numerical techniques.

Example 9–5 Bacteria Growth in a Batch Reactor

Glucose-to-ethanol fermentation is to be carried out in a batch reactor using an organism such as *Saccharomyces cerevisiae*. Plot the concentrations of cells, substrate, and product and the rates for growth, death, and maintenance, that is, r_g , r_d , and r_{sm} as functions of time. The initial cell concentration is 1.0 g/dm^3 , and the substrate (glucose) concentration is 250 g/dm^3 .



Additional data (Partial source: R. Miller and M. Melick, *Chem. Eng.*, 113 (February 16, 1987):

$$\begin{aligned}
 C_p^* &= 93 \text{ g/dm}^3 & Y_{c/s} &= 0.08 \text{ g/g} \\
 n &= 0.52 & Y_{p/s} &= 0.45 \text{ g/g} \\
 \mu_{\max} &= 0.46 \text{ h}^{-1} & Y_{p/c} &= 5.6 \text{ g/g} \\
 K_s &= 33.5 \text{ g/dm}^3 & k_d &= 0.01 \text{ h}^{-1} \\
 m &= 0.03 \text{ (g substrate) / (g cells} \cdot \text{h)}
 \end{aligned}$$

Solution

1. Mass balances:

$$\text{Cells: } V \frac{dC_c}{dt} = (r_g - r_d) V \quad (\text{E9-5.1})$$

$$\text{Substrate: } V \frac{dC_s}{dt} = Y_{s/c} (-r_g) V - r_{sm} V \quad (\text{E9-5.2})$$

$$\text{Product: } V \frac{dC_p}{dt} = r_p V = Y_{p/c} (r_g V) \quad (\text{E9-5.3})$$

The algorithm

2. Rate laws:

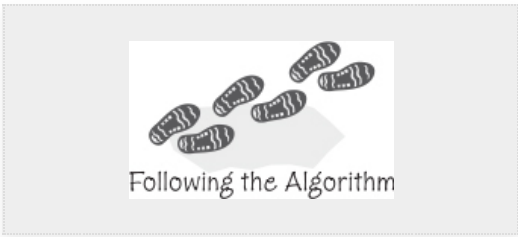
Growth: $r_g = \mu_{\max} \left(1 - \frac{C_p}{C_p^*}\right)^{0.52} \frac{C_c C_s}{K_s + C_s}$ (E9-5.4)

Death: $r_d = k_d C_c$ (E9-5.5)

Maintenance: $r_{sm} = m C_c$ (9-67)

3. Stoichiometry:

$r_p = Y_{p/c} r_g$ (E9-5.6)



4. Combining gives

$\frac{dC_c}{dt} = \mu_{\max} \left(1 - \frac{C_p}{C_p^*}\right)^{0.52} \frac{C_c C_s}{K_s + C_s} - k_d C_c$ (E9-5.7)

$\frac{dC_s}{dt} = -Y_{s/c} \mu_{\max} \left(1 - \frac{C_p}{C_p^*}\right)^{0.52} \frac{C_c C_s}{K_s + C_s} - m C_c$ (E9-5.8)

$\frac{dC_p}{dt} = Y_{p/c} r_g$

Cells Substrate Product

These equations were solved using an ODE equation solver (see Table E9-5.1). The results are shown in Figure E9-5.1 for the parameter values given in the problem statement.

TABLE E9-5.1 POLYMATH PROGRAM

Differential equations
1 d(Cc)/d(t) = rg-rd

$$2 \frac{d(C_s)}{d(t)} = Y_{sc} * (-r_g) - r_{sm}$$

$$3 \frac{d(C_p)}{d(t)} = r_g * Y_{pc}$$

Explicit equations

$$1 \text{ rd} = C_c * .01$$

$$2 Y_{sc} = 1/.08$$

$$3 Y_{pc} = 5.6$$

$$4 K_s = 33.5$$

$$5 m = .03$$

$$6 u_{max} = .46$$

$$7 r_{sm} = m * C_c$$

$$8 k_{obs} = u_{max} * (1 - C_p/93)^{.52}$$

$$9 r_g = k_{obs} * C_c * C_s / (K_s + C_s)$$

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	Cc	1.	16.55544
2	Cp	0	92.96161
3	Cs	250.	39.36185
4	kobs	0.46	0.007997
5	Ks	33.5	33.5
6	m	0.03	0.03
7	rd	0.01	0.1655544
8	rg	0.4056437	0.071523
9	rsm	0.03	0.4966631
10	t	0	12.
11	umax	0.46	0.46
12	Ypc	5.6	5.6
13	Ysc	12.5	12.5

(<http://www.umich.edu/~elements/6e/09chap/live.html>)



The substrate concentration C_s can never be less than zero. However, we note that when the substrate is completely consumed, the first term on the right-hand side of Equation (E9-5.8) (and line 2 of the Polymath program) will be zero but the second term for maintenance, mC_c , will not. Consequently, **if** the integration is carried further in time, the integration program will predict a **negative** value of C_s !! This inconsistency can be addressed in a number of ways, such as including an **if** statement in the Polymath program (e.g., if C_s is less than or equal to zero, then $m = 0$). The Wolfram sliders and typical Wolfram results are shown in Figures E9-5.2 and E9-5.3, respectively.

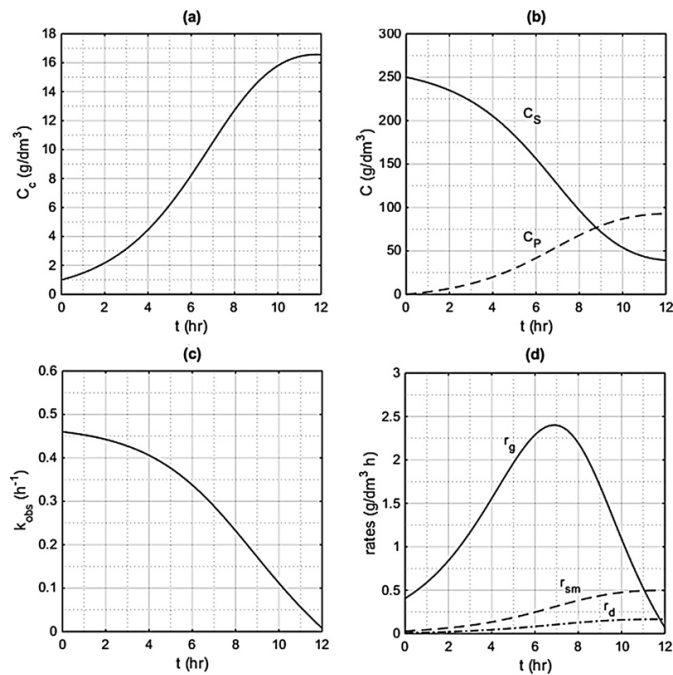


Figure E9-5.1 Concentrations and rates as a function of time.

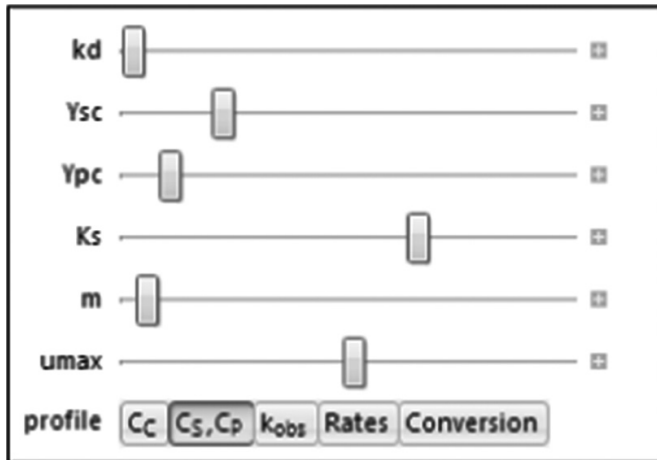
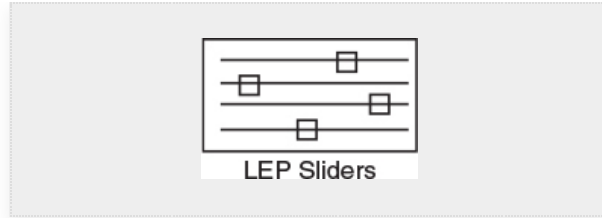


Figure E9-5.2 Wolfram sliders.

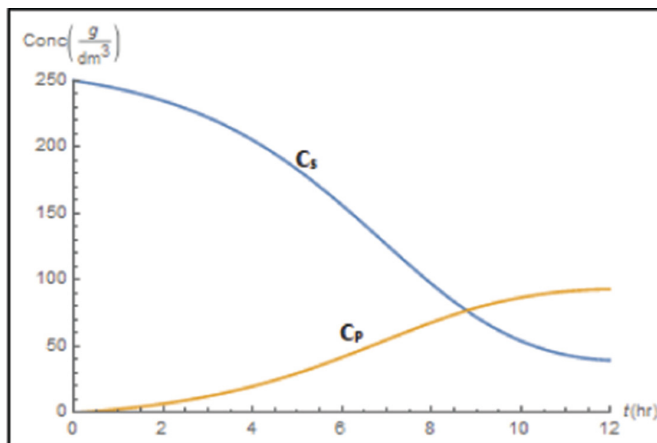


Figure E9-5.3 Wolfram concentration trajectory.

Analysis: In this example, we applied a modified CRE algorithm to biomass formation and solved the resulting equations using the ODE solver Polymath. We note in Figure E9-5.1(d) the growth rate, r_g , goes through a maximum, increasing at the start of the reaction as the concentration of cells, C_c , increases then decreasing as the substrate concentration

decreases, and at the end C_p approaches C_p^* and the growth rate approaches zero (nutrient) as does k_{obs} in Figure E9-5.1(c). One also observes in (d) the death rate r_d and substrate consumption for maintenance are very small and only become important at large cell concentrations. We see from Figures E9-5.1(a) and (b) that the cell concentration increases dramatically with time while the product concentration does not. The reason for this difference is that part of the substrate is consumed for maintenance and part for cell growth, leaving only the remainder of the substrate to be transformed into product.

9.4.5 Chemostats

Chemostats are essentially CSTRs that contain microorganisms. A typical chemostat is shown in Figure 9-24, along with the associated monitoring equipment and pH controller. One of the most important features of the chemostat is that it allows the operator to control the cell growth rate. This control of the growth rate is achieved by adjusting the volumetric feed rate (dilution rate).

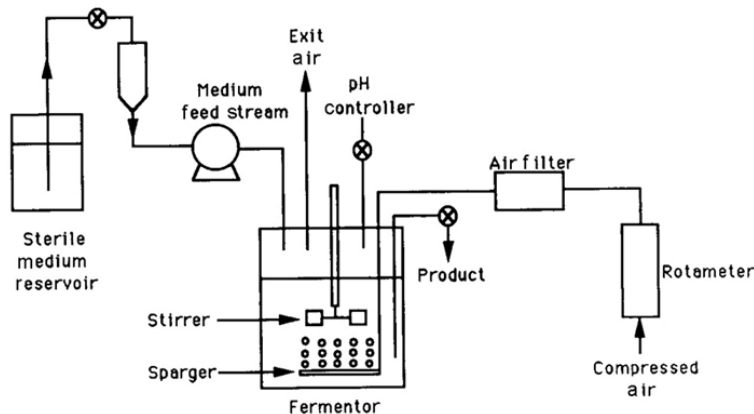


Figure 9-24 Chemostat (CSTR) system.

9.4.6 CSTR Bioreactor Operation

In this section, we return to the mass balance equations on the cells (Equation (9-75)) and substrate (Equation (9-76)), and consider the case where the volumetric flow rates in and out are the same, $v = v_0$, and that no live (i.e., viable) cells enter

the chemostat $C_{C0} = 0$. We next define a parameter common to bioreactors called the dilution rate, D . The dilution rate is

$$D = \frac{v_0}{V}$$

and is simply the reciprocal of the space time τ , that is, $D = \frac{1}{\tau}$. Dividing Equations (9-75) and (9-76) by V and using the definition of the dilution rate, and neglecting maintenance, that is, $m = 0$, we have

$$\text{Accumulation} = \text{In} - \text{Out} + \text{Generation}$$

$$\text{Cell : } \frac{dC_c}{dt} = 0 - DC_c + (r_g - r_d) \quad (9-82)$$

$$\text{Substrate : } \frac{dC_s}{dt} = DC_{s0} - DC_s + r_s \quad (9-83)$$

CSTR mass balances

Using the Monod equation, the growth rate is determined to be

$$r_g = \mu C_c = \frac{\mu_{\max} C_s C_c}{K_s + C_s} \quad (9-53)$$

Rate law

For steady-state operation we have

$$DC_c = r_g - r_d \quad (9-84)$$

Steady state

and

$$D(C_{s0} - C_s) = -r_s \quad (9-85)$$

We now neglect the death rate, r_d , and combine Equations (9-51) and (9-84) for steady-state operation to obtain the mass flow rate of cells out of the chemostat, $\dot{m}_c = C_c v_0$, and the rate of generation of cells, $r_g V$. Equating \dot{m}_c and $r_g V$, and then substituting for $r_g = \mu C_c$, we obtain

$$\dot{m}_c = C_c v_0 = r_g V = \mu C_c V \quad (9-86)$$

Dividing by $C_c V$ we see the cell concentration cancels to give the dilution rate D

$$\boxed{D = \frac{v_0}{V} = \mu} \quad (9-87)$$

Dilution rate

An inspection of Equation (9-87) reveals that the specific growth rate of the cells *can be controlled* by the operator by controlling the dilution rate D , that is, $D = \frac{v_0}{V}$. That is, simply by increasing the volumetric flow rate we can increase the specific growth rate μ . Using Equation (9-52)

How to control cell growth

$$\mu = \mu_{\max} \frac{C_s}{K_s + C_s} \quad \text{s}^{-1} \quad (9-52)$$

to substitute for μ in terms of the substrate concentration and then solving for the steady-state substrate concentration yields

$$C_s = \frac{DK_s}{\mu_{\max} - D} \quad (9-88)$$

Assuming that a single nutrient is limiting, cell growth is the only process contributing to substrate utilization, and that cell maintenance can be neglected, the stoichiometry is

$$-r_s = r_g Y_{s/c} \quad (9-89)$$

$$C_c = Y_{s/c} (C_{s0} - C_s) \quad (9-68)$$

Substituting for C_s using Equation (9-88) and rearranging, we obtain

$$\boxed{C_c = Y_{c/s} \left[C_{s0} - \frac{DK_s}{\mu_{\max} - D} \right]} \quad (9-90)$$

9.4.7 Washout

To learn the effect of increasing the dilution rate, we combine Equations (9-82) and (9-54), and set m and r_d to zero to get

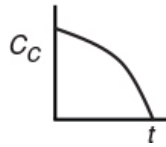
$$\frac{dC_c}{dt} = (\mu - D) C_c \quad (9-91)$$

We see that if $D > \mu$, then (dC_c/dt) will be negative, and the cell concentration will continue to decrease until we reach a point where all cells will be washed out:

$$C_c = 0$$

That is, as we continually increase we reach a point at which the concentration of live cells exiting the reactor will be zero and the point is called cell *wash-out*. The dilution rate at which washout will occur is obtained from Equation (9-90) by setting $C_c = 0$.

$$D_{\max} = \frac{\mu_{\max} C_{s0}}{K_s + C_{s0}} \quad (9-92)$$



Flow rate at which washout occurs

We next want to determine the other extreme for the dilution rate, which is the rate of maximum cell production. The cell production rate per unit volume of reactor is the mass flow rate of cells out of the reactor (i.e., $\dot{m}_c = C_c v_0$) divided by the volume V , or

$$\frac{\dot{M}_c}{V} = \frac{v_0 C_c}{V} = D C_c \quad (9-93)$$

Maximum rate of cell production ($D C_c$)

Using Equation (9-90) to substitute for C_c in Equation (9-93) yields

$$DC_c = DY_{c/s} \left(C_{s0} - \frac{DK_s}{\mu_{\max} - D} \right) \quad (9-94)$$

Figure 9-25 shows production rate, cell concentration, and substrate concentration as functions of dilution rate.

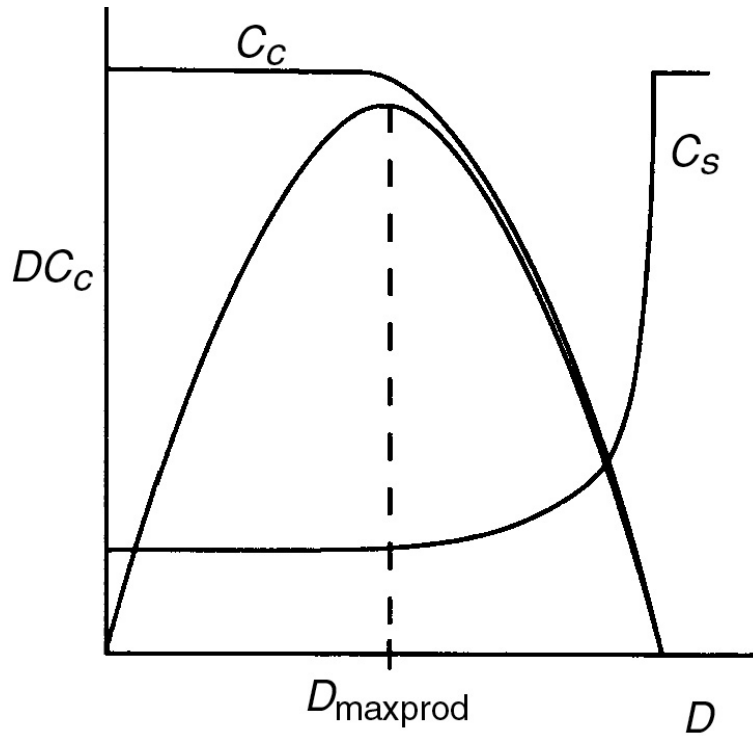


Figure 9-25 Cell and substrate concentrations and production rate as functions of dilution rate.

We observe a maximum in the production rate, and this maximum can be found by differentiating the production rate, Equation (9-94), with respect to the dilution rate D :

$$\frac{d(DC_c)}{dD} = 0 \quad (9-95)$$

Then

$$D_{\max\text{prod}} = \mu_{\max} \left(1 - \sqrt{\frac{K_s}{K_s + C_{s0}}} \right) \quad (9-96)$$

Maximum rate of cell production

The organism *Streptomyces aureofaciens* was studied in a 10-dm³ chemostat using sucrose as a substrate. The cell

concentration, C_c (mg/ml), the substrate concentration, C_s (mg/ml), and the production rate, DC_c (mg/ml/h), were measured at steady state for different dilution rates. The data are shown in Figure 9-26.²⁴ Note that the data follow the same trends as those discussed in Figure 9-25.

²⁴ B. Sikyta, J. Slezak, and M. Herold, *Appl. Microbiol.*, 9, 233.

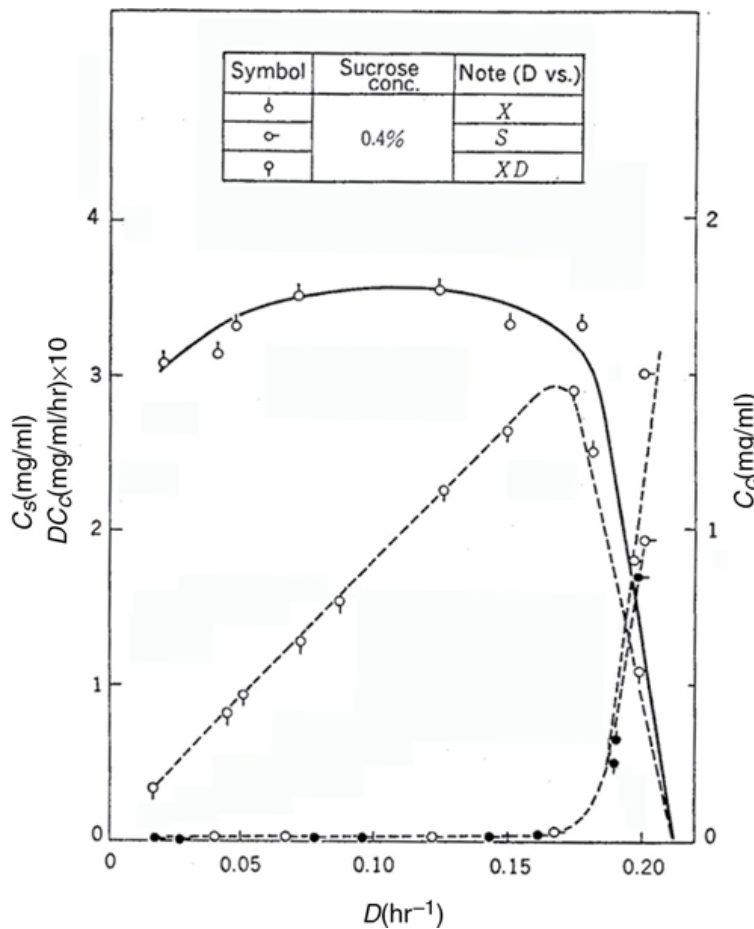


Figure 9-26 Continuous culture of *Streptomyces aureofaciens* in chemostats. Note: $X \equiv C_c$. Courtesy of S. Aiba, A. E. Humphrey, and N. F. Millis, *Biochemical Engineering*, 2nd ed. New York: Academic Press.

9.5 AND NOW... A WORD FROM OUR SPONSOR—SAFETY 9 (AWFOS—S9 PROCESS SAFETY TRIANGLE)[†]

[†] <http://umich.edu/~safeche/processtriangle.html>

Introduction

To ensure that chemical processes run safely, we must pay attention to safety indicators—those practices and situations that tell us if we are likely to have an accident. Process Safety Triangles are used to illustrate the different indicators and actions that can lead to an accident. This tool highlights how the smallest unsafe act can lead to a major accident. The triangle is applied from the bottom up, where each layer can be thought of as a preventative measure to the layer above it. The purpose is to show how an *unsafe* mindset can grow and produce tragic consequences.

9.5.1 Levels of the Process Safety Triangle

Let's go to page 4 of the *CCPS Process Safety* document that discusses three metrics: Lagging Indicators, Leading Indicators and Near Misses.

(https://www.aiche.org/sites/default/files/docs/pages/CCPS_ProcessSafety_Lagging_2011_2-24.pdf). Starting at the top of the pyramid and working down we have the following levels shown in Figure 9-27. A Google search on “process safety pyramid” will show you variations of the triangle/pyramid (<https://www.google.com/search?safe=strict&q=process+safety+pyramid&tbm=isch&source=univ&sa=X&ved=2ahUKEwiD2OuX5uvhAhVNY6wKHbYDDPgQsAR6BAgHEAE&biw=1266&bih=524&dpr=1.25>).

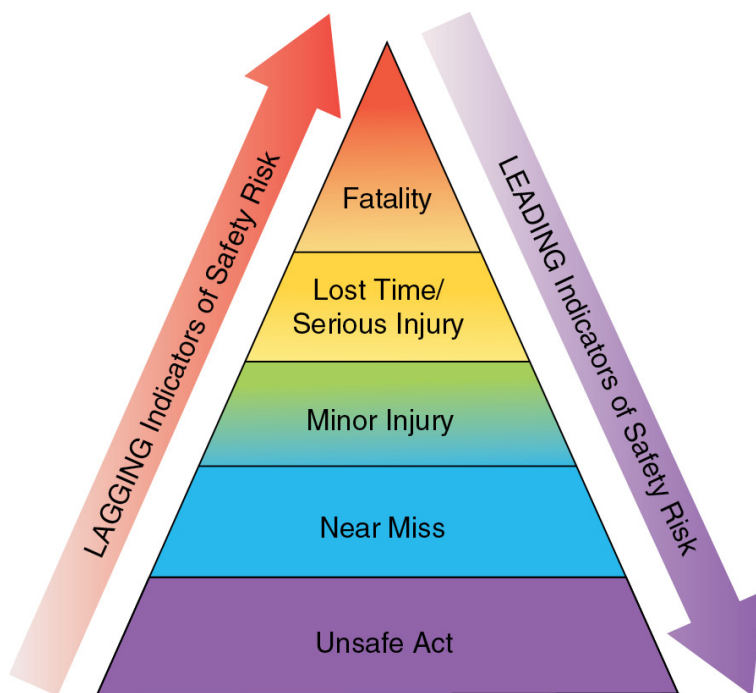


Figure 9-27 Face of process safety triangle.

Components

Fatality: Loss of life by an accident.[†]

[†] Google Search. Google. Web. 20 June 2018.

Lost Time/Serious Injury: The classification for an occupational injury which includes: (a) all disabling work injuries and (b) nondisabling work injuries. These injuries include: (1) eye injuries requiring treatment by a physician, (2) fractures, (3) injuries requiring hospitalization, (4) loss of consciousness, (5) injuries requiring treatment by a doctor, and (6) injuries requiring restriction of motion or work, or assignment to another job.[‡]

[‡] Center for Chemical Process Safety. "CCPS Process Safety Glossary." American Institute of Chemical Engineers, www.aiche.org/ccps/resources/glossary.

Minor Injuries: Any injury sustained that does not meet one of the requirements of a serious injury listed above. For example, any injury that can be treated quickly on site, such as a bruise, a minor cut, or scratch.

Near Misses: An event in which an accident (i.e., property damage, environmental impact, or human loss) or an operational interruption could have plausibly resulted if circumstances had been slightly different.[§]

[§] *Near Miss Reporting Systems* by the National Safety Council and Alliance (an OSHA Cooperative Program). Document can be found at <https://www.nsc.org/Portals/0/Documents/WorkplaceTrainingDocuments/Near-Miss-Reporting-Systems.pdf>.

Unsafe Acts: Any act that deviates from a generally recognized safe way or specified method of doing a job and which increases the probabilities for an accident.[¶]

[¶] US Legal, Inc. "USLegal." *Unsafe Act Law and Legal Definition* (definitions.uslegal.com/u/unsafe-act/).

9.5.2 Application to Process Safety

One of the main purposes of the process safety triangle is the illustration of how unsafe acts can lead to a major incident. The process safety triangle is also used to visualize the different layers of protection and help redesign systems to ensure better preventative practices. The bottom level, unsafe acts, is categorized as a leading metric. Leading metrics are preventative actions taken to avoid an incident from occurring. Unsafe behaviors of employees, such as not wearing personal protective equipment or the lack of protection layers for a system, are the fundamental causes of process safety incidents. The wider the base of your process safety triangle is the wider the top level is. This triangle illustrates how the more unsafe behaviors you have, the more likely a fatality from a process safety incident is to occur.

Near misses and the levels above it are categorized as lagging metrics. In many companies, *near misses* are analyzed at the same level as an accident. Lagging metrics are events that happen in a process that are reported for the improvement of the safety of the process. Analyzing past incidents has proven that if near misses are treated like injuries and incidents by reporting them, then the likelihood of a fatality from a process safety incident decreases. All past accidents have had warning

signs (near misses) that indicated something needed to change and could have prevented the accident from occurring.[§]

Reporting near misses makes others aware of a potential issue and allows for measures to be implemented to prevent the escalation to a process safety incident. Most, if not all, companies require that all unsafe acts—be logged in safety report whether or not an injury occurs.

The key takeaways from the process safety triangle are that eliminating unsafe acts drastically reduces the risk of a process safety incident occurring. Reporting near misses allows for the process to be reviewed and improve to prevent injuries and fatalities from occurring.

9.5.3 Examples of Process Safety Triangle

Below is an example of a process safety triangle with an estimation of each reported type of action on the triangle (Figure 9-28).

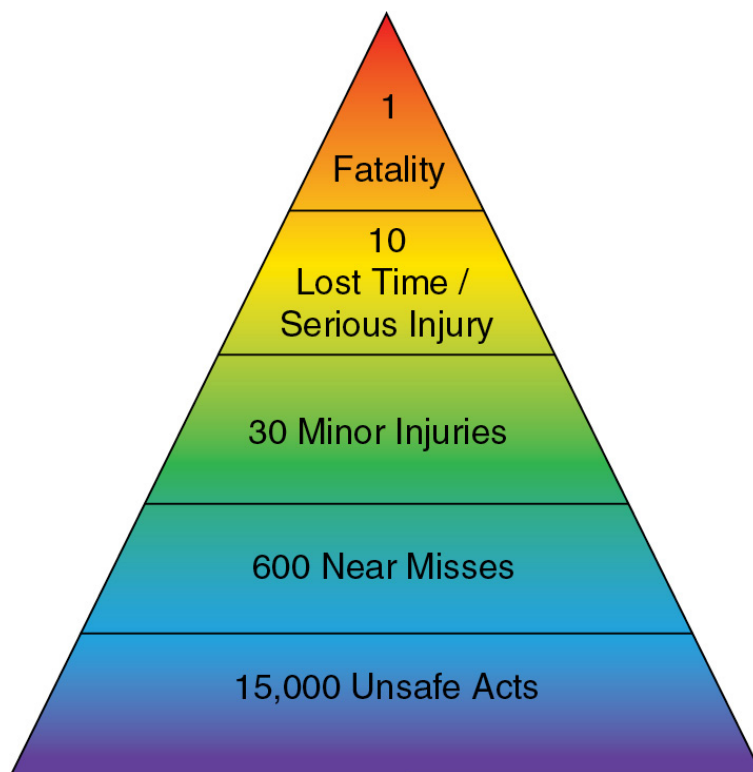


Figure 9-28 Face of process safety triangle with number estimates (*Near Miss Reporting Systems* by

the National Safety Council and Alliance [an OSHA Cooperative Program]. Document can be found at <https://www.nsc.org/Portals/0/Documents/WorkplaceTrauma/Near-Miss-Reporting-Systems.pdf>.

Closure. The theme running through most of this chapter is the pseudo-steady-state hypothesis (PSSH) as it applies to chemical reactions and to enzymatic reactions. The reader should be able to apply the PSSH to reactions in such problems as P9-4_B to P9-8_B in order to develop rate laws. After completing this chapter, the reader should be able to describe and analyze enzymatic reactions and the different types of inhibition as displayed on a Lineweaver–Burk plot. The reader should be able to explain the use of microorganisms to produce chemical products, along with the stages of cell growth and how the Monod equation for cell growth is coupled with mass balances on the substrate, cells, and product to obtain the concentration–time trajectories in a batch reactor. The reader should also be able to apply the growth laws and balance equations to a chemostat (CSTR) to predict the maximum product flow rate and the washout rate.

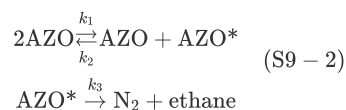
SUMMARY

1. In the PSSH, we set the rate of formation of the active intermediates equal to zero. If the active intermediate A* is involved in m different reactions, we set it to

$$r_{A^*,\text{net}} \equiv \sum_{i=1}^m r_{A^*i} = 0 \quad (\text{S9-1})$$

This approximation is justified when the active intermediate is highly reactive and present in low concentrations.

2. The azomethane (AZO) decomposition mechanism is



$$r_{\text{N}_2} = \frac{k(\text{AZO})^2}{1+k'(\text{AZO})} \quad (\text{S9-3})$$

By applying the PSSH to AZO*, we show the rate law, which exhibits first-order dependence with respect to AZO at high AZO concentrations and second-order dependence with respect to AZO at low AZO concentrations.

3. Enzyme kinetics: enzymatic reactions follow the sequence



Using the PSSH for (E · S) and a balance on the total enzyme, E_t, which includes both the bound (E · S) and unbound enzyme (E) concentrations

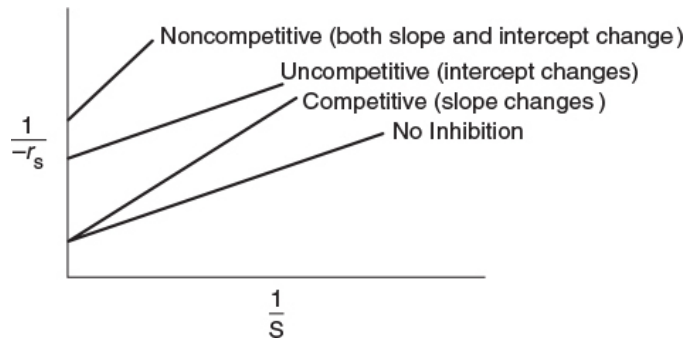
$$E_t = (E) + (E \cdot S)$$

we arrive at the Michaelis–Menten equation

$$-r_s = \frac{V_{\max}(S)}{K_M + (S)} \quad (S9-4)$$

where V_{\max} is the maximum reaction rate at large substrate concentrations ($S \gg K_M$) and K_M is the Michaelis constant. K_M is the substrate concentration at which the rate is half the maximum rate ($S_{1/2} = K_M$).

4. The three different types of inhibition—competitive, uncompetitive, and noncompetitive (mixed)—are shown on the Lineweaver–Burk plot:



5. Bioreactors:

Cells + Substrate \rightarrow More cells + Product

1. Phases of bacteria growth:
 - I. Lag
 - II. Exponential
 - III. Stationary
 - IV. Death
2. Unsteady-state **mass balance** on a chemostat

$$\frac{dC_c}{dt} = D(C_{c0} - C_c) + r_g - r_d \quad (S9-5)$$

$$\frac{dC_s}{dt} = D(C_{s0} - C_s) + r_s \quad (S9-6)$$

3. Monod growth **rate law**

$$r_g = \mu_{\max} \frac{C_c C_s}{K_s + C_s} \quad (S9-7)$$

4. **Stoichiometry**

$$Y_{c/s} = \frac{\text{Mass of new cells formed}}{\text{Mass of substrate consumed}} \quad (S9-8)$$

$$Y_{s/c} = \frac{1}{Y_{c/s}} \quad (S9-9)$$

Substrate consumption

$$-r_{s/c} = Y_{s/c} r_g + m C_c \quad (S9-10)$$

5. **Maximum cell concentration and cell washout**

The dilution rate at which the cells become washed out is

$$D_{\max} = \frac{\mu_{\max} C_{s0}}{K_s + C_{s0}}$$

The dilution rate that gives the maximum rate of production of the cells exiting the reactor, m_c is

$$D_{\max\text{prod}} = \mu_{\max} \left(1^{\text{TM}} \frac{\sqrt{K_s}}{K_s + C_{s0}} \right)$$

CRE WEB SITE MATERIALS

(<http://www.umich.edu/~elements/6e/09chap/obj.html#/>)

Useful Links

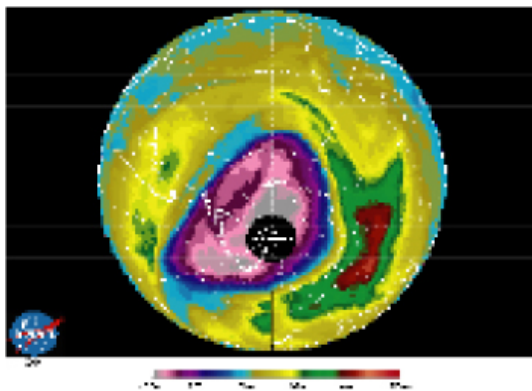


Evaluation



Web Modules

Earth Probe TOMs Total Ozone September 8, 2000



Ozone Layer

(http://umich.edu/~elements/6e/web_mod/ozone/index.htm)



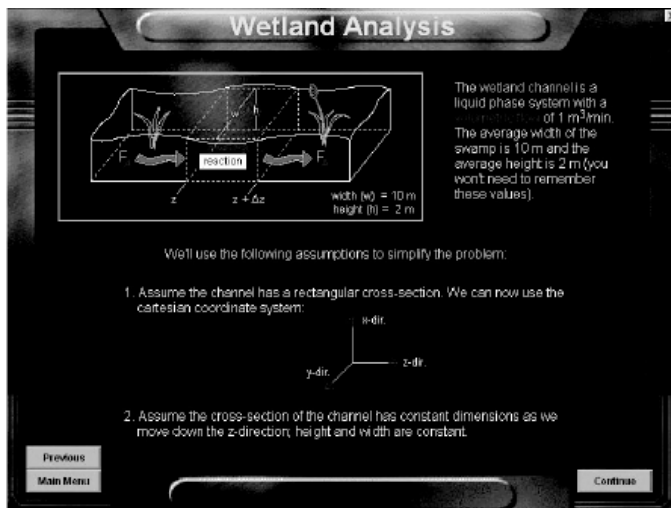
Glow Sticks,

(http://www.umich.edu/~elements/6e/web_mod/new/glowsticks/index.htm)

Photo courtesy of Goddard Space Flight Center (NASA). See the Web Modules on the CRE Web site for color pictures of the ozone layer and the glow sticks.

Interactive Computer Games

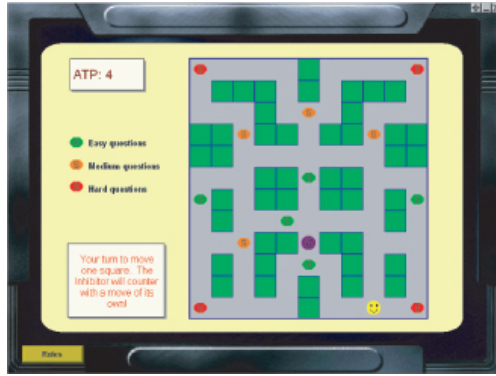
(<http://umich.edu/~elements/6e/icm/index.html>)



Ecology (<http://umich.edu/~elements/6e/icm/ecology.html>)

Enzyme Man

(<http://umich.edu/~elements/6e/icm/enzyme.html>)



R9-1 Pharmacokinetics in Drug Delivery

(<http://www.umich.edu/~elements/6e/09chap/prof-07prof5.html>)

Pharmacokinetic models of drug delivery for medication administered either orally or intravenously are developed and analyzed.

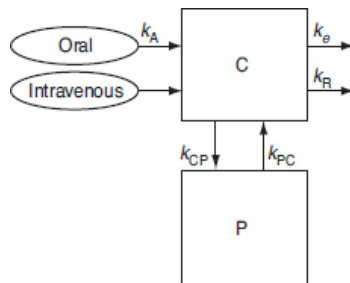


Figure A Two-compartment model.

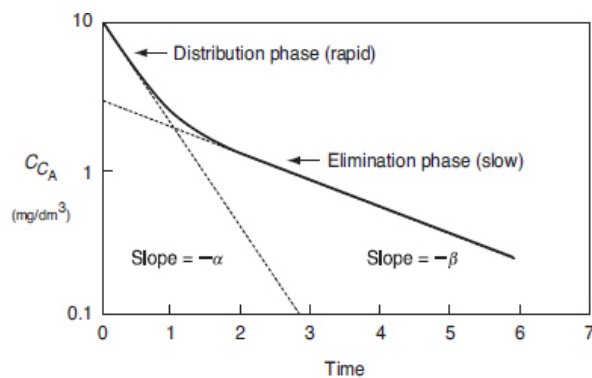


Figure B Drug-response curve.

R9-2 Around 2005, the author of this book carried out a research project on ethanol that was published in the medical journal *Alcohol*, 35 (1), 3–12 (2005).

Abbreviated salient features from the article can be found in the Summary Notes (<http://www.umich.edu/~elements/6e/09chap/summary.html#sec3>) and in the Summary Notes (<http://www.umich.edu/~elements/6e/09chap/prof-pharmacokinetics.html>). Physiologically Based Pharmacokinetic (PBPK) Models. Case Study: Alcohol Metabolism in Humans (<http://www.umich.edu/~elements/6e/09chap/prof-pharmacokinetics.html>).

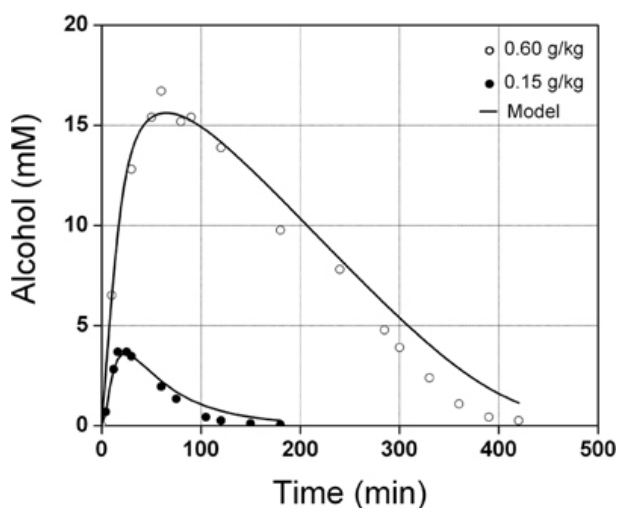


Figure R9-2 Predicted blood alcohol—time trajectories compared with the data of Wilkinson et al.²⁵

²⁵ P. K. Wilkinson, et al., "Pharmacokinetics of ethanol after oral administration in the fasting state," *J. Pharmacokinet. Biopharm.*, 5(3), 207–224 (1977).

Go to the LEP Wolfram sliders to vary some of the parameters and write two conclusions.

The author of this textbook and two students published an article on ethanol metabolics in the medical journal *Alcohol* that can be found at (<http://www.umich.edu/~elements/6e/09chap/pdf/Alcohol.pdf>).

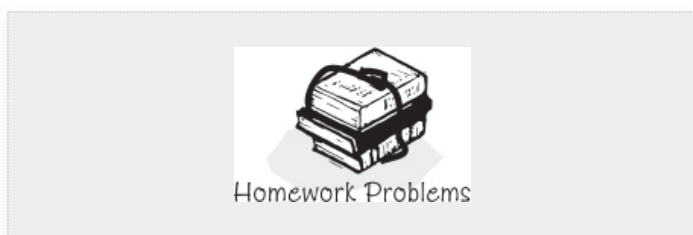
QUESTIONS, SIMULATIONS, AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$A = \bullet B = \blacksquare C = \blacklozenge D = \blacklozenge\blacklozenge$$

In each of the following questions and problems, rather than just drawing a box around your answer, write a sentence or two describing how you solved the problem, the assumptions you made, the reasonableness of your answer, what you learned, and any other facts that you want to include.

To enhance the quality of your sentences, you may wish to refer to W. Strunk and E. B. White, *The Elements of Style*, 4th ed. New York: Macmillan, 2000 and Joseph M. Williams, *Style: Ten Lessons in Clarity & Grace*, 6th ed. Glenview, IL: Scott, Foresman, 1999.



Questions

Q9-1_A QBR (*Question Before Reading*). What factors affect the enzymatic rate law and cell growth law both positive and negative ways.

Q9-2_A i>clicker. Go to the Web site (http://www.umich.edu/~elements/6e/09chap/iclicker_ch9_q1.html) and view at least five i>clicker questions. Choose one that could be used as is, or a variation thereof, to be included on the next exam. You also could consider the opposite case: explaining why the question should *not* be on the next exam. In either case, explain your reasoning.

Q9-3_A Go to the LearnChemE screencast link for Chapter 9 (<http://www.umich.edu/~elements/6e/09chap/learn-cheme-videos.html>).

1. View one of the screencast 5- to 6-minute video (1) PSSH, (2) Cell Growth, (3) Michaelis-Menten Kinetics in a CSTR, and (4) Competitive Inhibition tutorials and list two of the most important points that the presenter was making.
2. In the cell growth screencast, why is there a minus right before r_s and not before r_g ?

Q9-4_A What key points does the Process Safety Triangle want to emphasize? Which point do you think some companies have recently been required to report? What is the overall takeaway lesson from the Process Safety Triangle?

Computer Simulations and Experiments

P9-1_A

1. Example 9-1: The Stern–Volmer Equation

Wolfram and Python

1. Explain how I would change if the concentrations of CS_2 and M were increased.
 2. Explain how the light intensity varies with an increase in concentration of M .
 3. Write two conclusions from your experiment in (i)–(ii).
2. **Example 9-2: Evaluation of the Michaelis–Menten Parameters V_{\max} and K_M**

Wolfram and Python

1. At very low values of K_M in the Michaelis–Menton plot (e.g., $K_M = 0.0001$), how does the rate of substrate consumption, $-r_s$, vary with substrate concentration, C_{urea} ?
2. At very low values of K_M in the Eadie–Hofstee plot, what are the values of K_M and V_{\max} such that the substrate rate, $-r_s$, becomes zero?
3. Write two conclusions from your experiment in (i)–(ii).

Polymath

4. The following additional runs were carried out when an inhibitor was present:

$C_{\text{urea}}(\text{kmol/m}^3)$	$C_{\text{inhibitor}}(\text{kmol/m}^3)$	$-r_{\text{urea}}(\text{kmol/m}^3 \cdot \text{s})$
0.01	0.1	0.125
0.005	0.1	0.065

What type of inhibition is taking place?

5. Sketch the curves for no inhibition as well as competitive, uncompetitive, noncompetitive (mixed), and substrate inhibition on a Woolf–Hanes plot and on an Eadie–Hofstee plot.

3. **Example 9-3: Batch Enzymatic Reactors**

Wolfram and Python

1. As the conversion approaches one, what does the reaction time, in seconds, approach?
2. What happens to X versus t when K_M is varied?
3. Vary each parameter and write a set of conclusions.

Polymath

4. What would the conversion be after 15 minutes if the initial concentration of urea were increased by a factor of 10?
5. What is the minimum value of K_M so that conversion is below 0.5 after half an hour?

4. **Example 9-4: Estimate the Yield Coefficients** What is the total mass of substrate consumed in grams per mass of cells plus what is consumed to form product? Is there disparity here?

5. **Example 9-5: Bacteria Growth in a Batch Reactor**

Wolfram and Python

1. Which parameter will you vary so that C_C goes through a maxima at $t = 9$ hr? Explain the results.
2. What is the minimum value of K_S such that C_S is always higher than C_p ?
3. What is the maximum value of μ_{\max} so that r_g continuously increases up to $t = 12$ hr?
4. What is the value of $Y_{S/C}$ such that virtually 100% conversion is achieved at the end of the reaction?
5. Write a set of conclusions based on your experiment (i)–(iv) above.

Polymath

6. Modify the code to carry out the fermentation in a fed-batch (e.g., semibatch) reactor in which the substrate is fed at a rate of $0.5 \text{ dm}^3/\text{h}$ and a concentration of 5 g/dm^3 to an initial liquid volume of 1.0 dm^3 containing a cell mass with an initial concentration of $C_{Ci} = 0.2 \text{ mg/dm}^3$ and an initial substrate concentration of $C_{Si} = 0.5 \text{ mg/dm}^3$. Plot and analyze the concentration of cells, substrate, and product as a function of time, along with the mass of product up to 24 hours.
7. Repeat (i) when the growth is uncompetitively inhibited by the substrate with $K_I = 0.7 \text{ g/dm}^3$.
8. Set $C_p^* = 10000 \text{ g/dm}^3$, and compare your results with the base case.

6. **LEP 9 Enzyme Inhibition.**

1. Vary V_{\max} and K_m between their minimum and maximum values and describe what you find.
2. Vary K_I and describe how each of the three types of inhibition is affected.
3. Write three conclusions based on your experiments in (i) and (ii).

7. **LEP 9-7 Example on Alcohol Metabolism on the CRE Web Site.** *This problem is a gold mine for things to be learned about the effect of alcohol on the human body.*

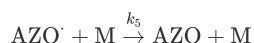
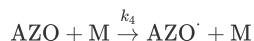
Hint: Read the journal article in the Summary Notes (Alcohol 35, 1 (2005)), available at <http://www.umich.edu/~elements/6e/09chap/prof-pharmacokinetics.html>.

1. Write a summary paragraph describing what you learned from reading the article.
- Wolfram and Python**
2. Vary the initial concentration for ethanol in the stomach and describe how the concentrations of ethanol and acetaldehyde in the blood are affected.
3. Set V_{\max} for acetaldehydes between 10% and 50% of its normal value and compare the concentration-time trajectories with the base cases.
4. Write two conclusions about alcohol metabolism.

Interactive Computer Games

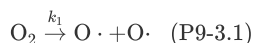
P9-2_A

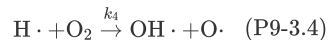
1. **ICG Enzyme Man.** Load the ICG on your computer and carry out the exercise. Performance number = _____.
(<http://www.umich.edu/~elements/6e/icm/enzyme.html>)
2. Apply to this problem one or more of the six ideas discussed in Table P-4 in the Complete Preface-Introduction on the Web site
(<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>).
3. Rederive Equation (9-9) assuming the inert gas M (e.g., N_2) involved is also the reaction with the added steps by



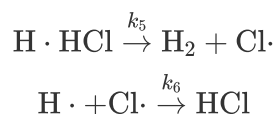
Problems

P9-3_C (*Flame retardants*) Hydrogen radicals are important to sustaining combustion reactions. Consequently, if chemical compounds that can scavenge the hydrogen radicals are introduced, the flames can be extinguished. While many reactions occur during the combustion process, we shall choose CO flames as a model system to illustrate the process (S. Senkan et al., *Combustion and Flame*, 69, 113). In the absence of inhibitors





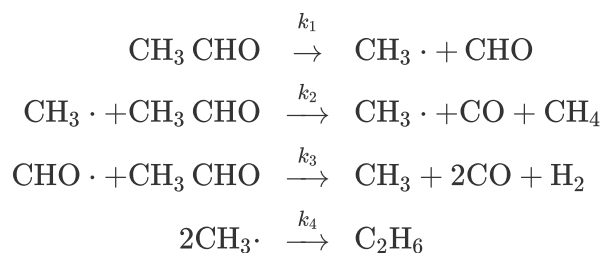
The last two reactions are rapid compared to the first two. When HCl is introduced to the flame as a retardant with forward and reverse specific rate constants k_5 and k_6 , the following additional reactions occur:



Assume that all reactions are elementary and that the PSSH holds for the $\text{O} \cdot$, $\text{OH} \cdot$, and $\text{Cl} \cdot$ radicals.

1. Derive a rate law for the consumption of CO when no retardant is present.
2. Derive an equation for the concentration of $\text{H} \cdot$ as a function of time, assuming constant concentration of O_2 , CO, and H_2O for both uninhibited combustion and combustion with HCl present. Sketch $\text{H} \cdot$ versus time for both cases.
3. Use Polymath to find out what happens when $k_1 = 0.0001$, $k_4 = 0.02$, $k_5 = 0.05$, and $k_6 = 0.005$ appropriate units. Write one sentence conclusion.

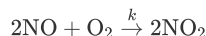
P9-4A The pyrolysis of acetaldehyde is believed to take place according to the following sequence:



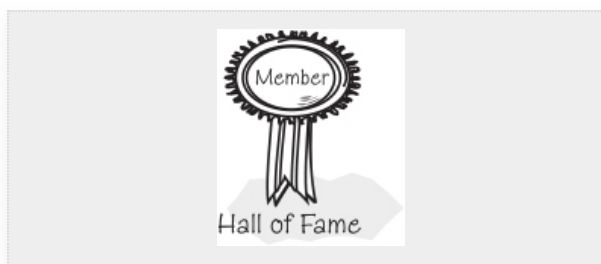
1. Derive the rate expression for the rate of disappearance of acetaldehyde, $-r_{\text{Ac}}$.
2. Under what conditions does it reduce to the equation at the beginning of [Section 9.1](#) on page [368](#)?
3. Sketch a reaction pathway diagram for this reaction. *Hint:* See margin note on page [373](#).

P9-5B

1. **OEQ (Old Exam Question).** For each of the reactions in parts (a), (b), and (c), suggest a mechanism and apply the PSSH to learn if the mechanism is consistent with the rate law.
2. The gas-phase homogeneous oxidation of nitrogen monoxide (NO) to dioxide (NO₂)



is known to have a form of third-order kinetics, which suggests that the reaction is elementary as written, at least for low partial pressures of the nitrogen oxides. However, the rate constant k actually *decreases* with increasing absolute temperature, indicating an apparently *negative* activation energy. Because the activation energy of any elementary reaction must be positive, some explanation is in order.



Provide an explanation, starting from the fact that an active intermediate species, NO₃, is a participant in some other known reactions that involve oxides of nitrogen. Draw the reaction pathway. *Hint:* See margin in Section 9.1.2.

3. The rate law for formation of phosgene, COCl₂, from chlorine, Cl₂, and carbon monoxide, CO, has the rate law

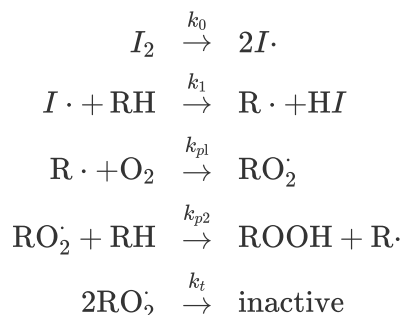
$$r_{\text{COCl}_2} = k_{\text{CO}} C_{\text{CO}} C_{\text{Cl}_2}^{3/2}$$

Suggest a mechanism for this reaction that is consistent with this rate law and draw the reaction pathway. *Hint:* Cl formed from the dissociation of Cl₂ is one of the two active intermediates.

4. Suggest an active intermediate(s) and mechanism for the reaction $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$. Use the PSSH to show whether or not your mechanism is consistent with the rate law

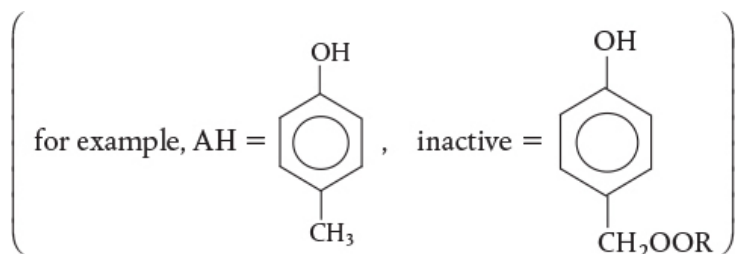
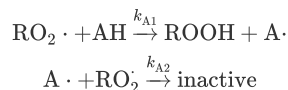
$$r_{\text{HBr}} = \frac{k_1 C_{\text{H}_2} C_{\text{Br}}^{3/2}}{C_{\text{HBr}} + k_2 C_{\text{Br}_2}}$$

P9-6C (Tribology) Why do you change your motor oil? One of the major reasons for engine–oil degradation is the oxidation of the motor oil. To retard the degradation process, most oils contain an antioxidant (see *Ind. Eng. Chem.*, 26, 902 (1987)). Without an inhibitor to oxidation present, the suggested mechanism at low temperatures is



where I_2 is an initiator and RH is the hydrocarbon in the oil.

When an antioxidant is added to retard degradation at low temperatures, the following additional termination steps occur:



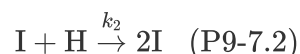
1. Derive a rate law for the degradation of the motor oil in the absence of an antioxidant at low temperatures.
2. Derive a rate law for the rate of degradation of the motor oil in the presence of an antioxidant for low temperatures.
3. How would your answer to part (a) change if the radicals $I\cdot$ were produced at a constant rate in the engine and then found their way into the oil?
4. Sketch a reaction pathway diagram for both high and low temperatures, with and without antioxidant.
5. See the open-ended problem G.2 in [Appendix G](#) and on the CRE Web site for more on this problem.

P9-7A Epidemiology. Consider the application of the PSSH to epidemiology. We shall treat each of the following

steps as elementary, in that the rate will be proportional to the number of people in a particular state of health. A healthy person, H, can become ill, I, spontaneously, such as by contracting smallpox spores:



or the person may become ill through contact with another ill person:



The ill person may become healthy:



or the ill person may expire:

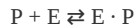
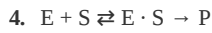
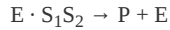


Application of the above sequence to the 2020 Coronavirus Pandemic can be found on page 737.

1. Derive an equation for the death rate.
2. At what concentration of healthy people does the death rate become critical? (**Ans:** When $[\text{H}] = (k_3 + k_4)/k_2$.)
3. Comment on the validity of the PSSH under the conditions of Part (b).
4. If $k_1 = 10^{-8} \text{ h}^{-1}$, $k_2 = 10^{-16} (\text{people} \cdot \text{h})^{-1}$, $k_3 = 5 \times 10^{-10} \text{ h}^{-1}$, $k_4 = 10^{-11} \text{ h}^{-1}$, and $H_0 = 10^9$ people, use Polymath to plot H, I, and D versus time. Vary k_i and describe what you find. Check with your local *disease control center* or search online to modify the model and/or substitute appropriate values of k_i . Extend the model, taking into account what you learn from other sources (e.g., the Internet).
5. Apply to this problem one or more of the six ideas discussed in Table P-4 in the Complete Preface-Introduction on the Web site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>).

P9-8_B Derive the rate laws for the following enzymatic reactions and sketch and compare, where possible, with the plots shown in Figure E9-2.1.

1. $\text{E} + \text{S} \rightleftharpoons \text{E} \cdot \text{S} \rightleftharpoons \text{P} + \text{E}$
2. $\text{E} + \text{S} \rightleftharpoons \text{E} \cdot \text{S} \rightarrow \text{P} + \text{E}$
3. $\text{E} + \text{S}_1 \rightleftharpoons \text{E} \cdot \text{S}_1$
 $\text{E} \cdot \text{S}_1 + \text{S}_2 \rightleftharpoons \text{E} \cdot \text{S}_1\text{S}_2$



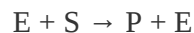
5. Which of the reactions (a)–(d), if any, lend themselves to analysis by a Lineweaver–Burk plot?

P9-9_B OEQ (Old Exam Question). Beef catalase has been used to accelerate the decomposition of hydrogen peroxide to yield water and oxygen (*Chem. Eng. Educ.*, 5, 141). The concentration of hydrogen peroxide is given as a function of time for a reaction mixture with a pH of 6.76 maintained at 30°C.

t (min)	0	10	20	50	100
$C_{H_2O_2}$ (mol/L)	0.02	0.01775	0.0158	0.0106	0.005

1. Determine the Michaelis–Menten parameters V_{\max} and K_M .
2. If the total enzyme concentration is tripled, what will the substrate concentration be after 20 minutes?
3. Apply to this problem one or more of the six ideas discussed in Table P-4 in the Complete Preface-Introduction on the Web site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>).
4. List ways you can work this problem incorrectly.

P9-10_B OEQ (Old Exam Question). It has been observed that substrate inhibition occurs in the following enzymatic reaction:



1. Show that the rate law for substrate inhibition is consistent with the plot in Figure P9-10_B of $-r_s$ (mmol/L·min) versus the substrate concentration S (mmol/L).
2. If this reaction is carried out in a CSTR that has a volume of 1000 dm³, to which the volumetric flow rate is 3.2 dm³/min, determine the three possible steady states, noting, if possible, which are stable. The entrance concentration of the substrate is 50 mmol/dm³. What is the highest conversion?
3. What would be the effluent substrate concentration if the total enzyme concentration is reduced by 33%?
4. List ways you can work this problem incorrectly.
5. How could you make this problem more difficult?

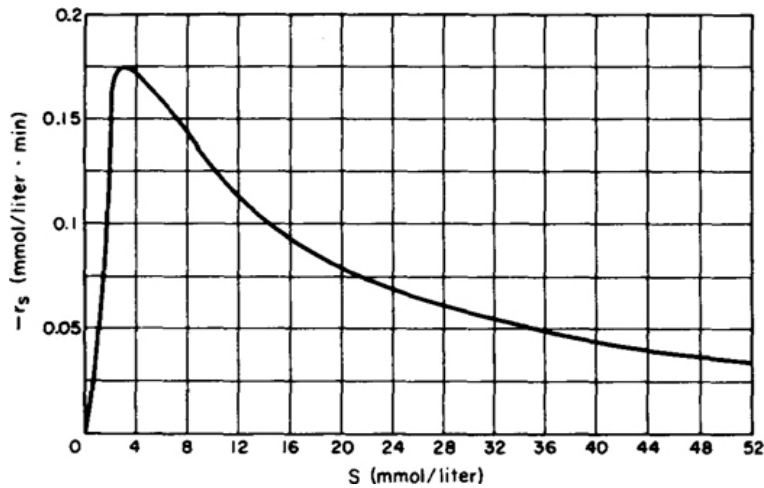


Figure P9-10B Michaelis–Menten plot for substrate inhibition.

P9-11B The following data on baker's yeast in a particular medium at 23.4°C were obtained in the presence and in the absence of an inhibitor, sulfanilamide. The reaction rate ($-r_S$) was measured in terms of the oxygen uptake rate Q_{O_2} , obtained as a function of oxygen partial pressure.

- Assume the rate follows Michaelis–Menten kinetics with respect to oxygen. Calculate the maximum (i.e., V_{\max}), and the Michaelis–Menten constant K_M .
(Ans: $V_{\max} = 52.63 \mu\text{L O}_2/\text{h} \cdot \text{mg cells.}$)
- Using the Lineweaver–Burk plot, determine the type of inhibition sulfanilamide that causes the O_2 uptake to change.

$P_{\text{O}_2}^*$	Q_{O_2} (no sulfanilamide)	Q_{O_2} (20 mg sulfanilamide/mL added to medium)
0.0	00.0	00.0
0.5	23.5	17.4
1.0	33.0	25.6
1.5	37.5	30.8
2.5	42.0	36.4
3.5	43.0	39.6
5.0	43.0	40.0

* P_{O_2} = oxygen partial pressure, mmHg; Q_{O_2} = oxygen uptake rate, μL of O_2 per hour per mg of cells.

- List ways you can work this problem incorrectly.
- Apply to this problem one or more of the six ideas discussed in Table P-4 in the Complete Preface-Introduction on the Web site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>).

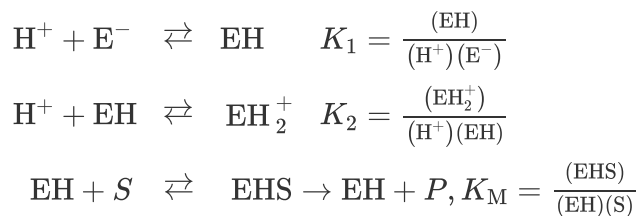
P9-12_B OEQ (Old Exam Question). The enzymatic hydrolysis of starch was carried out with and without maltose and α -dextrin added. (Adapted from S. Aiba, A. E. Humphrey, and N.F. Mills, *Biochemical Engineering*, New York: Academic Press, 1973.)

Starch \rightarrow α -dextrin \rightarrow Limit dextrin \rightarrow Maltose

<u>No Inhibition</u>				
C_S (g/dm^3)	12.5	9.0	4.25	1.0
$-r_S$ (relative)	100	92	70	29
<u>Maltose added ($I = 12.7 \text{ mg}/\text{dm}^3$)</u>				
C_S (g/dm^3)	10	5.25	2.0	1.67
$-r_S$ (relative)	77	62	38	34
<u>α-dextrin added ($I = 3.34 \text{ mg}/\text{dm}^3$)</u>				
C_S (g/dm^3)	33	10	3.6	1.6
$-r_S$ (relative)	116	85	55	32

Determine the types of inhibition for maltose and for α -dextrin.

P9-13_B The hydrogen ion, H^+ , binds with the enzyme (E^-) to activate it in the form EH . The hydrogen ion, H^+ , also binds with EH to deactivate it by forming EH_2^+



where E^- and EH_2^+ are inactive.

1. Determine whether the preceding sequence can explain the optimum in enzyme activity with pH shown in Figure P9-13B.
2. List ways you can work this problem incorrectly.
3. Apply to this problem one or more of the six ideas discussed in Table P-4 in the Complete Preface-Introduction on the Web site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>).

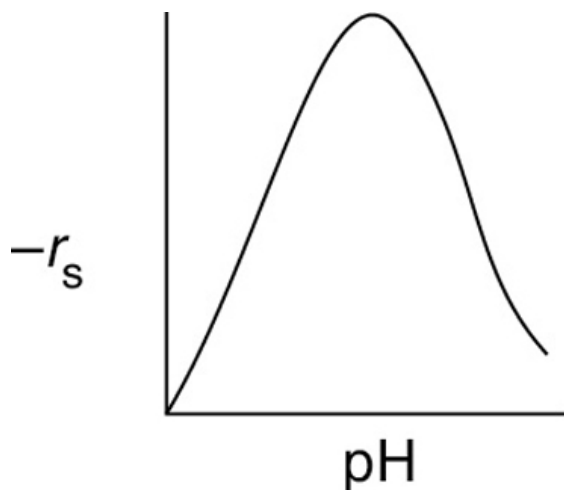


Figure P9-13B Enzyme pH dependence.

P9-14B OEQ (*Old Exam Question*). An Eadie–Hofstee Plot is shown in Figure P9-14B for different types of enzyme inhibition.

1. Match the line with the type of inhibition.
 1. Line A Inhibition Mechanism. Ans: _____
 2. Line B Inhibition Mechanism. Ans: _____
 3. Line C Inhibition Mechanism. Ans: _____

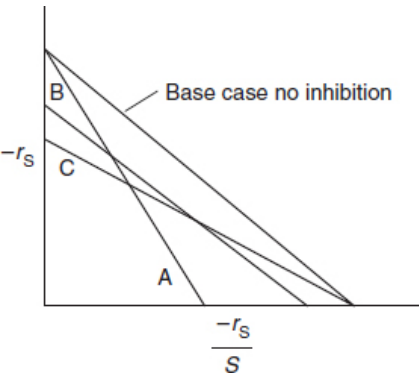


Figure P9-14B Eadie–Hofstee Plot.

2. Draw a Hanes–Woolf plot analogous to Figure P9-14B for the three types of inhibition and the case of no inhibition.

P9-15B An enzymatic reaction that follows, Michaels-Menten kinetics rate law with initial enzyme concentration C_{E0} is

$$-r_A = \frac{k_2 C_{E0}(S)}{1 + K_M(S)} \quad (\text{P9-15.1})$$

The rate constant, k_2 , was measured as a function of inhibitor concentration and shown in Table P9-15B

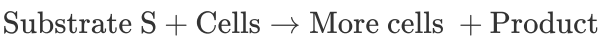
TABLE P9-15B SUBSTRATE CONCENTRATION AND K_2 INHIBITION DATA[†]

C_s (μ mol/dm ³)	0.1	0.	1.0	2	3	4.0	6.0	8.0
		04						
k_2 (min ⁻¹)	0.0	0.	0.0	0.	0.01	0.01	0.01	0.01
	15	04	62	09	05	15	23	28

[†] Nature Reviews, Lit. cit.

Determine the type of inhibition and write the full rate law.

P9-16B The biomass reaction



takes place in a 12-dm³ CSTR (chemostat) where the entering concentration of substrate is 200 g/dm³. The rate

law follows the Monod equation with $\mu_{\max} = 0.5 \text{ s}^{-1}$ and $K_S = 50 \text{ g/dm}^3$. What is the volumetric flow rate, v_0 (dm^3/h), that will give the maximum production rate of cells (g/h)?

P9-17_B The production of a product P from a particular gram-negative bacteria follows the Monod growth law

$$r_g = \frac{\mu_{\max} C_s C_c}{K_S + C_s}$$

with $\mu_{\max} = 1 \text{ h}^{-1}$, $K_S = 0.25 \text{ g/dm}^3$, and $Y_{c/s} = 0.5 \text{ g/g}$.

1. The reaction is to be carried out in a batch reactor with the initial cell concentration of $C_{c0} = 0.1 \text{ g/dm}^3$ and substrate concentration of $C_{s0} = 20 \text{ g/dm}^3$.

$$C_c = C_{c0} + Y_{c/s}(C_{s0} - C_s)$$

Plot r_g , $-r_s$, $-r_c$, C_s , and C_c as a function of time.

2. The reaction is now to be carried out in a CSTR with $C_{s0} = 20 \text{ g/dm}^3$ and $C_{c0} = 0$. What is the dilution rate at which washout occurs?
3. For the conditions in part (b), what is the dilution rate that will give the maximum product rate (g/h) if $Y_{p/c} = 0.15 \text{ g/g}$? What are the concentrations C_c , C_s , C_p , and $-r_s$ at this value of D ?
4. How would your answers to (b) and (c) change if cell death could not be neglected with $k_d = 0.02 \text{ h}^{-1}$?
5. How would your answers to (b) and (c) change if maintenance could not be neglected with $m = 0.2 \text{ g/h/dm}^3$?
6. Redo part (a) and use a **logistic growth law**

$$r_g = \mu_{\max} \left(1 - \frac{C_c}{C_{\infty}}\right) C_c$$

and plot C_c and r_c as a function of time. The term C_{∞} is the maximum cell mass concentration and is called the *carrying capacity*, and is equal to $C_{\infty} = 1.0 \text{ g/dm}^3$. Can you find an analytical solution for the batch reactor? Compare with part (a) for $C_{\infty} = Y_{c/s} C_{s0} + C_{c0}$.

7. List ways you can work this problem incorrectly.
8. Apply to this problem one or more of the six ideas discussed in Table P-4 in the Complete Preface-Introduction on the Web site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>).

P9-18_B Redo Problem P9-17_B (a), (c), and (d) using the Tessier equation

$$r_g = \mu_{\max} [1 - e^{-C_s/k}] C_c$$

with $\mu_{\max} = 1.0 \text{ h}^{-1}$ and $k = 8 \text{ g/dm}^3$.

1. List ways you can work this problem incorrectly.
2. How could you make this problem more difficult?

P9-19_B The bacteria X-II can be described by a simple Monod equation with $\mu_{\max} = 0.8 \text{ h}^{-1}$ and $K_S = 4 \text{ g/dm}^3$, $Y_{p/c} =$

0.2 g/g, and $Y_{s/c} = 2$ g/g. The process is carried out in a CSTR in which the feed rate is $1000 \text{ dm}^3/\text{h}$ at a substrate concentration of 10 g/dm^3 .

1. What size fermentor is needed to achieve 90% conversion of the substrate? What is the exiting cell concentration?
2. How would your answer to (a) change if all the cells were filtered out and returned to the feed stream?
3. Consider now two 5000-dm^3 CSTRs connected in series. What are the exiting concentrations C_s , C_c , and C_p from each of the reactors?
4. Determine, if possible, the volumetric flow rate at which washout occurs and also the flow rate at which the cell production rate ($C_c v_0$) in grams per day is a maximum.
5. Suppose you could use the two 5000-dm^3 reactors as batch reactors that take 2 hours to empty, clean, and fill. What would your production rate be in (grams per day) if your initial cell concentration is 0.5 g/dm^3 ? How many 500-dm^3 batch reactors would you need to match the CSTR production rate?
6. List ways you can work this problem incorrectly.
7. Apply to this problem one or more of the six ideas discussed in Table P-4 in the Complete Preface-Introduction on the Web site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>).

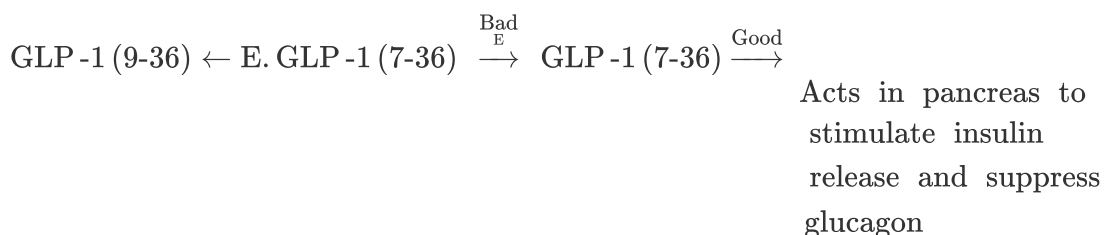
P9-20A A CSTR is being operated at steady state. The cell growth follows the Monod growth law without inhibition. The exiting substrate and cell concentrations are measured as a function of the volumetric flow rate (represented as the dilution rate), and the results are shown below. Of course, measurements are not taken until steady state is achieved after each change in the flow rate. Neglect substrate consumption for maintenance and the death rate, and assume that $Y_{p/c}$ is zero. For run 4, the entering substrate concentration was 50 g/dm^3 and the volumetric flow rate of the substrate was $2 \text{ dm}^3/\text{h}$.

Run	$C_s \text{ (g/dm}^3\text{)}$	$D \text{ (day}^{-1}\text{)}$	$C_c \text{ (g/dm}^3\text{)}$
1	1	1	0.9
2	3	1.5	0.7
3	4	1.6	0.6
4	10	1.8	4

1. Determine the Monod growth parameters μ_{\max} and K_S .
2. Estimate the stoichiometric coefficients, $Y_{c/s}$ and $Y_{s/c}$.
3. Apply to this problem one or more of the six ideas discussed in Table P-4 in the Complete Preface-Introduction on the Web site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>).
4. How could you make this problem more difficult?

P9-21_C Diabetes is a global epidemic affecting more than 240 million people worldwide. The vast majority of the cases are Type 2. Recently a drug, Januvia (J), was discovered to treat Type 2 diabetes. When food enters the stomach, a peptide, GLP-1 (glucagon-like peptide 1) is released, which leads to glucose-dependent insulin secretion and glucagon suppression. The half-life of GLP-1 is very short because it is rapidly degraded by an enzyme dipeptidyl peptidase-IV (DPP-IV), which cleaves the two terminal amino acids of the peptide thus deactivating it. DP-IV rapidly cleaves the active form of GLP-1 (GLP-1[7-36] amide) to its inactive form (GLP-1[9-36] amide) with a half-life of 1 minute, that is, $t_{1/2} = 1 \text{ min.}$, and it is thought to be the primary enzyme responsible for this hydrolysis.²⁶

²⁶ Also see (a) J. J. Holst and D. F. Deacon, *Diabetes*, 47, 1663 (1998); (b) B. Balkan, et al., *Diabetologia*, 42, 1324 (1999); (c) K. Augustyns, et al., *Curr. Med. Chem.*, 6, 311 (1999).



Inhibition of the DPP-IV Enzyme, (E), therefore, is expected to significantly reduce the extent of the inactivation of GLP-1[7-36] and should lead to an increase in circulating levels of the active form of the hormone. Supporting evidence for this comes from DPP-IV-enzyme-deficient mice, which have elevated levels of GLP-1[7-36]²⁷ amide. As a very rough approximation,

let's treat the reaction as follows: The new drug, an inhibitor of the DPP-IV enzyme (E), is Januvia (J), which prevents the enzyme from deactivating GLP-1.

²⁷ D. Marguet, et al., *Proc. Natl. Acad. Sci.*, 97, 6864 (2000).



Inhibited



By delaying the degradation of GLP-1, the inhibitor is able to extend the action of insulin and also suppress the release of glucagon.

1. Plot the ratio of reaction of $-r_{\text{GLP}}$ (without inhibition) to the rate $-r_{\text{GLP}}$ (with inhibition) as a function of DDP-4 inhibitor constant for both competitive inhibition and uncompetitive inhibition.
2. Assuming the body is a well-mixed reactor, develop a model similar to Problems **P8-5** and **P8-6** for the dosage schedule for Januvia.

P9-22_B Alternative Energy Source.²⁸ In the summer of 2009, ExxonMobil decided to invest 600 million dollars on developing algae as an alternative fuel and their TV commercials on this initiative were recently shown (e.g., December 2019). Algae would be grown and their oil extracted to provide an energy source. It is estimated that one acre of a biomass pond can provide 6000 gal of gasoline per year, which would require the capture of a CO₂ source more concentrated than air (e.g., fuel gas from a refinery) and also contribute to the sequestration of CO₂. The biomass biosynthesis during the day is

²⁸ The contributions of John Benemann to this problem are appreciated.



Consider a 5000-gal pond with perforated pipes into which CO₂ is injected and slowly bubbled into the solution to keep the water saturated with CO₂.

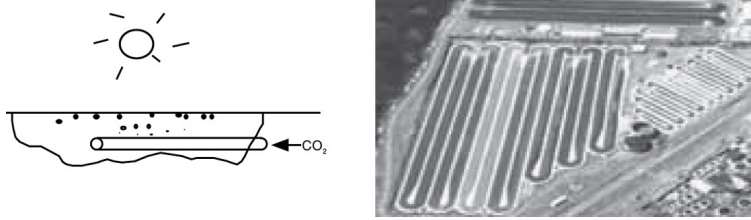


Figure P9-22B Commercial microalgae production in open raceway, paddle-wheel mixed ponds. Courtesy of Cyanotech Co., Hawaii.

The doubling time during the day is 12 h at high-noon sunlight and zero during the night. As a first approximation, the growth during the 12 hours of daylight law is

$$r_g = f\mu C_C$$

with $f = \text{sunlight} = \sin(\pi t/12)$ between 6 A.M. and 6 P.M., otherwise $f = 0$, C_C is the algae concentration (g/dm^3) and $\mu = 0.9 \text{ day}^{-1}$ (assumes constant CO_2 saturation at 1 atm is $1.69 \text{ g}/\text{kg}$ water). The pond is 30-cm deep and for effective sunlight penetration, the algae concentration cannot exceed $200 \text{ mg}/\text{dm}^3$.

1. Derive an equation for the ratio of the algae cell concentration C_C at time t to initial cell concentration C_{C0} , that is, (C_C/C_{C0}) . Plot and analyze (C_C/C_{C0}) versus time up to 48 hours.
2. If the pond is initially seeded with $0.5 \text{ mg}/\text{dm}^3$ of algae, how long will it take the algae to reach a cell density (i.e., concentration) of $200 \text{ mg}/\text{dm}^3$, which is the concentration at which sunlight can no longer effectively penetrate the depth of the pond? Plot and analyze r_g and C_C as a function of time. As a first approximation, assume the pond is well mixed.
3. Suppose the algae limit the sun's penetration significantly even before the concentration reaches $200 \text{ mg}/\text{dm}^3$ with, for example, $\mu = \mu_0 (1 - C_C/200)$. Plot and analyze r_g and C_C as a function of time. How long would it take to completely stop growth at $200 \text{ mg}/\text{dm}^3$?
4. Now, let's consider continuous operation. Once the cell density reaches $200 \text{ mg}/\text{dm}^3$, one-half of the pond is harvested and the remaining broth is mixed with fresh nutrient. What is the steady-state algae productivity in gm/year , again assuming the pond is well mixed?
5. Now consider a constant feed of waste water and removal of algae at a dilution rate of one reciprocal day. What is the mass flow rate of algae out of the 5000-gal pond (g/d)? Assume the pond is well mixed.
6. Now consider that the reaction is to be carried out in an enclosed, transparent reactor. The reactor can be pressurized with CO_2 up to 10 atm with $K_S = 2 \text{ g}/\text{dm}^3$. Assume that after the initial pressurization, no

more CO₂ can be injected. Plot and analyze the algae concentration as a function of time.

7. An invading algae can double twice as fast as the strain you are cultivating. Assume that it initially is at 0.1 mg/l concentration. How long until it is the dominant species (over 50% of the cell density)?

P9-23_A Short calculations on the algae ponds.

1. If the pond is initially seeded with 0.5 mg/dm³ of algae, how long will it take the algae to reach a cell density (i.e., concentration) of 200 mg/dm³? Sketch a rough plot of r_g and C_C over time.
2. Suppose the algae limit the sun's penetration significantly even before the concentration reaches 200 mg/dm³ by using $\mu = \mu_0 (1 - C_C/200)$. Assume $\mu_0 = 0.9 \text{ day}^{-1}$. Qualitatively, what happens to the growth rate as the concentration of cells increases? Approximately how long would it take for the concentration to reach 200 mg/dm³? Why?
3. An invading algae species can double twice as fast as the strain you are cultivating. Assume that it is initially at a concentration of 0.01 mg/dm³. How long until it becomes the dominant species in the pond (over 50% of the cell density)?

• Additional Homework Problems

A number of homework problems that can be used for exams or supplementary problems or examples are found on the CRE Web site,

www.umich.edu/~elements/6e/index.html.

SUPPLEMENTARY READING

Web

Review the following Web site:

www.pharmacokinetics.com



Text

1. A discussion of complex reactions involving active intermediates is given in

A. K. DATTA, *Heat and Mass Transfer: A Biological Context*, 2nd ed. Boca Raton, FL: CRC Press, 2017.

A. A. FROST and R. G. PEARSON, *Kinetics and Mechanism*, 2nd ed. New York: Wiley, 1961, Chap. 10. Old but great examples.

K. J. LAIDLER, *Chemical Kinetics*, 3rd ed. New York: HarperCollins, 1987.

M. J. PILLING, *Reaction Kinetics*, New York: Oxford University Press, 1995.

2. Further discussion of enzymatic reactions:

Just about everything you want to know about basic enzyme kinetics can be found in I. H. SEGEL, *Enzyme Kinetics*, New York: Wiley-Interscience, 1975.

An excellent description of parameter estimation, biological feedback, and reaction pathways can be found in E. O. VOIT, *Computational Analysis of Biochemical Systems*, Cambridge, UK: Cambridge University Press, 2000.

A. CORNISH-BOWDEN, *Analysis of Enzyme Kinetic Data*, New York: Oxford University Press, 1995.

D. L. NELSON and M. M. COX, *Lehninger Principles of Biochemistry*, 3rd ed. New York: Worth Publishers, 2000.

M. L. SHULER and F. KARGI, *Bioprocess Engineering Principles*, 2nd ed. Upper Saddle River, NJ: Prentice Hall, 2002.

3. Material on bioreactors can be found in

T. J. BAILEY and D. OLLIS, *Biochemical Engineering*, 2nd ed. New York: McGraw-Hill, 1987.

H. W. BLANCH and D. S. CLARK, *Biochemical Engineering*, New York: Marcel Dekker, 1996.

4. Also see

THORNTON W. BURGESS, *The Adventures of Old Mr. Toad*, New York: Dover Publications, Inc., 1916.

GARRISON KEILLOR, *Pretty Good Joke Book: A Prairie Home Companion*, St. Paul, MN: HighBridge Co., 2000.

HOWARD MASKILL, *The Investigation of Organic Reactions and Their Mechanisms*, Oxford, UK: Blackwell Publishing Ltd, 2006.

10. Catalysis and Catalytic Reactors

It isn't that they can't see the solution. It is that they can't see the problem.

—G. K. Chesterton

Overview. The objectives of this chapter are to develop an understanding of catalysts, reaction mechanisms, and catalytic reactor design. Specifically, after reading this chapter one should be able to

- Define a catalyst and describe its properties.
- Describe the steps in a catalytic reaction and in chemical vapor deposition (CVD).
- Suggest a mechanism and apply the concept of a rate-limiting step to derive a rate law.
- Use nonlinear regression to determine the rate law and rate-law parameters that best fit the data.
- Use the rate-law parameters to design PBRs and fluidized CSTRs.
- Describe the analogy between catalytic steps and CVD in microelectronic fabrication.
- Analyze catalyst decay and reactors that can be used to help offset decay.

The various sections of this chapter roughly correspond to these objectives.

10.1 CATALYSTS

Catalysts have been used by humankind for over 2000 years.¹ The first observed uses of catalysts were in the making of wine, cheese, and bread. For example, it was found that it was always necessary to add small amounts of bread from the previous batch to make the current batch. However, it wasn't until 1835 that Berzelius began to tie together observations of earlier chemists by suggesting that small amounts of a foreign substance could greatly affect the course of chemical reactions. This mysterious force attributed to the substance was called *catalytic* (from the ancient Greek *katálusis*, “to dissolve away the inertness”). In 1894, Ostwald expanded

Berzelius's explanation by stating that catalysts were substances that accelerate the rate of chemical reactions without being consumed during the reaction. During the 180 years since Berzelius's work, catalysts have come to play a major economic role in the world market. In the United States alone, sales of process catalysts will reach over \$20 billion by 2020, the major uses being in petroleum refining and in chemical production.

¹ S. T. Oyama and G. A. Somorjai, *J. Chem. Educ.*, 65, 765.

10.1.1 Definitions

What is catalysis?

A *catalyst* is a substance that affects the rate of a reaction but emerges from the process unchanged. A catalyst usually changes a reaction rate by promoting a different molecular path ("mechanism") for the reaction. For example, gaseous hydrogen and oxygen are virtually inert at room temperature, but react rapidly when exposed to platinum. The reaction coordinate (cf. Figure 3-2) shown in Figure 10-1 is a measure of the progress along the reaction path as H₂ and O₂ approach each other and pass over the energy barrier to form H₂O. *Catalysis is the occurrence, study, and use of catalysts and catalytic processes.* Commercial chemical catalysts are immensely important. Approximately one-third of the material gross national product of the United States involves a catalytic process somewhere between raw material and finished product.² The development and use of catalysts is a major part of the constant search for new ways of increasing product yield and selectivity in chemical reactions. Because a catalyst makes it possible to obtain an end product by a different pathway with a lower energy barrier, it can affect both the yield and the selectivity.

² V. Haensel and R. L. Burwell, Jr., *Sci. Am.*, 225(10), 46.

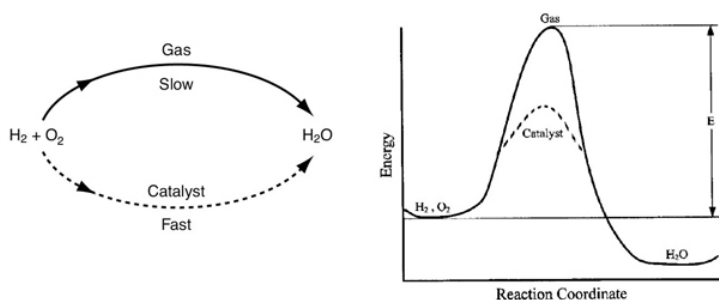
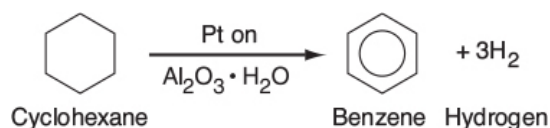


Figure 10-1 Different reaction paths.

Catalysts can accelerate the reaction rate but cannot change the equilibrium.

Normally when we talk about a catalyst, we mean one that speeds up a reaction, although strictly speaking, a catalyst can either accelerate or slow the formation of a particular product species. *A catalyst changes only the rate of a reaction; it does not affect the equilibrium.*

The 2007 Nobel Prize for Chemistry was awarded to Gerhard Ertl for his pioneering work on heterogeneous catalytic reactions. A *heterogeneous catalytic reaction* involves more than one phase; usually the catalyst is a solid and the reactants and products are in liquid or gaseous form. One example is the production of benzene, which is mostly manufactured today from the dehydrogenation of cyclohexane (obtained from the distillation of petroleum crude oil) using platinum-on-alumina as the catalyst:



The simple and complete separation of the fluid product mixture from the solid catalyst makes heterogeneous catalysis economically attractive, especially because many catalysts are quite valuable and their reuse is demanded.

A heterogeneous catalytic reaction occurs at or very near the fluid–solid interface. The principles that govern heterogeneous catalytic reactions can be applied to both catalytic and noncatalytic fluid–solid reactions. The two other types of heterogeneous reactions involve gas–liquid and gas–liquid–

solid systems. Reactions between a gas and a liquid are usually mass transfer–limited as will be discussed in Chapter 14.

10.1.2 Catalyst Properties

Ten grams of this catalyst possess more surface area than a U.S. football field.

Because a catalytic reaction occurs at the fluid–solid interface, a large interfacial area is almost always essential in attaining a significant reaction rate. In many catalysts, this area is provided by an inner porous structure (i.e., the solid contains many fine pores, and the surface of these pores supplies the area needed for the high rate of reaction), see Figures 10-4(b) and 10-9. The area possessed by some porous catalysis materials is surprisingly large. A typical silica-alumina cracking catalyst has a pore volume of $0.6 \text{ cm}^3/\text{g}$ and an average pore radius of 4 nm. The corresponding surface area can be the order of $300 \text{ m}^2/\text{g}$ of these *porous catalysts*. Examples include the Raney nickel used in the hydrogenation of vegetable and animal oils, platinum-on-alumina used in the reforming of petroleum naphthas to obtain higher octane ratings, and promoted iron used in ammonia synthesis. Sometimes pores are so small that they will admit only small molecules and prevent large ones from entering and being catalyzed. Materials with this type of pore are called *molecular sieves*, and they may be derived from natural substances such as certain clays and zeolites, or they may be totally synthetic, such as some crystalline aluminosilicates (see Figure 10-2). These sieves can form the basis for quite selective catalysts; the pores can control the residence time of various molecules near the catalytically active surface to a degree that essentially allows *only* the desired molecules to react. One example of the high selectivity of zeolite catalysts is the formation of para-xylene from toluene and methane shown in Figure 10-2(b).³ Here, methane and toluene enter through the zeolite pore and react on the interior surface to form a mixture of ortho-, meta-, and para-xylenes. However, the size of the pore mouth is such that only para-xylene can exit through the pore mouth, as meta- and ortho-xylene with their methyl group on the side cannot fit through the pore mouth. There are interior sites that

can isomerize ortho-xylene and meta-xylene to para-xylene. Hence, we have a very high selectivity to form para-xylene.

³ R. I. Masel, *Chemical Kinetics and Catalysis*, New York: Wiley Interscience, 2001, p. 741.

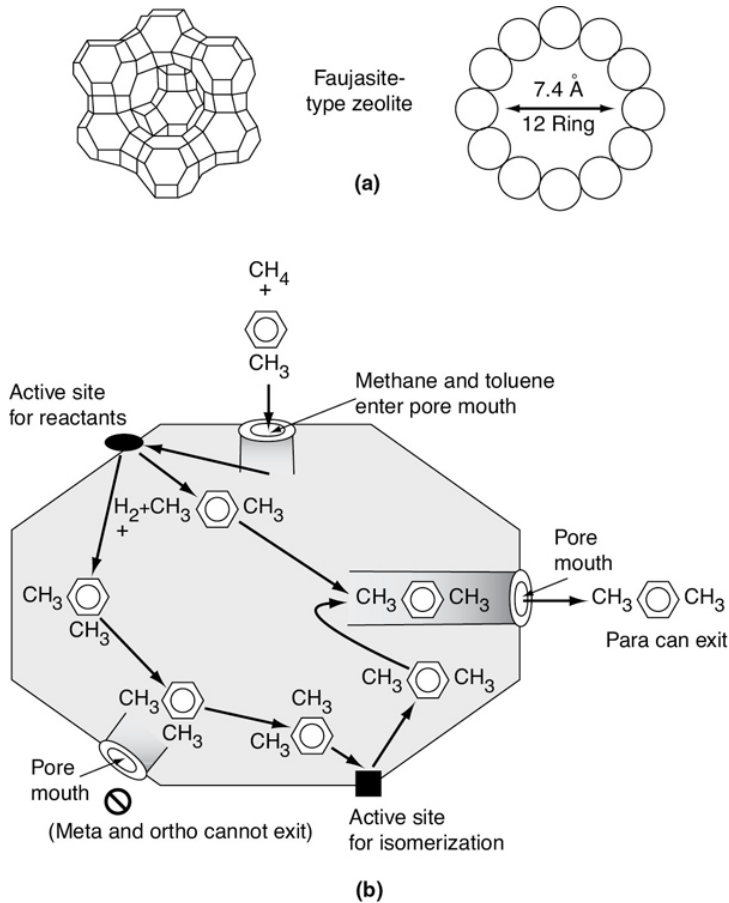


Figure 10-2 (a) Framework structures and (b) pore cross sections of two types of zeolites. (a) Faujasite-type zeolite has a three-dimensional channel system with pores at least 7.4 Å in diameter. A pore is formed by 12 oxygen atoms in a ring. (b) Schematic of reaction CH_4 and $\text{C}_6\text{H}_5\text{CH}_3$. (Note that the size of the pore mouth and the interior of the zeolite are not to scale.) ((a) From N. Y. Chen and T. F. Degnan, *Chem. Eng. Prog.*, 84(2), 33 (1988). Reproduced by permission of the American Institute of Chemical Engineers. Copyright © 1988 AIChE. All rights reserved.)

Catalyst types:

- Porous
- Molecular sieves
- Monolithic
- Supported
- Unsupported

Typical zeolite catalyst

High selectivity to para-xylene

A very thorough and well-written book.

In some cases, a catalyst consists of minute particles of an active material dispersed over a less-active substance called a *support*. The active material is frequently a pure metal or metal alloy. Such catalysts are called *supported catalysts*, as distinguished from *unsupported catalysts*. Catalysts can also have small amounts of active ingredients added called *promoters*, which increase their activity. Examples of supported catalysts are the packed-bed catalytic converter in an automobile, the platinum-on-alumina catalyst used in petroleum reforming, and the vanadium pentoxide on silica used to oxidize sulfur dioxide in manufacturing sulfuric acid. Typical unsupported catalysts include platinum gauze for ammonia oxidation, promoted iron for ammonia synthesis, and the silica-alumina dehydrogenation catalyst used in butadiene manufacture.

10.1.3 Catalytic Gas–Solid Interactions

In this section, we focus our attention on gas-phase reactions catalyzed by solid surfaces. For a catalytic reaction to occur, at least one and frequently all of the reactants must become attached to the surface. This attachment is known as *adsorption* and takes place by two different processes: physical adsorption and chemisorption. *Physical adsorption* is similar to condensation. The process is exothermic, and the heat of adsorption is relatively small, being on the order of 1–15 kcal/mol. Here, the forces of attraction between the gas molecules and the solid surface are weak. These van der Waals

forces consist of interaction between permanent dipoles, between a permanent dipole and an induced dipole, and/or between neutral atoms and molecules. The amount of gas physically adsorbed decreases rapidly with increasing temperature, and above its critical temperature only very small amounts of a substance are physically adsorbed.

The type of adsorption that affects the rate of a chemical reaction is *chemisorption*. Here, the adsorbed atoms or molecules are held to the surface by valence forces of the same type as those that occur between bonded atoms in molecules. As a result, the electronic structure of the chemisorbed molecule is perturbed significantly, causing it to be extremely reactive. Interaction with the catalyst causes bonds of the adsorbed reactant to be stretched, making them easier to break.

Figure 10-3 shows the bonding from the adsorption of ethylene on a platinum surface to form chemisorbed ethylidyne. Like physical adsorption, chemisorption is an exothermic process, but the heats of adsorption are generally of the same magnitude as the heat of a chemical reaction (i.e., 40–400 kJ/mol). If a catalytic reaction involves chemisorption, it must be carried out within the temperature range where chemisorption of the reactants is appreciable.

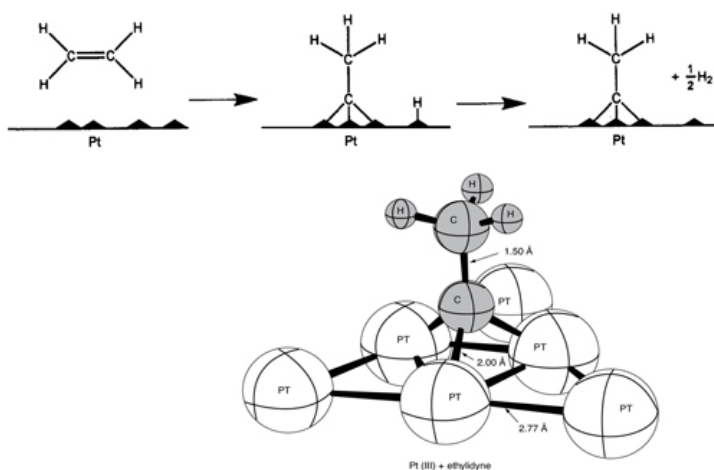


Figure 10-3 Ethylidyne chemisorbed on platinum.
(Adapted from G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis*. © 1994 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.)

Chemisorption on active sites is what catalyzes the reaction.

In a landmark contribution to catalytic theory, H. S. Taylor suggested that a reaction is not catalyzed over the entire solid surface but only at certain *active sites* or *centers*.⁴ He visualized these sites as unsaturated atoms in the solids that resulted from surface irregularities, dislocations, edges of crystals, and cracks along grain boundaries. Other investigators have taken exception to this definition, pointing out that other properties of the solid surface are also important. The active sites can also be thought of as places where highly reactive intermediates (i.e., chemisorbed species) are stabilized long enough to react. This stabilization of a reactive intermediate is key in the design of any catalyst. Consequently, for our purposes we will define an *active site* as *a point on the catalyst surface that can form strong chemical bonds with an adsorbed atom or molecule*.

⁴ H. S. Taylor, *Proc. R. Soc. London, A108*, 105 (1928).

TOF

One parameter used to quantify the activity of a catalyst is the *turnover frequency (TOF)*, f . It is the number of molecules reacting per active site per second at the conditions of the experiment. When a metal catalyst such as platinum is deposited on a support, the metal atoms are considered active sites. The *dispersion*, D , of the catalyst is the fraction of the metal atoms deposited on a catalyst that are *on* the surface. The TOFs for a number of reactions are shown in the *Additional Material for Chapter 10* on the Web site (http://www.umich.edu/~elements/6e/10chap/expanded_ch10_TOF.pdf).

10.1.4 Classification of Catalysts

One common way to classify catalysts is in terms of the type of reaction they catalyze.

Table 10-1 gives a list of representative reactions and their corresponding catalysts. Further discussion of each of these reaction classes and the materials that catalyze them can be

found on the CRE Web site's *Professional Reference Shelf*
R10.1 (<http://www.umich.edu/~elements/6e/10chap/prof.html>).

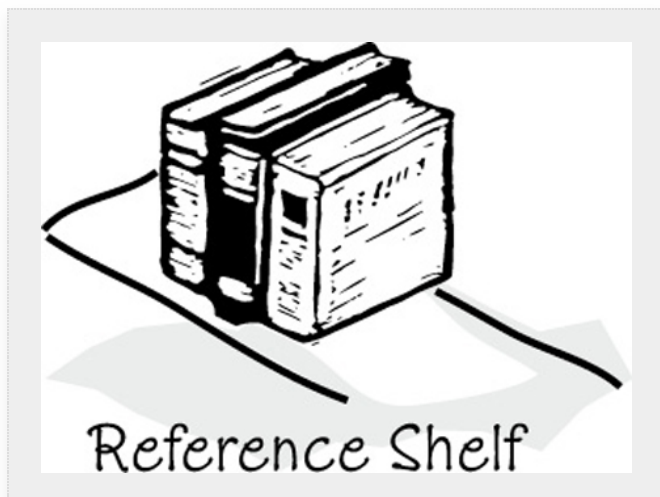
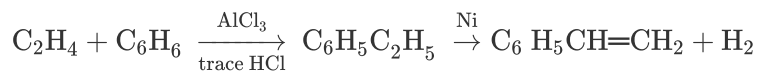


TABLE 10-1 TYPES OF REACTIONS AND REPRESENTATIVE
 CATALYSTS

<i>Reaction Catalysts</i>	
1. Halogenation–dehalogenation	CuCl ₂ , AgCl, Pd
2. Hydration–dehydration	Al ₂ O ₃ , MgO
3. Alkylation–dealkylation	AlCl ₃ , Pd, Zeolites
4. Hydrogenation–dehydrogenation	Co, Pt, Cr ₂ O ₃ , Ni
5. Oxidation	Cu, Ag, Ni, V ₂ O ₅
6. Isomerization	AlCl ₃ , Pt/Al ₂ O ₃ , Zeolites

If, for example, we were to form styrene from an equimolar mixture of ethylene and benzene, we could first carry out an

alkylation reaction to form ethyl benzene, which is then dehydrogenated to form styrene. We need both an alkylation catalyst and a dehydrogenation catalyst:



10.2 STEPS IN A CATALYTIC REACTION

A photograph of different types and sizes of catalysts is shown in [Figure 10-4\(a\)](#). A schematic diagram of a tubular reactor packed with catalytic pellets is shown in [Figure 10-4\(b\)](#). The overall process by which heterogeneous catalytic reactions proceed can be broken down into the sequence of individual steps shown in [Table 10-2](#) and pictured in [Figure 10-5](#) for an isomerization reaction.



Figure 10-4(a) Catalyst particles of different shapes (spheres, cylinders) and sizes (0.1–1 cm). (Photo courtesy of BASF Corporation.)

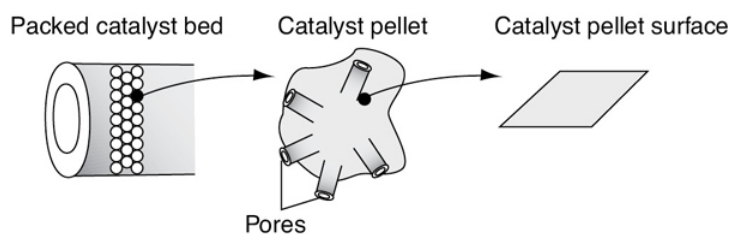


Figure 10-4(b) Catalytic packed-bed reactor—schematic.

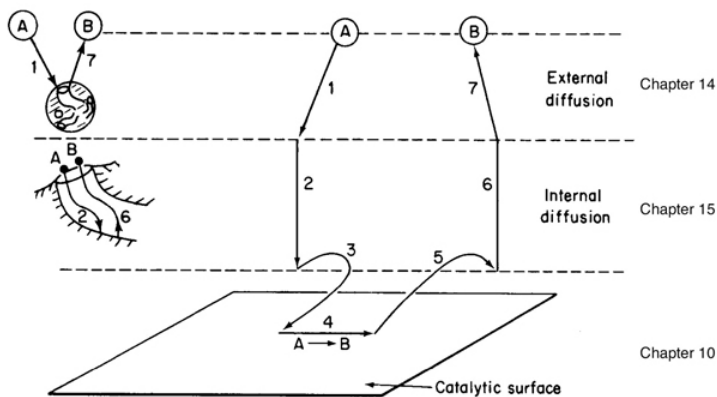


Figure 10-5 Steps in a heterogeneous catalytic reaction.

Each step in Table 10-2 is shown schematically in Figure 10-5.

A reaction takes place on the surface, but the species involved in the reaction must get to and from the surface.

The overall rate of reaction is limited by the rate of the slowest step in the sequence. When the diffusion steps (1, 2, 6, and 7 in Table 10-2) are very fast compared with the surface reaction-rate steps (3, 4, and 5), the concentrations in the immediate vicinity of the active sites are indistinguishable from those in the bulk fluid. In this situation, the transport or diffusion steps do not affect the overall rate of the reaction. In other situations, if the reaction steps are very fast compared with the diffusion steps, mass transport does affect the reaction rate. In systems where diffusion from the bulk gas or liquid to the external catalyst surface or to the mouths of catalyst pores affects the rate, that is, Steps 1 and 7, changing the flow conditions past the catalyst should change the overall reaction rate (see Chapter 14). Once inside the porous catalysts, on the other hand, diffusion within the catalyst pores, that is, Steps 2 and 6, may limit the rate of reaction and, as a result, the overall rate will be unaffected by external flow conditions even though diffusion affects the overall reaction rate (see Chapter 15).

TABLE 10-2 STEPS IN A CATALYTIC REACTION

--

1. Mass transfer (diffusion) of the reactant(s) (e.g., species A) from the bulk fluid to the external surface of the catalyst pellet, that is, the pore mouth.
2. Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface
3. Adsorption of reactant A onto the catalyst surface
4. Reaction on the surface of the catalyst (e.g., $A \rightarrow B$)
5. Desorption of the products (e.g., B) from the surface
6. Diffusion of the products from the interior of the pellet to the pore mouth at the external surface
7. Mass transfer of the products from the external pellet surface to the bulk fluid

There are many variations of the situation described in [Table 10-2](#). Sometimes, of course, two reactants are necessary for a reaction to occur, and both of these may undergo the steps listed above. Other reactions between two substances may have only one of them adsorbed.

In this chapter we focus on:

3. Adsorption
4. Surface reaction
5. Desorption

With this introduction, we are ready to treat individually the steps involved in catalytic reactions. In this chapter, only Steps 3, 4, and 5—that is, adsorption, surface reaction, and desorption—are considered as we assume that the diffusion steps (1, 2, 6, and 7) are very fast so that the overall reaction

rate is not affected by mass transfer in any fashion. Further treatment of the effects involving diffusion limitations is provided in [Figure 14-5](#) in [Chapter 14](#) and [Figure 15-5](#) in [Chapter 15](#).

Where Are We Heading?[†] As we saw in [Chapter 7](#), one of the tasks of a chemical reaction engineer is to analyze rate data and to develop a rate law that can be used in reactor design. Rate laws in heterogeneous catalysis seldom follow power-law models (Eq. 3-3) and hence are inherently more difficult to formulate from the data. To develop an in-depth understanding and insight as to how the rate laws are formed from heterogeneous catalytic data, we are going to proceed in somewhat of a reverse manner than what is normally done in industry when one is asked to develop a rate law. That is, we will first postulate catalytic mechanisms and *then* derive rate laws for the various mechanisms. The mechanism will typically have an adsorption step, a surface reaction step, and a desorption step, one of which is usually rate-limiting. Suggesting mechanisms and rate-limiting steps is not the first thing we normally do when presented with data. However, by deriving equations for different mechanisms, we will observe the various forms of the rate law one can have in heterogeneous catalysis. *Knowing* the different forms that catalytic rate equations can take, it will be easier to view the trends in the data and deduce the appropriate rate law. This deduction is usually what is done first in industry before a mechanism is proposed. Knowing the form of the rate law, one can then numerically evaluate the rate-law parameters and postulate a reaction mechanism and rate-limiting step that are consistent with the experimental data. Finally, we use the rate law to design catalytic reactors. This procedure is shown in [Figure 10-6](#). The dashed lines represent feedback to obtain new data in specific regions (e.g., concentrations, temperature) to evaluate the rate-law parameters more precisely or to differentiate between reaction mechanisms.

[†] “If you don’t know where you are going, you’ll probably wind up someplace else.” Yogi Berra, New York Yankees.

An algorithm

Knowing the various forms a catalytic rate law can take will help us interpret the data.

An overview

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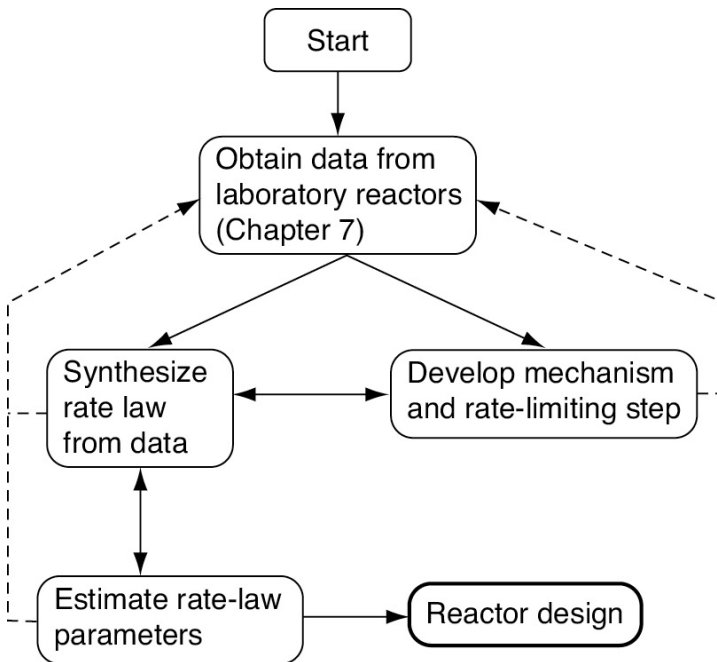


Figure 10-6 Collecting information for catalytic reactor design.

We will now discuss each of the steps shown in [Figure 10-5](#) and [Table 10-2](#). As mentioned earlier, this chapter focuses on Steps 3, 4, and 5 (the adsorption, surface reaction, and

desorption steps) by assuming that Steps 1, 2, 6, and 7 are very rapid. Consequently, to understand when this assumption is valid, we shall give a quick overview of Steps 1, 2, 6, and 7. These steps involve diffusion of the reactants to and within the catalyst pellet. While these diffusion steps are covered in detail in [Figure 14-5 in Chapter 14](#) and [Figure 15-5 in Chapter 15](#), it's worthwhile to give a brief description of these two mass-transfer steps to better understand the entire sequence of steps. If you have had the core course in *Mass Transfer* or *Transport Phenomena* you can skip [Sections 10.2.1 and 10.2.2](#), and go directly to [Section 10.2.3](#).

10.2.1 Mass Transfer Step 1: Diffusion from the Bulk to the External Surface of the Catalyst—An Overview

For the moment, let's assume that the transport of A from the bulk fluid to the external surface of the catalyst is the slowest step in the sequence shown in [Figure 10-5](#). We lump all the resistance to transfer of reactant species A from the bulk fluid to the surface, in the *mass transfer boundary layer* surrounding the pellet. In this step the reactant A, which is at a bulk concentration C_{Ab} must travel (diffuse) through the boundary layer of thickness δ to the external surface of the pellet where the concentration is C_{As} , as shown in [Figure 10-7](#). The rate of transfer (and hence rate of reaction, $-r'_A$) for this slowest step is

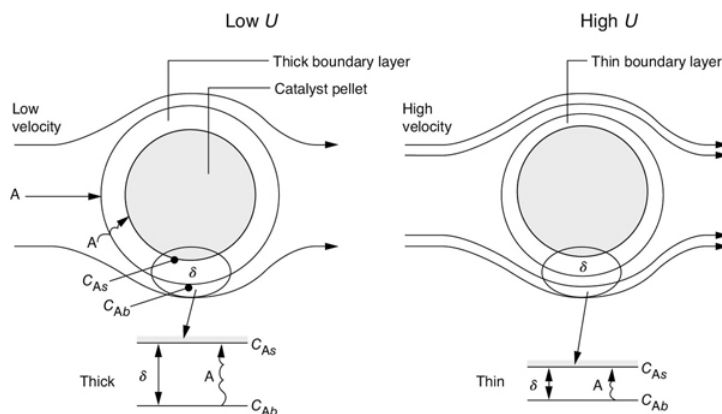


Figure 10-7 Diffusion through the external boundary layer (also see [Figures 14-2 and 14-3](#)).

$$\text{Rate} = k_C (C_{Ab} - C_{As})$$

where the mass transfer coefficient, k_C , is a function of the hydrodynamic conditions, namely the fluid velocity, U , and the particle diameter, D_p .

External and internal mass transfer in catalysis are covered in detail in [Chapters 14 and 15](#).

As we will see ([Chapter 14](#)), the mass transfer coefficient is inversely proportional to the boundary layer thickness, δ , and directly proportional to the diffusion coefficient (i.e., the diffusivity D_{AB}).

$$k_C = \frac{D_{AB}}{\delta}$$

At low velocities of fluid flow over the pellet, the boundary layer across which A and B must diffuse is thick, and it takes a long time for A to travel to the surface, resulting in a small mass transfer coefficient k_C . As a result, mass transfer across the boundary layer is slow and limits the rate of the overall reaction. As the velocity over the pellet is increased, the boundary layer becomes thinner and the mass transfer rate is increased. At very high velocities, the boundary layer thickness, δ , is so small that it no longer offers any significant resistance to the diffusion across the boundary layer. As a result, external mass transfer no longer limits the rate of reaction. This external resistance also decreases as the particle size is decreased. As the fluid velocity increases and/or the particle diameter decreases, the mass transfer coefficient increases until a plateau is reached, as shown in [Figure 10-8](#). On this plateau, $C_{Ab} \approx C_{As}$, and one of the other steps in the sequence, that is, Steps 2–6, is the slowest step and limits the overall reaction rate. Further details on external mass transfer are discussed in [Chapter 14](#).

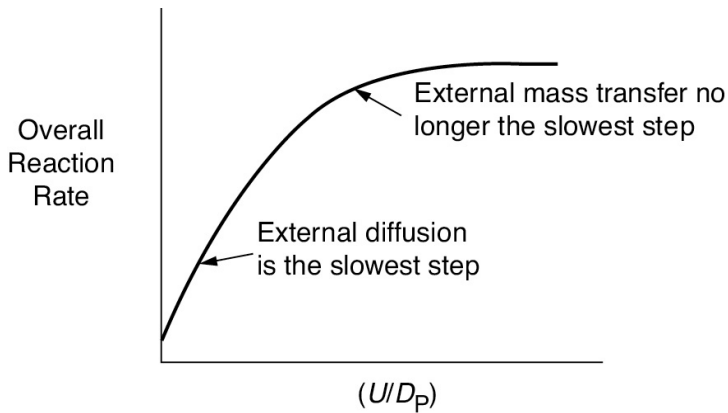


Figure 10-8 Effect of particle size and fluid velocity on the overall reaction rate.

High external fluid velocities decrease the resistance to external mass transfer.

10.2.2 Mass Transfer Step 2: Internal Diffusion—An Overview

Now consider that we are operating at a fluid velocity where external diffusion is no longer the rate-limiting step and that internal diffusion is the slowest step. In Step 2 of Figure 10-5, the reactant A diffuses from the external pellet surface at a concentration is C_A . As A diffuses into the interior of the pellet, it reacts with catalyst deposited on the sides of the catalyst pellet's inner pore walls.

The smaller the size of the catalyst pellet, the smaller the resistance to internal mass transfer (i.e., diffusion).

For large pellets, it takes a long time for the reactant A to diffuse into the interior, compared to the time that it takes for the reaction to occur on the interior pore surface. Under these circumstances, the reactant is only consumed near the exterior surface of the pellet and the catalyst near the center of the pellet is wasted catalyst. On the other hand, for very small pellets it takes very little time to diffuse into and out of the pellet interior and, as a result, internal diffusion no longer limits the rate of reaction. When internal mass transfer *does* not limit the rate of reaction, the concentration inside the pores of the catalyst pellet is equal to the concentration at the external pellet surface, C_{As} . As a result the corresponding rate law is

$$\text{Rate} = k_r C_{As}$$

where C_{As} is the concentration at the external pellet surface and k_r is an overall rate constant, which is a function of particle size. The overall rate constant, k_r , increases as the pellet diameter decreases. In Chapter 15, we show that Figure 15-5 can be combined with Equation (15-34) to arrive at the plot of k_r as a function of D_p , shown in Figure 10-9(b).

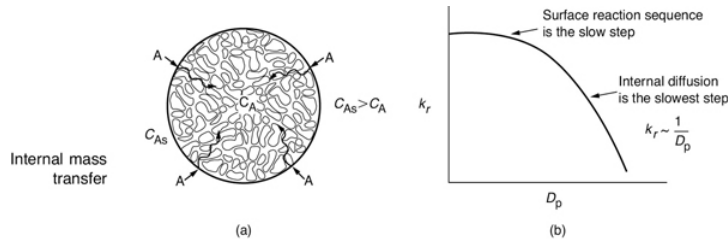


Figure 10-9 Effect of particle size on the overall reaction-rate constant. (a) Branching of a single pore with deposited metal; (b) decrease in rate constant with increasing particle diameter (see Chapter 15).

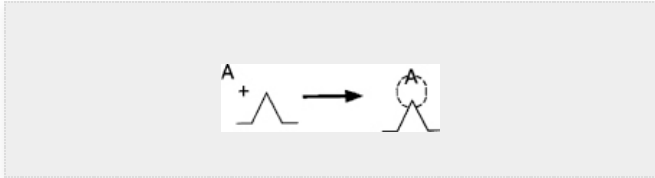
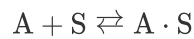
We see in Figure 10-9 that for small particle sizes, internal diffusion is *no longer* the slow step and that the surface reaction sequence of adsorption, surface reaction, and desorption (Steps 3, 4, and 5 in Figure 10-5) limit the overall rate of reaction. Consider now one more important point about internal diffusion and surface reaction. Steps (2–6) are **not at all** affected by flow conditions external to the pellet.

In the material that follows, we are going to choose our pellet size and external fluid velocity such that neither external diffusion (Chapter 14), nor internal diffusion (Chapter 15), limits the reaction. Instead, we assume that either Step 3 (adsorption), Step 4 (surface reaction), or Step 5 (desorption), or a combination of these steps, limits the overall rate of reaction.

10.2.3 Adsorption Isotherms

Because chemisorption is a necessary part of a catalytic process, we shall discuss it before treating catalytic reaction rates. The letter S will represent an active site; alone, it will denote a vacant site, with no atom, molecule, or complex

adsorbed on it. The combination of S with another letter (e.g., A·S) will mean that one unit of species A has been chemically adsorbed on the site S. Species A can be an atom, molecule, or some other atomic combination, depending on the circumstances. Consequently, the adsorption of A on a site S is represented by



The total molar concentration of active sites per unit mass of catalyst is equal to the number of active sites per unit mass divided by Avogadro's number and will be labeled C_t (mol/g-cat). The molar concentration of vacant sites, C_o (mol/g-cat), is the number of vacant sites per unit mass of catalyst divided by Avogadro's number. In the absence of catalyst deactivation, we assume that the total concentration of active sites, C_t , remains constant. Some further definitions include

P_i = partial pressure of species i in the gas phase (atm, bar, or kPa)

$C_{i:S}$ = surface concentration of sites occupied by species i (mol/g-cat)

A conceptual model depicting species A and B adsorbed on two different sites is shown in Figure 10-10.

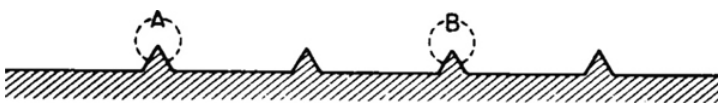


Figure 10-10 Vacant and occupied sites.

For the system shown in Figure 10-10, the total concentration of sites is

Site balance

$$C_t = C_v + C_{A \cdot S} + C_{B \cdot S} \quad (10-1)$$

This equation is referred to as a *site balance*. A typical value for the total concentration of sites could be the order of 10^{22} sites/g-cat. To express the site concentration in terms of (moles/g-cat) we divide by Avogadro's number to get "moles of sites/g-cat."

Now consider the adsorption of a nonreacting gas onto the surface of a catalyst. Adsorption data are frequently reported in the form of adsorption *isotherms*. Isotherms portray the amount of a gas adsorbed on a solid at different pressures at a given temperature.

Postulate models; then see which one(s) fit(s) the data.

First, an adsorption mechanism is proposed, and then the isotherm (see [Figure 10-11](#), page 455) obtained from the mechanism is compared with the experimental data. If the isotherm predicted by the model agrees with the experimental data, the model may reasonably describe what is occurring physically in the real system. If the predicted curve does not agree with the experimental data, the model fails to match the physical situation in at least one important characteristic and perhaps more.

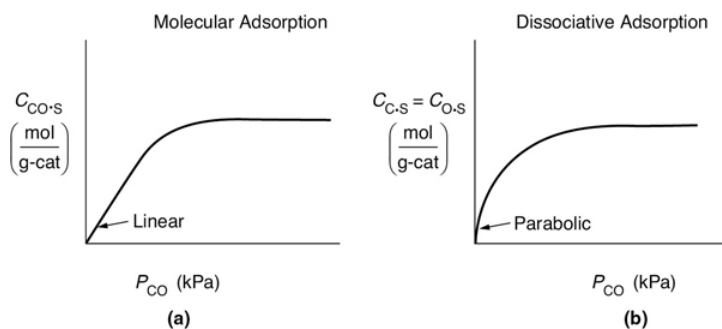
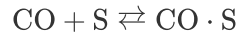


Figure 10-11 Langmuir isotherms for (a) molecular adsorption (b) dissociative adsorption of CO.

We will consider two types of adsorption: *molecular adsorption* and *dissociative adsorption*. To illustrate the difference between molecular adsorption and dissociative adsorption, we will postulate two models for the adsorption of

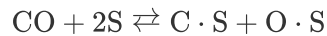
carbon monoxide on a metal surface active site. In the molecular adsorption model, carbon monoxide is adsorbed as molecules, CO,



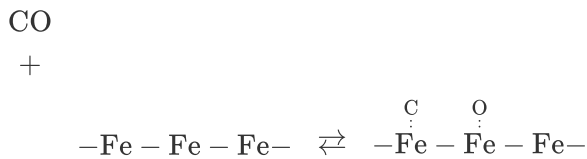
as is the case on nickel



In the dissociative adsorption model, carbon monoxide is adsorbed as oxygen and carbon atoms instead of molecular CO



as is the case on iron⁵



⁵ R. I. Masel, *Principles of Adsorption and Reaction on Solid Surfaces*, New York: Wiley, 1996.

Two models:

1. Adsorption as CO
2. Adsorption as C and O

The former is called *molecular* or *nondissociated adsorption* (e.g., CO) and the latter is called *dissociative adsorption* (e.g., C and O). Whether a molecule adsorbs nondissociatively or dissociatively depends on the surface.

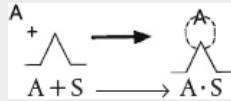
Molecular Adsorption: The adsorption of carbon monoxide molecules will be considered first. Because the carbon monoxide does not react further after being adsorbed, we need only to consider the molecular adsorption process:



Molecular adsorption

In obtaining a rate law for the rate of adsorption, the reaction in Equation (10-2) can be treated as an *elementary reaction*. The rate of attachment of the carbon monoxide molecules to the active site on the surface is proportional to the number of collisions that CO molecules make with a surface active site per second. In other words, a specific fraction of the molecules that strike the surface become adsorbed. The collision rate is, in turn, directly proportional to the carbon monoxide partial pressure, P_{CO} . Because carbon monoxide molecules adsorb only on vacant sites and not on sites already occupied by other carbon monoxide molecules, the rate of attachment is also directly proportional to the concentration of vacant sites, C_v . Combining these two facts along with the law of mass action means that the rate of attachment of carbon monoxide molecules to the surface is directly proportional to the product of the partial pressure of CO (P_{CO}) and the concentration of vacant sites (C_v); that is,

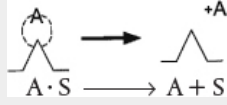
$$\text{Rate of attachment} = k_A P_{\text{CO}} C_v$$



$$P_{\text{CO}} = C_{\text{CO}} RT$$

The rate of detachment of molecules from the surface can be a first-order process; that is, the detachment of carbon monoxide molecules from the surface is usually directly proportional to the concentration of sites occupied by the adsorbed molecules (e.g., $C_{\text{CO}\cdot\text{S}}$):

$$\text{Rate of detachment} = k_{-A} C_{\text{CO}\cdot\text{S}}$$



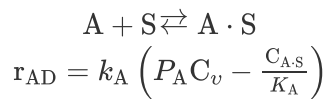
The net rate of adsorption is equal to the rate of molecular attachment to the surface minus the rate of detachment from the surface. If k_A and k_{-A} are the constants of proportionality for the attachment and detachment processes, then

$$r_{AD} = k_A P_{CO} C_v - k_{-A} C_{CO \cdot S} \quad (10-3)$$

The ratio $K_A = k_A/k_{-A}$ is the *adsorption equilibrium constant*. Using K_A to rearrange Equation (10-3) gives

$$r_{AD} = k_A \left(P_{CO} C_v - \frac{C_{CO \cdot S}}{K_A} \right) \quad (10-4)$$

Adsorption



The adsorption rate constant, k_A , for molecular adsorption is virtually independent of temperature, while the desorption constant, k_{-A} , increases exponentially with increasing temperature. Consequently, *the equilibrium adsorption constant K_A decreases exponentially with increasing temperature*.

Site balance

Because carbon monoxide is the only material adsorbed on the catalyst, the site balance gives

$$C_t = C_v + C_{CO \cdot S} \quad (10-5)$$

$$\begin{aligned}
 -r'_A &= r_{AD} = \left(\frac{\text{mol}}{\text{g-cat}\cdot\text{s}} \right) \\
 k_A &= \left(\frac{1}{\text{atm}\cdot\text{s}} \right) \\
 P_A &= (\text{atm}) \\
 C_v &= \left(\frac{\text{mol}}{\text{g-cat}} \right) \\
 K_A &= \left(\frac{1}{\text{atm}} \right) \\
 C_{A\cdot S} &= \left(\frac{\text{mol}}{\text{g-cat}} \right)
 \end{aligned}$$

At equilibrium, the net rate of adsorption equals zero, that is, $r_{AD} \equiv 0$. Setting the left-hand side of Equation (10-4) equal to zero and solving for the concentration of CO adsorbed on the surface, we get

$$C_{\text{CO}\cdot\text{S}} = K_A C_v P_{\text{CO}} \quad (10-6)$$

Using Equation (10-5) to give in terms of $C_{\text{CO}\cdot\text{S}}$ and the total number of sites C_t , we can solve for the equilibrium value of $C_{\text{CO}\cdot\text{S}}$ in terms of constants and the pressure of carbon monoxide

$$C_{\text{CO}\cdot\text{S}} = K_A C_v P_{\text{CO}} = K_A P_{\text{CO}} (C_t - C_{\text{CO}\cdot\text{S}})$$

Rearranging gives us a Langmuir isotherm⁶

⁶ Named after Irving Langmuir (1881–1957), who first proposed it. He received the Nobel Prize in 1932 for his discoveries in surface chemistry (https://www.nobelprize.org/nobel_prizes/chemistry/laureates/1932/langmuir-bio.html).

$$C_{\text{CO}\cdot\text{S}} = \frac{K_A P_{\text{CO}} C_t}{1 + K_A P_{\text{CO}}} \quad (10-7)$$

Langmuir adsorption isotherm

This equation thus gives the equilibrium concentration of carbon monoxide adsorbed on the surface, $C_{\text{CO}\cdot\text{S}}$, as a function of the partial pressure of carbon monoxide, and is an equation for the adsorption isotherm. This particular type of isotherm equation is called a *Langmuir isotherm*.⁷ **Figure 10-11(a)** shows a single-site Langmuir isotherm for molecular adsorption in terms of the adsorbed concentration (mass of CO

adsorbed per unit mass of catalyst) *as a function* of the partial pressure of CO, that is, Equation (10-7).

² Ibid.

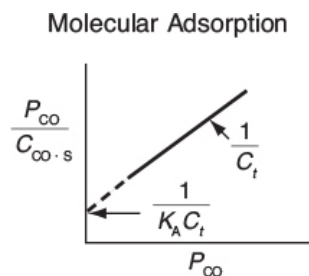
Now, for the case of dissociative adsorption, Equation (10-11), **Figure 10-11(b)** shows the concentration of the dissociated atoms of C and O adsorbed per unit mass of catalyst of a function of partial pressure of CO, that is, Equation (10-11).

One method of checking whether or not a model (e.g., molecular adsorption vs. dissociative adsorption) predicts the behavior of the experimental data is to linearize the model's equation and then plot the indicated variables against one another. For example, the molecular adsorption isotherm, Equation (10-7), may be arranged in the form

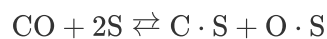
$$\frac{P_{\text{CO}}}{C_{\text{CO}\cdot\text{s}}} = \frac{1}{K_{\text{A}} C_{\text{t}}} + \frac{P_{\text{CO}}}{C_{\text{t}}} \quad (10-8)$$

Molecular adsorption

and the linearity of a plot of $P_{\text{CO}}/C_{\text{CO}\cdot\text{s}}$ as a function of P_{CO} will determine whether the data conform to molecular adsorption, that is, a Langmuir single-site isotherm.



Dissociative Adsorption: We next derive the isotherm for carbon monoxide disassociating into separate atoms as it adsorbs on the surface, that is,



Dissociative adsorption

When the carbon monoxide molecule dissociates upon adsorption, it is referred to as the *dissociative adsorption* of carbon monoxide. As in the case of molecular adsorption, the rate of adsorption is proportional to the partial pressure of carbon monoxide in the system because this rate is governed by the number of gaseous CO collisions with the surface. For a molecule to dissociate as it adsorbs, however, two adjacent vacant active sites are required, rather than the single site needed when a substance adsorbs in its molecular form. The probability of two vacant sites occurring adjacent to one another is proportional to the square of the concentration of vacant sites, cf. the law of mass action. These two observations mean that the rate of adsorption is proportional to the product of the carbon monoxide partial pressure and the square of the vacant-site concentration, $P_{\text{CO}}C_v^2$.

For desorption to occur, two occupied sites must be adjacent, meaning that the rate of desorption is proportional to the product of the occupied-site concentration, $(\text{C}\cdot\text{S}) \times (\text{O}\cdot\text{S})$. The net rate of adsorption can then be expressed as

$$r_{\text{AD}} = k_{\text{A}}P_{\text{CO}}C_v^2 - k_{-\text{A}}C_{\text{O}\cdot\text{S}}C_{\text{C}\cdot\text{S}} \quad (10-9)$$

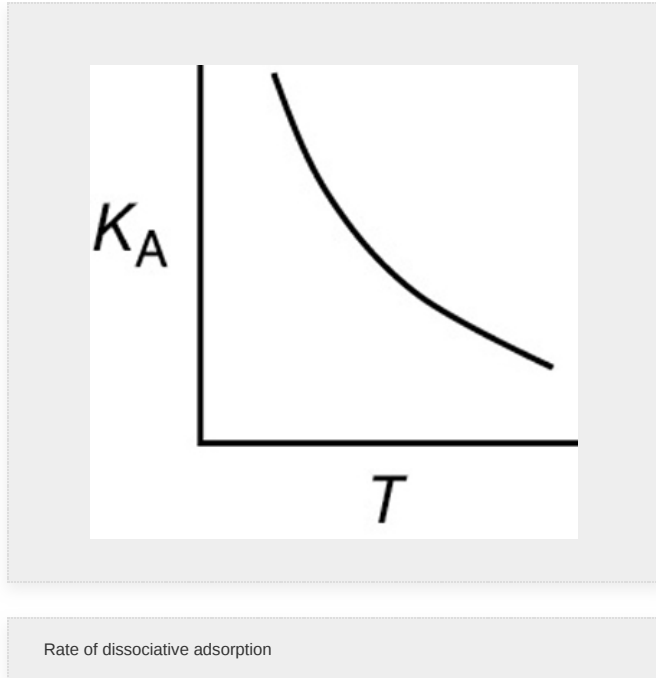


Factoring out k_{A} , the equation for *dissociative adsorption* is

$$r_{\text{AD}} = k_{\text{A}} \left(P_{\text{CO}}C_v^2 - \frac{C_{\text{C}\cdot\text{S}}C_{\text{O}\cdot\text{S}}}{K_{\text{A}}} \right)$$

where

$$K_{\text{A}} = \frac{k_{\text{A}}}{k_{-\text{A}}}$$



For dissociative adsorption, both k_A and k_{-A} increase exponentially with increasing temperature, while the *adsorption equilibrium constant* K_A decreases with increasing temperature because adsorption is an exothermic reaction step.

At equilibrium, $r_{AD} \equiv 0$, and

$$k_A P_{CO} C_v^2 = k_{-A} C_{C.S} C_{O.S}$$

For $C_{C.S} = C_{O.S}$

$$(K_A P_{CO})^{1/2} C_v = C_{O.S} \quad (10-10)$$

Substituting for $C_{C.S}$ and $C_{O.S}$ in a site balance equation (10-1),

$$\begin{aligned} C_t &= C_v + C_{O.S} + C_{C.S} \\ &= C_v + (K_A P_{CO})^{1/2} C_v = C_v \left(1 + 2(K_A P_{CO})^{1/2} \right) \end{aligned}$$

Site balance:

Solving for C_v

$$C_v = C_t / \left(1 + 2(K_A P_{CO})^{1/2} \right)$$

This value may be substituted into Equation (10-10) to give an expression that can be solved for the equilibrium value of $C_{O,S}$ as a function of the partial pressure of CO. The resulting equation for the isotherm shown in Figure 10-11(b) is

$$C_{O,S} = \frac{(K_A P_{CO})^{1/2} C_t}{1 + 2(K_A P_{CO})^{1/2}} \quad (10-11)$$

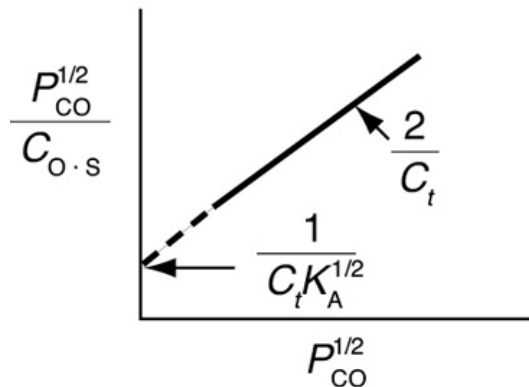
Langmuir isotherm for carbon monoxide dissociative adsorption as atomic carbon and oxygen

Taking the inverse of both sides of the equation, then multiplying through by $(P_{CO})^{1/2}$, yields

$$\frac{(P_{CO})^{1/2}}{C_{O,S}} = \frac{1}{C_t(K_A)^{1/2}} + \frac{2(P_{CO})^{1/2}}{C_t} \quad (10-12)$$

If dissociative adsorption is the correct model, a plot of $(P_{CO}^{1/2}/C_{O,S})$ versus $P_{CO}^{1/2}$ should be linear with slope $(2/C_t)$.

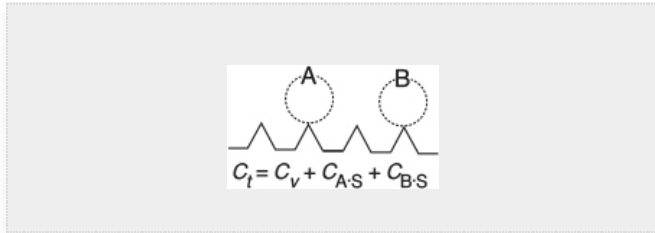
Dissociative Adsorption



When more than one substance is present, the adsorption isotherm equations are somewhat more complex. The principles are the same, though, and the isotherm equations are easily derived. It is left as an exercise to show that the adsorption isotherm of A in the presence of another adsorbate B is given by the relationship

$$C_{A,S} = \frac{K_A P_A C_t}{1 + K_A P_A + K_B P_B} \quad (10-13)$$

When the adsorption of both A and B are first-order processes, the desorptions are also first order, and both A and B are adsorbed as molecules. The derivations of other Langmuir isotherms are relatively easy.

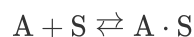


In obtaining the Langmuir isotherm equations, several aspects of the adsorption system were presupposed in the derivations. The most important of these, and the one that has been subject to the greatest doubt, is that a *uniform* surface is assumed. In other words, any active site has the same attraction for an impinging molecule as does any other active site. Isotherms different from the Langmuir isotherm, such as the Freundlich isotherm, may be derived based on various assumptions concerning the adsorption system, including different types of nonuniform surfaces.

Note assumptions in the model and check their validity.

10.2.4 Surface Reaction

The rate of adsorption of species A onto a solid surface site



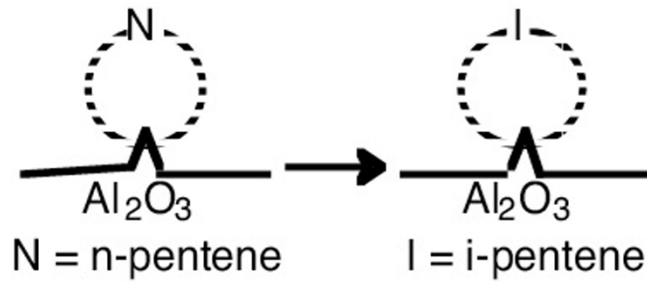
is given by

$$r_{AD} = k_A \left(P_A C_v - \frac{C_{A \cdot S}}{K_A} \right) \quad (10-14)$$

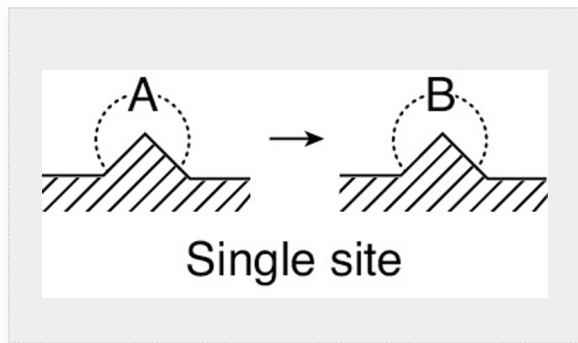
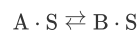
After a reactant has been adsorbed onto the surface, that is, $A \cdot S$, it is capable of reacting in a number of ways to form the reaction product. Three of these ways are:

1. **Single site.** The surface reaction may be a single-site mechanism in which only the site on which the reactant is adsorbed is involved in the reaction. For example, an adsorbed molecule of A may isomerize (or perhaps

decompose) directly on the site to which it is attached, such as pentene isomerization



The pentane isomerization can be written in generic form as



Each step in the reaction mechanism is elementary, so the surface reaction rate law is

$$r_S = k_S C_{A,S} - k_{-S} C_{B,S} = k_S \left(C_{A,S} - \frac{C_{B,S}}{K_S} \right) \quad (10-15)$$

Single Site

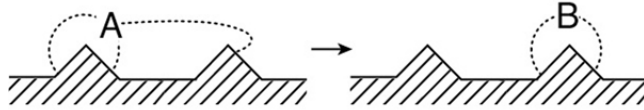
$$k_S = \left(\frac{1}{s} \right)$$

where K_S is the surface-reaction equilibrium constant $K_S = k_S/k_{-S}$

$$K_S = (\text{dimensionless})$$

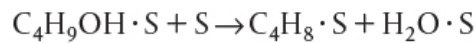
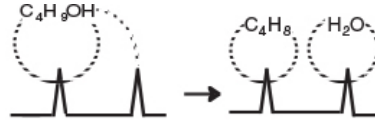
2. **Dual site.** The surface reaction may be a dual-site mechanism in which the adsorbed reactant interacts with another site (either unoccupied or occupied) to form the product.

First type of dual-site mechanism



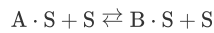
Dual site

For example, adsorbed A may need to react with an adjacent vacant site to further become destabilized to yield a vacant site and a site on which the product is adsorbed. In case of the dehydration of butanol, the reaction products adsorb on two adjacent sites.



$$r_s = k_s \left[(C_{\text{C}_4\text{H}_9\text{OH} \cdot \text{S}})(C_v) - \frac{(C_{\text{C}_4\text{H}_8 \cdot \text{S}})(C_{\text{H}_2\text{O} \cdot \text{S}})}{K_s} \right]$$

For the generic reaction



the corresponding surface-reaction rate law is

$$r_s = k_s \left[C_{\text{A} \cdot \text{S}} C_v - \frac{C_{\text{B} \cdot \text{S}} C_v}{K_s} \right] \quad (10-16)$$

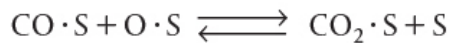
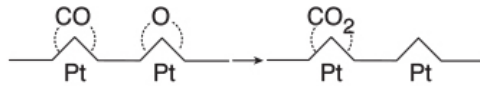
Dual Site

$$r_s = \left(\frac{\text{mol}}{\text{g-cat} \cdot \text{S}} \right)$$

$$k_s = \left(\frac{\text{g-cat}}{\text{mol} \cdot \text{S}} \right)$$

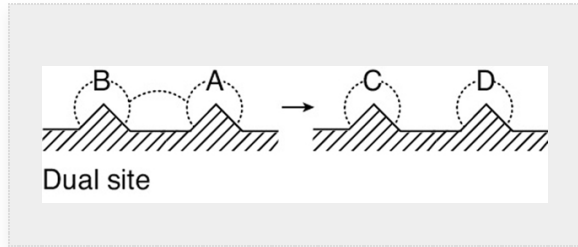
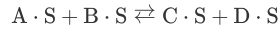
$$K_s = (\text{dimensionless})$$

A second dual-site mechanism is the reaction between two adsorbed species, such as the reaction of CO with O.



$$r_s = k_s \left[(C_{\text{CO} \cdot \text{S}})(C_{\text{O} \cdot \text{S}}) - \frac{(C_{\text{CO}_2 \cdot \text{S}})(C_v)}{K_s} \right]$$

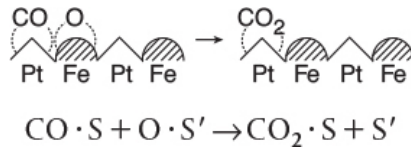
For the generic reaction



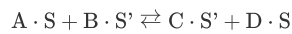
the corresponding surface-reaction rate law is

$$r_S = k_S \left(C_{A \cdot S} C_{B \cdot S} - \frac{C_{C \cdot S} C_{D \cdot S}}{K_S} \right) \quad (10-17)$$

A **third dual-site mechanism** is the reaction of two species adsorbed on different types of sites S and S' , such as the reaction of CO with O.

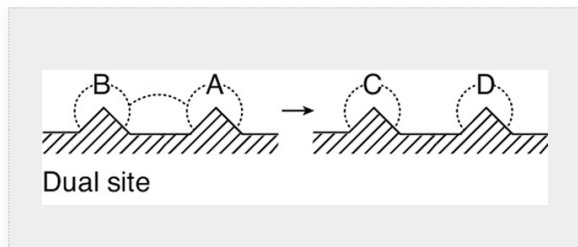


For the generic reaction



the corresponding surface-reaction rate law is

$$r_S = k_S \left(C_{A \cdot S} C_{B \cdot S'} - \frac{C_{C \cdot S'} C_{D \cdot S}}{K_S} \right) \quad (10-18)$$



Langmuir-Hinshelwood kinetics

Reactions involving either single- or dual-site mechanisms, which were described earlier, are sometimes referred to as following *Langmuir-Hinshelwood kinetics*.

3. **Eley-Rideal.** A third mechanism is the reaction between an adsorbed molecule and a molecule in the gas phase, such as the reaction of propylene and benzene (cf. the reverse reaction in Figure 10-13 on page 463.)

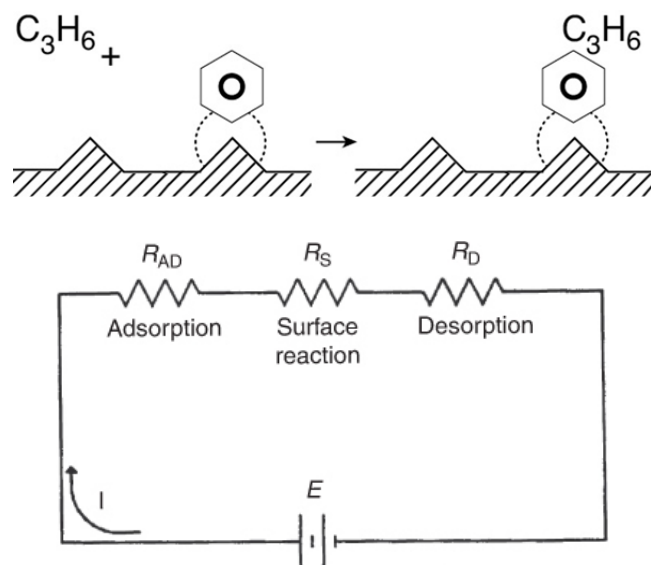


Figure 10-12 Electrical analog to heterogeneous reactions.

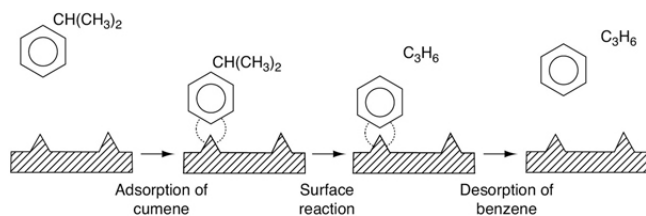
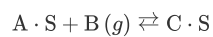


Figure 10-13 Sequence of steps in a reaction-limited catalytic reaction.

For the generic reaction

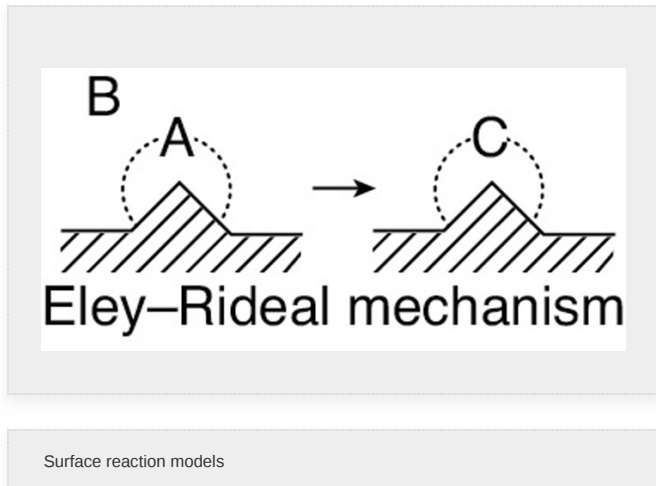


the corresponding surface-reaction rate law is

$$k_s = \left(\frac{1}{\text{atm} \cdot \text{s}} \right)$$

$$K_S = \left(\frac{1}{\text{atm}} \right)$$

$$r_S = k_S \left[C_{A \cdot S} P_B - \frac{C_{C \cdot S}}{K_S} \right] \quad (10-19)$$



This type of mechanism is referred to as an *Eley-Rideal mechanism*.

$$K_{DC} = (\text{atm})$$

$$k_D = \left(\frac{1}{\text{s}}\right)$$

10.2.5 Desorption

In each of the preceding cases, the products of the surface reaction adsorbed on the surface are subsequently desorbed into the gas phase. For the desorption of a species (e.g., C)



the rate of desorption of C is

$$r_{DC} = k_D \left(C_{C \cdot S} - \frac{P_C C_v}{K_{DC}} \right) \quad (10-20)$$

where K_{DC} is the desorption equilibrium constant with units of atm. Now let's look at the above desorption step of $C \cdot S$ from right to left. We note that the desorption step for $C \cdot S$ is just the reverse of the adsorption step. Consequently, the rate of desorption of C, r_{DC} , is just opposite in sign to the rate of adsorption of C, r_{ADC}

$$r_{DC} = -r_{ADC}$$

In addition, we see that the desorption equilibrium constant K_{DC} is just the reciprocal of the adsorption equilibrium

constant for C, K_C

$$K_{DC} = \frac{1}{K_C}$$

in which case the rate of desorption of C can be written

$$r_{DC} = k_D (C_{C.S} - K_C P_C C_v) \quad (10-21)$$

$$K_{DC} = (\text{atm})$$

$$K_C = \left(\frac{1}{\text{atm}} \right)$$

In the material that follows, the form of the equation for the desorption step that we will use to develop our rate laws will be similar to Equation (10-21).

10.2.6 The Rate-Limiting Step

When heterogeneous reactions are carried out at steady state, the rates of each of the three reaction steps in series (adsorption, surface reaction, and desorption) are equal to one another

$$-r'_A = r_{AD} = r_S = r_D$$

However, one particular step in the series is usually found to be *rate-limiting* or *rate-controlling*. That is, if we could make that particular step go faster, the entire reaction would proceed at an accelerated rate. Consider the analogy to the electrical circuit shown in Figure 10-12. A given concentration of reactants is analogous to a given driving force or electromotive force (EMF). The current I (with units of coulombs/s) is analogous to the rate of reaction, $-r'_A$ (mol/s·g-cat), and a resistance R_i (with units of Ohms, Ω) is associated with each step in the series. Because the resistances are in series, the total resistance R_{tot} is just the sum of the individual resistances, for adsorption (R_{AD}), surface reaction (R_S), and desorption (R_D). The current, I , for a given voltage, E , is

$$I = \frac{E}{R_{\text{tot}}} = \frac{E}{R_{AD} + R_S + R_D}$$

The concept of a rate-limiting step

Who is slowing us down?

Because we observe only the total resistance, R_{tot} , it is our task to find which resistance is much larger (say, 100 Ω) than the other two resistances (say, 0.1 Ω). Thus, if we could lower the largest resistance, the current I (i.e., $-r'_A$), would be larger for a given voltage, E . Analogously, we want to know which step in the adsorption–reaction–desorption series is limiting the overall rate of reaction.

An algorithm to determine the rate-limiting step



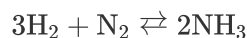
The approach in determining catalytic and heterogeneous mechanisms is usually termed the *Langmuir-Hinshelwood approach*, since it is derived from ideas proposed by Hinshelwood based on Langmuir's principles for adsorption.⁸ The Langmuir-Hinshelwood approach was popularized by Hougen and Watson and occasionally includes their names.⁹ It consists of first assuming a sequence of steps in the reaction. In writing this sequence, one must choose among such mechanisms as molecular or atomic adsorption, and single- or dual-site reaction. Next, rate laws are written for the individual steps as shown in the preceding section, assuming that all steps are reversible. Finally, a rate-limiting step is postulated, and steps that are not rate-limiting are used to eliminate all coverage-dependent terms. The most questionable assumption in using this technique to obtain a rate law is the hypothesis that the activity of the surface is essentially uniform as far as the various steps in the reaction are concerned.

⁸ C. N. Hinshelwood, *The Kinetics of Chemical Change*, Oxford: Clarendon Press, 1940.

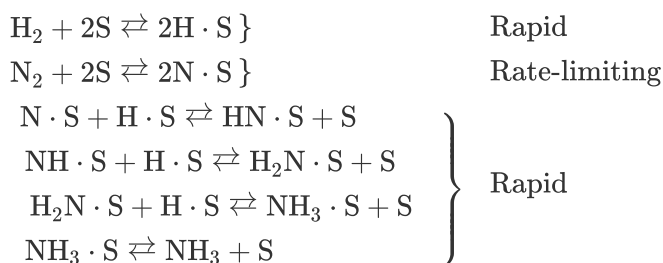
⁹ O. A. Hougen and K. M. Watson, *Ind. Eng. Chem.*, 35, 529 (1943).

Industrial Example of Adsorption-Limited Reaction

An example of an adsorption-limited reaction is the synthesis of ammonia from hydrogen and nitrogen



over an iron catalyst that proceeds by the following mechanism:¹⁰



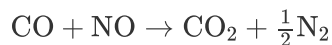
¹⁰ From the literature cited in G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis*, New York: Wiley, 1994, p. 482.

Dissociative adsorption of N_2 is rate-limiting.

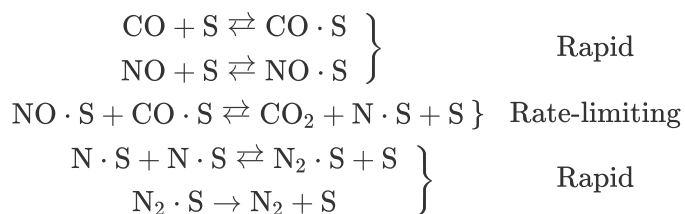
The rate-limiting step is believed to be the adsorption of the N_2 molecule as an N atom on an iron active site.

Industrial Example of Surface-Limited Reaction

An example of a surface-limited reaction is the reaction of two noxious automobile exhaust products, CO and NO



carried out over a copper catalyst to form more environmentally acceptable products, N_2 and CO_2



Surface reaction is rate-limiting.

Analysis of the rate law suggests that CO_2 and N_2 are weakly adsorbed, that is, have infinitesimally small adsorption constants (see Problem P10-9B).

What If Two Steps Are Equally Rate Limiting?

If two steps, say surface reaction and desorption, are equally slow then one must resort to applying the Pseudo-Steady-State Hypothesis (PSSH) to the adsorbed species as shown in the Chapter 10 expanded material (http://www.umich.edu/~elements/6e/10chap/expanded_ch10_PSSH.pdf).

10.3 SYNTHESIZING A RATE LAW, MECHANISM, AND RATE-LIMITING STEP

We now wish to develop rate laws for catalytic reactions that are not diffusion-limited. In developing the procedure of how to obtain a rate law, a mechanism and a rate-limiting step, consistent with experimental observation, we shall discuss the catalytic decomposition of cumene to form benzene and propylene. The overall reaction is



- Adsorption
- Surface reaction
- Desorption

A conceptual model depicting the sequence of steps in this platinum-catalyzed reaction is shown in Figure 10-13. Figure 10-13 is only a schematic representation of the adsorption of cumene; a more realistic model is the formation of a complex of the π orbitals of benzene with the catalytic surface, as shown in Figure 10-14.

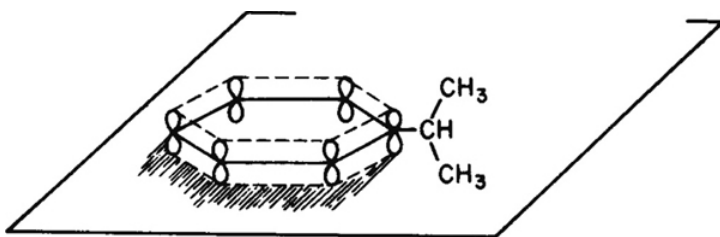


Figure 10-14 π -orbital complex on surface.

The nomenclature in Table 10-3 will be used to denote the various species in this reaction: **C = cumene**, **B = benzene**, and **P = propylene**. The reaction sequence for this decomposition is shown in Table 10-3.

TABLE 10-3 STEPS IN A LANGMUIR-HINSHELWOOD KINETIC MECHANISM

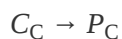
$C + S \xrightleftharpoons[k_{-A}]{k_A} C \cdot S \quad \text{Adsorption of cumene on the surface} \quad (10-22)$		
$C \cdot S \xrightleftharpoons[k_{-S}]{k_S} B \cdot S + P \quad \begin{array}{l} \text{Surface reaction to form adsorbed} \\ \text{benzene and propylene in the} \\ \text{gas phase} \end{array} \quad (10-23)$		
$B \cdot S \xrightleftharpoons[k_{-D}]{k_D} B + S \quad \text{Desorption of benzene from surface} \quad (10-24)$		

These three steps represent the mechanism for cumene decomposition.

Equations (10-22)–(10-24) represent the *mechanism* proposed for this reaction.

Ideal gas law $P_C = C_C RT$

When writing rate laws for these steps, we treat each step as an elementary reaction; the only difference is that the species concentrations in the gas phase are replaced by their respective partial pressures



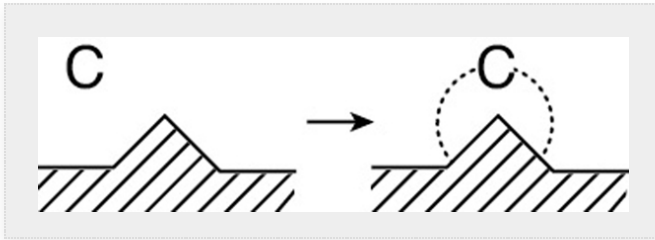
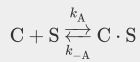
There is no theoretical reason for this replacement of the concentration, C_C , with the partial pressure, P_C ; it is just the convention initiated in the 1930s and used ever since.

Fortunately, P_C can be calculated easily and directly from C_C using the ideal gas law (i.e., $P_C = C_C RT$).

The rate expression for the adsorption of cumene as given in Equation (10-22) is

$$r_{AD} = k_A P_C C_v - k_{-A} C_{C \cdot S}$$

$$\text{Adsorption: } r_{AD} = k_A \left(P_C C_v - \frac{C_{C \cdot S}}{K_C} \right) \quad (10-25)$$



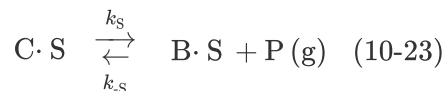
If r_{AD} has units of (mol/g-cat·s) and $C_{C \cdot S}$ has units of (mol cumene adsorbed/g-cat) and P_C has units of kPa, bar or atm, then typical units of k_A , k_{-A} , and K_C would be

$$[k_A] \equiv (\text{kPa} \cdot \text{s})^{-1} \text{ or } (\text{atm} \cdot \text{h})^{-1} \text{ or } (\text{bar} \cdot \text{h})^{-1}$$

$$[k_{-A}] \equiv \text{h}^{-1} \text{ or } \text{s}^{-1}$$

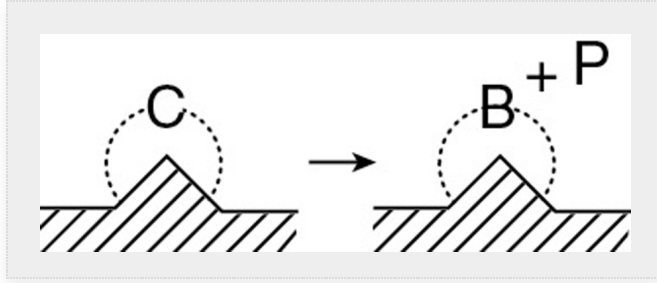
$$[K_C] \equiv \left[\frac{k_A}{k_{-A}} \right] \equiv \text{kPa}^{-1} \text{ or } (\text{bar}^{-1}) \text{ or } (\text{atm}^{-1})$$

The rate law for the surface-reaction step producing adsorbed benzene and propylene in the gas phase



is

$$r_S = k_S C_{C \cdot S} - k_{-S} P_P C_{B \cdot S}$$



$$\text{Surface reaction: } r_S = k_S \left(C_{C \cdot S} - \frac{P_P C_{B \cdot S}}{K_S} \right) \quad (10-26)$$

with the *surface reaction equilibrium constant* being

$$K_S = \frac{k_S}{k_{-S}}$$

Typical units for k_S and K_S are s^{-1} and kPa (or atm or bar) respectively.

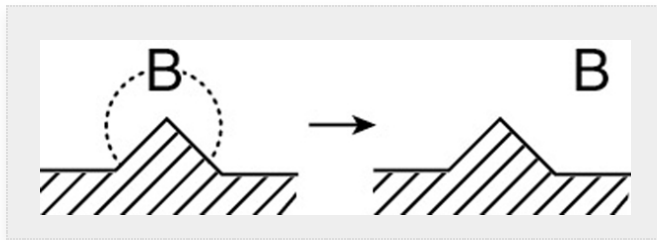
Propylene is not adsorbed on the surface. Consequently, its concentration on the surface is zero, that is,

$$C_{P \cdot S} = 0$$

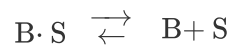
The rate of benzene desorption (see Equation (10-24)) is

$$r_D = k_D C_{B \cdot S} - k_{-D} P_B C_v \quad (10-27)$$

$$\text{Desorption: } r_D = k_D \left(C_{B \cdot S} - \frac{P_B C_v}{K_{DB}} \right) \quad (10-28)$$



Typical units of k_D and K_{DB} are s^{-1} and kPa or bar, respectively. By viewing the desorption of benzene



from right to left, we see that desorption is just the reverse of the adsorption of benzene. Consequently, as mentioned earlier,

it is easily shown that the benzene adsorption equilibrium constant K_B is just the reciprocal of the benzene desorption constant K_{DB}

$$K_B = \frac{1}{K_{DB}}$$

and Equation (10-28) can be written as

$$\text{Desorption: } r_D = k_D (C_{B,S} - K_B P_B C_v) \quad (10-29)$$

Because there is no accumulation of reacting species on the surface, the rates of each step in the sequence are all equal as discussed in Figure 10-12:

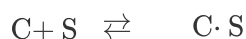
$$-r'_C = r_{AD} = r_S = r_D \quad (10-30)$$

For the mechanism postulated in the sequence given by Equations (10-22)–(10-24), we wish to determine which step is rate-limiting. We first assume one of the steps to be rate-limiting (rate-controlling) and then formulate the reaction-rate law in terms of the partial pressures of the species present. From this expression, we can determine the variation of the initial reaction rate with the initial partial pressures and the initial total pressure. If the predicted rate varies with pressure in the same manner as the rate observed experimentally, the implication is that the assumed mechanism and rate-limiting step are correct.

We will first start our development of the rate laws with the assumption that the adsorption step is rate-limiting and derive the rate law, and then proceed in the following reactions to assume that each of the other two steps' surface reaction and desorption limit the overall rate and then derive the rate law for each of these other two limiting cases.

10.3.1 Is the Adsorption of Cumene Rate-Limiting?

To answer this question, we shall first assume that the adsorption of cumene is *indeed* the rate-limiting step (RLS)



derive the corresponding rate law, and then check to see whether it is consistent with experimental observation. By postulating that this (or any other) step is rate-limiting, we are assuming that the adsorption rate constant of this step (in this case k_A) is small with respect to the specific rates of the other steps (in this case k_S and k_D).¹¹ The rate of adsorption is

¹¹ Strictly speaking, one should compare the product $k_A P_C$ with k_S and k_D .

$$-r'_C = r_{AD} = k_A \left(P_C C_v - \frac{C_{C \cdot S}}{K_C} \right) \quad (10-25)$$

Need to express C_v and $C_{C \cdot S}$ in terms of P_C , P_B , and P_P .

$$r_{AD} = k_A P_C \left[C_v - \frac{C_{C \cdot S}}{K_C P_C} \right]$$

$$\frac{\text{mol}}{\text{s} \cdot \text{kg-cat}} = \left(\frac{1}{\text{s atm}} \right) \cdot (\text{atm}) \cdot \left[\frac{\text{mol}}{\text{kg-cat}} \right] = \left[\frac{1}{\text{S}} \right] \frac{\text{mol}}{\text{kg-cat}}$$

Dividing r_{AD} by $k_A P_C$, we note $\frac{r_{AD}}{k_A P_C} = \frac{\text{mol}}{\text{kg-cat}}$. The reason we do this is that in order to compare terms, the ratios $\left(-\frac{r_{AD}}{k_A P_C} \right)$, $\left(\frac{r_S}{k_S} \right)$, and $\left(\frac{r_D}{k_D} \right)$ must all have the same units $\left[\frac{\text{mol}}{\text{kg-cat}} \right]$. Luckily for us, the end result is the same, however.

Because we cannot measure either C_v or $C_{C \cdot S}$, we must replace these variables in the rate law with measurable quantities in order for the equation to be meaningful.

For steady-state operation we have

$$-r'_C = r_{AD} = r_S = r_D \quad (10-30)$$

For adsorption-limited reactions, k_A is very small and k_S and k_D are very, very large by comparison. Consequently, the ratios r_S / k_S and r_D / k_D are very small (approximately zero), whereas the ratio r_{AD} / k_A is relatively large.

The surface reaction-rate law is

$$r_S = k_S \left(C_{C \cdot S} - \frac{C_{B \cdot S} P_P}{K_S} \right) \quad (10-31)$$

Again, for adsorption-limited reactions, the surface-specific reaction rate k_S is large by comparison, and we can set

$$\frac{r_S}{k_S} \simeq 0 \quad (10-32)$$

and solve Equation (10-31) for $C_{C \cdot S}$

$$C_{C \cdot S} = \frac{C_{B \cdot S} P_P}{k_S} \quad (10-33)$$

Side Comment: A conceptual mistake often made in deriving the rate laws for the individual steps is to set the rates of steps other than the rate-limiting step (RLS) equal to zero (e.g., $r_S = 0$ rather than setting $\frac{r_S}{k_S} \simeq 0$). If one were to set $r_S = 0$ we observe from Equation (10-30) that the entire reaction rate would be zero.

From Equation (10-33) we see that in order to be able to express $C_{C \cdot S}$ solely in terms of the partial pressures of the species present, we must evaluate $C_{B \cdot S}$. The rate of desorption of benzene is

$$r_D = k_D (C_{B \cdot S} - K_B P_B C_v) \quad (10-29)$$

Using $\frac{r_S}{k_S} \simeq 0 \simeq \frac{r_D}{k_D}$ find $C_{B \cdot S}$ and $C_{C \cdot S}$ in terms of partial pressures.

However, for adsorption-limited reactions, k_D is large by comparison, and we can set

$$\frac{r_D}{k_D} \simeq 0 \quad (10-34)$$

and then solve Equation (10-29) for $C_{B \cdot S}$

$$C_{B \cdot S} = K_B P_B C_v \quad (10-35)$$

After combining Equations (10-33) and (10-35), we have

$$C_{C \cdot S} = K_B \frac{P_B P_P}{K_S} C_v \quad (10-36)$$

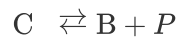
Replacing $C_{C \cdot S}$ in the rate equation by Equation (10-36) and then factoring C_v , we obtain

$$r_{AD} = k_A \left(P_C - \frac{K_B P_B P_P}{K_S K_C} \right) C_v = k_A \left(P_C - \frac{P_B P_P}{K_P} \right) C_v \quad (10-37)$$

Thermodynamics: Let's look at how the thermodynamic constant-pressure equilibrium constant, K_p , found its way into Equation (10-37) and how we can find its value for any reaction. First we observe that at equilibrium $r_{AD} = 0$, Equation (10-37) rearranges to

$$\frac{P_{Be}P_{Pe}}{P_{Ce}} = \frac{K_C K_S}{K_B}$$

We also know from thermodynamics (Appendix C) that for the reaction



also at equilibrium ($-r'_C \equiv 0$), we have the following relationship for partial pressure equilibrium constant K_P

$$K_P = \frac{P_{Be}P_{Pe}}{P_{Ce}}$$

Consequently, the following relationship must hold

$$\boxed{\frac{K_S K_C}{K_B} = K_P} \quad (10-38)$$

The thermodynamic equilibrium constant, K_p

The equilibrium constant can be determined from *thermodynamic data* and is related to the change in the Gibbs free energy, ΔG° , by the equation (see Equation (C-2) in Appendix C)

$$\boxed{RT \ln K = -\Delta G^\circ} \quad (10-39)$$

where R is the ideal gas constant and T is the absolute temperature.

Back to the rate law task at hand. The concentration of vacant sites, C_v , can now be eliminated from Equation (10-37) by utilizing the *site balance* to give the total concentration of sites, C_t , which is assumed constant¹²

$$\text{Total sites} = \text{Vacant sites} + \text{Occupied sites}$$

¹² *#SurfaceReactionRate*, Some (I won't mention any names, but they know who they are) prefer to write the surface reaction rate in terms of the fraction of the surface of sites covered (i.e., f_A rather than the number of sites $C_{A,S}$ covered, the difference being the multiplication factor of the total site concentration, C_t . In any event, the final form of the rate law is the same because C_t , K_A , k_S , and so on, are all lumped into the reaction-rate constant, k .

Because cumene and benzene are adsorbed on the surface, the concentration of occupied sites is $(C_{C,S} + C_{B,S})$, and the total concentration of sites is

$$C_t = C_v + C_{C,S} + C_{B,S} \quad (10-40)$$

Site balance

Substituting Equations (10-35) and (10-36) into Equation (10-40), we have

$$C_t = C_v + \frac{K_B}{K_S} P_B P_C C_v + K_B P_B C_v$$

Solving for C_v , we have

$$C_v = \frac{C_t}{1 + P_B P_C K_B / K_S + K_B P_B} \quad (10-41)$$

Combining Equations (10-41) and (10-37), we find that the rate law for the catalytic decomposition of cumene, assuming that the adsorption of cumene is the rate-limiting step, is

$$-r'_C = r_{AD} = \frac{C_t k_A (P_C - P_P P_B / K_P)}{1 + K_B P_P P_B / K_S + K_B P_B} \quad (10-42)$$

Cumene reaction rate law iff adsorption were the limiting step

We now, as we usually do, sketch a plot of the initial rate of reaction as a function of the initial partial pressure, in this case cumene, P_{C0} . Initially, no products are present; consequently, $P_P = P_B = 0$. The initial rate is given by

$$-r'_{C0} = C_t k_A P_{C0} = k P_{C0} \quad (10-43)$$

If the cumene decomposition is adsorption rate limited, then from Equation (10-43) we see that the initial rate will be linear with the initial partial pressure of cumene, as shown in Figure 10-15.

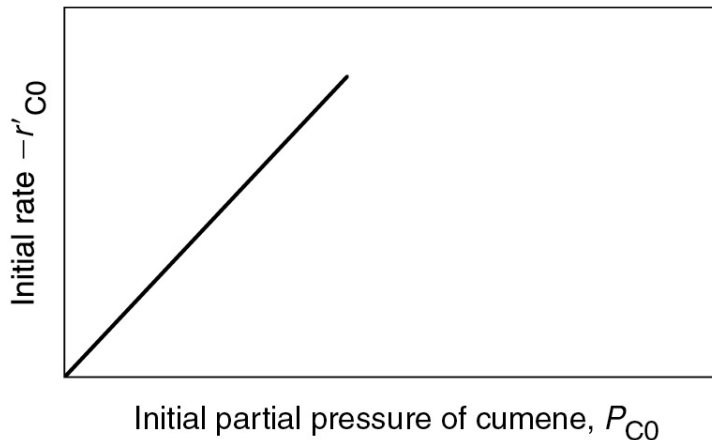


Figure 10-15 Adsorption-limited reaction.

If adsorption were rate-limiting, the data should show $-r'_{CO}$ increasing linearly with P_{C0} .

Before checking to see whether Figure 10-15 is consistent with experimental observation, we shall derive the corresponding rate laws for the other possible rate-limiting steps and then develop corresponding initial rate plots for the case when the surface reaction is rate-limiting and then for the case when the desorption of benzene is rate-limiting.

10.3.2 Is the Surface Reaction Rate-Limiting?

We next assume the surface reaction step



is the rate-limiting step (RLS) and derive a rate law in terms of the partial pressures of C and B. The rate law for the surface reaction is

$$r_S = k_S \left(C_{C \cdot S} - \frac{P_P C_{B \cdot S}}{K_S} \right) \quad (10-26)$$

Single-site mechanism

Since we cannot readily measure the concentrations of the adsorbed species, we must utilize the adsorption and desorption steps to eliminate $C_{C \cdot S}$ and $C_{B \cdot S}$ from this equation.

From the adsorption rate expression in Equation (10-25) and the condition that k_A and k_D are very large by comparison with k_S when the surface reaction is limiting (i.e., $r_{AD}/k_A \approx 0$),¹³ we obtain a relationship for the surface concentration for adsorbed cumene

¹³ See footnote 11 on page 466.

$$C_{C \cdot S} = K_C P_C C_v$$

In a similar manner, the surface concentration of adsorbed benzene can be evaluated from the desorption rate expression, Equation (10-29), together with the approximation

$$\text{when } \frac{r_{AD}}{k_A} \approx \frac{r_D}{k_D}$$

Using $\frac{r_{AD}}{k_A} \approx 0 \approx \frac{r_D}{k_D}$ find $C_{B \cdot S}$ and $C_{C \cdot S}$ in terms of partial pressures.

then we get the same result for $C_{B \cdot S}$ as before when we had adsorption limitation, that is,

$$C_{B \cdot S} = K_B P_B C_v$$

Substituting for $C_{B \cdot S}$ and $C_{C \cdot S}$ in Equation (10-26) gives us

$$r_S = k_S \left(P_C K_C - \frac{K_B P_B P_P}{K_S} \right) C_v = k_S K_C \left(P_C - \frac{P_B P_P}{K_P} \right) C_v \quad (10-26a)$$

where the thermodynamic equilibrium constant was used to replace the ratio of surface reaction and adsorption constants, that is,

$$K_P = \frac{K_C K_S}{K_B} \quad (10-26b)$$

The only variable left to eliminate is and we use a site balance to accomplish this, that is,

$$C_t = C_v + C_{B \cdot S} + C_{C \cdot S} \quad (10-40)$$

Site balance

Substituting for concentrations of the adsorbed species, $C_{B \cdot S}$, and $C_{C \cdot S}$, factoring out C_v , and rearranging yields

$$C_v = \frac{C_t}{1 + K_B P_B + K_C P_C}$$

Substituting for C_v in Equation (10-26a)

$$-r'_C = r_S = \frac{\overbrace{k_S C_t K_C}^k (P_C - P_P P_B / K_P)}{1 + P_B K_B + K_C P_C} \quad (10-44)$$

Cumene rate law iff surface-reaction-limiting

The initial rate of reaction is

$$-r'_{C0} = \frac{\overbrace{k_S C_t K_C}^k P_{C0}}{1 + K_C P_{C0}} = \frac{k P_{C0}}{1 + K_C P_{C0}} \quad (10-45)$$

Using Equation (10-45), we make the sketch of the initial rate of reaction, $-r'_{C0}$, as a function of the initial partial pressure of cumene, P_{C0} , as shown in Figure 10-16 for the case when surface-reaction limit is the limiting step.

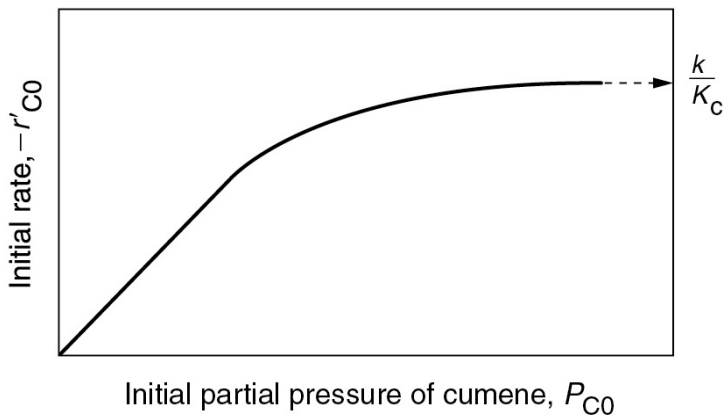


Figure 10-16 Surface-reaction-limited.

At low partial pressures of cumene

$$1 \gg K_C P_{C0}$$

and we observe that the initial rate will increase linearly with the initial partial pressure of cumene:

iff surface reaction were rate-limiting, the data would show this behavior.

$$-r'_{C0} \approx kP_{C0}$$

At high partial pressures

$$K_C P_{C0} \gg 1$$

and Equation (10-45) becomes

$$-r'_{C0} \simeq \frac{kP_{C0}}{K_C P_{C0}} = \frac{k}{K_C}$$

and the initial rate is independent of the initial partial pressure of cumene.

10.3.3 Is the Desorption of Benzene the Rate-Limiting Step (RLS)?

To answer this question, we now want to determine the initial rate, $-r'_{C0}$, and a function of partial pressure of cumene, P_C , for the desorption step



The rate expression for the desorption of benzene is

$$r_D = k_D (C_{B \cdot S} - K_B P_B C_v) \quad (10-29)$$

From the rate expression for surface reaction, Equation (10-26), we set

For desorption-limited reactions, both k_A and k_S are very large compared with k_D , which is small.

$$\frac{r_S}{k_S} \simeq 0$$

to obtain

$$C_{B \cdot S} = K_S \left(\frac{C_{C \cdot S}}{P_P} \right) \quad (10-46)$$

Similarly, for the adsorption step, Equation (10-25), we set

$$\frac{r_{AD}}{k_A} \simeq 0$$

then substitute for $C_{C.S}$ in Equation (10-46) to obtain

$$C_{B.S} = \frac{K_C K_S P_C C_v}{P_P} \quad (10-47)$$

Combining Equations (10-26b), (10-29), and (10-47) gives us

$$r_D = k_D K_C K_S \left(\frac{P_C}{P_P} - \frac{P_B}{K_P} \right) C_v \quad (10-48)$$

where K_C is the cumene adsorption constant, K_S is the surface reaction equilibrium constant, and K_P is the thermodynamic gas-phase equilibrium constant, Equation (10-38), for the reaction. The expression for C_v is obtained from a site balance:

$$\text{Site balance : } C_t = C_{C.S} + C_{B.S} + C_v \quad (10-40)$$

After substituting for the respective surface concentrations, we solve the site balance for C_v

$$C_v = \frac{C_t}{1 + K_C K_S P_C / P_P + K_C P_C} \quad (10-49)$$

Replacing C_v in Equation (10-48) by Equation (10-49) and multiplying the numerator and denominator by P_P , we obtain the rate expression for desorption control

Cumene decomposition rate law **iff** desorption were limiting

$$-r'_C = r_D = \frac{\overbrace{k_D C_t K_S K_C}^k (P_C - P_B P_P / K_P)}{P_P + P_C K_C K_S + K_C P_P P_C} \quad (10-50)$$

To determine the dependence of the initial rate of reaction on the initial partial pressure of cumene, we again set $P_P = P_B = 0$, and the rate law reduces to

$$-r'_{C0} = k_D C_t$$

If desorption limits, the initial rate is independent of the initial partial pressure of cumene.

with the corresponding plot of $-r'_{C0}$ shown in Figure 10-17. If desorption were rate limiting, we would see that the initial rate of reaction would be independent of the initial partial pressure of cumene.

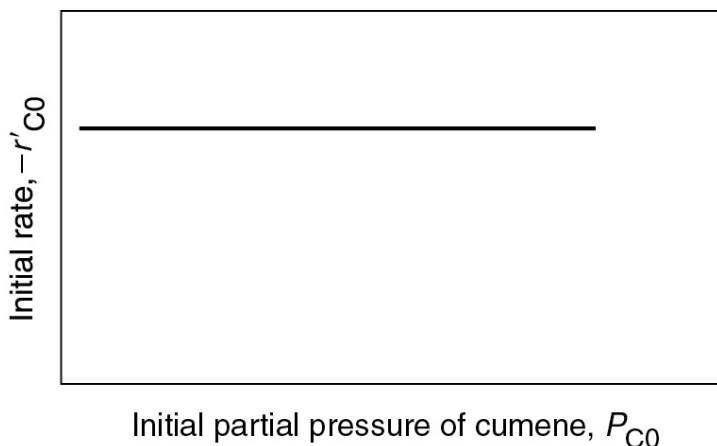


Figure 10-17 Desorption-limited reaction.

10.3.4 Summary of the Cumene Decomposition



Now that we know what the functionality of initial rate versus partial pressure looks like when we assume each of the step is the RLS, it gives us a *foot up* in interpreting reaction rate data. The experimental observations of $-r'_{C0}$ as a function of P_{C0} are shown in Figure 10-18. From the plot in Figure 10-18, we can clearly see that neither adsorption nor desorption is rate-limiting. For the reaction and mechanism given by



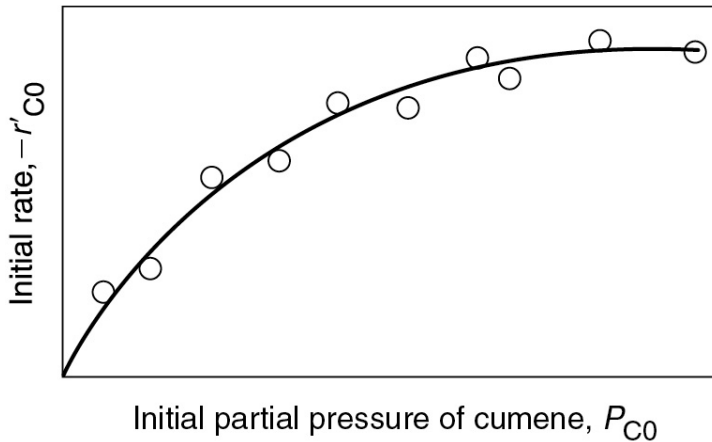
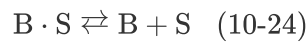
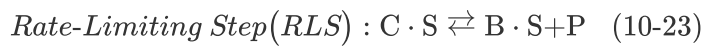


Figure 10-18 Actual initial rate as a function of partial pressure of cumene.



the rate law derived by assuming that the surface reaction is the rate-limiting step (RLS) agrees with the data.

Cumene decomposition is surface-reaction-limited.

Surface-reaction-limited mechanism is consistent with experimental data.

The rate law for the case of no inerts adsorbing on the surface is

$$-r'_C = \frac{k(P_C - P_B P_P / K_p)}{1 + K_B P_B + K_C P_C} \quad (10-44)$$

The forward cumene decomposition reaction is a single-site mechanism involving only adsorbed cumene, while the reverse reaction of propylene in the gas phase reacting with adsorbed benzene is an Eley–Rideal mechanism.

If we were to have an adsorbing inert in the feed, the inert would not participate in the reaction but would occupy active sites on the catalyst surface:



Our site balance is now

$$C_t = C_v + C_{C.S} + C_{B.S} + C_{I.S} \quad (10-51)$$

Because the adsorption of the inert is at equilibrium, the concentration of sites occupied by the inert is

$$C_{I.S} = K_I P_I C_v \quad (10-52)$$

Substituting for the inert sites in the site balance, the rate law for surface reaction control when an adsorbing inert is present is

$$-r'_C = \frac{k(P_C - P_B P_P / K_P)}{1 + K_C P_C + K_B P_B + K_I P_I} \quad (10-53)$$

Adsorbing inerts

One observes that the rate decreases as the partial pressure of adsorbing inerts, P_I , increases.

10.3.5 Reforming Catalysts

We now consider a dual-site mechanism, which is a reforming reaction found in petroleum refining to upgrade the octane number of gasoline.

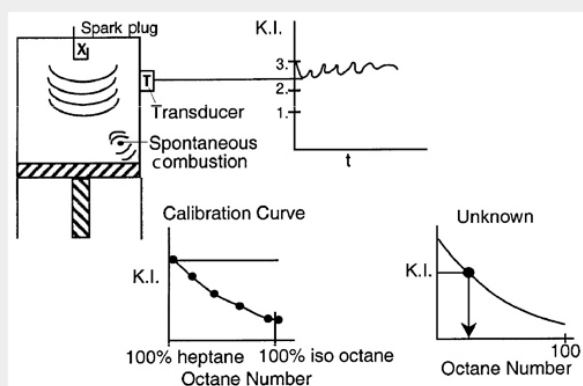
Side Note: Octane Number. Fuels with low octane numbers can produce spontaneous combustion in the car cylinder before the air/fuel mixture is compressed to its desired volume and ignited by the spark plug. The following figure shows the desired combustion wave-front moving down from the spark plug along with the unwanted spontaneous combustion wave in the lower right-hand corner. This spontaneous combustion produces detonation waves, which constitute engine knock. The lower the octane number, the greater the chance of spontaneous combustion and engine knock.

The octane number of a gasoline is determined from a calibration curve relating knock intensity to the % iso-octane in a mixture of iso-octane and heptane. One way to calibrate the octane number is to place a transducer on the side of the cylinder to measure the knock intensity (K.I.) (pressure pulse) for various mixtures of heptane and iso-octane. The octane number is the percentage of iso-octane in this mixture. That is, pure iso-octane has an octane number of 100, 80% iso-octane/20% heptane has an octane number of 80, and so on. The knock intensity is measured for this 80/20 mixture and recorded. The relative percentages of iso-octane and heptane are changed (e.g., 90/10), and the test is repeated. After a series of experiments, a calibration curve is constructed. The gasoline to be calibrated is then used in the test engine, where the standard knock intensity is measured. Knowing the knock intensity, the octane rating of the fuel is read off the calibration curve. A gasoline with an octane rating of 92 means that it matches the performance of a mixture of 92% iso-octane and 8% heptane. Another way to calibrate octane number is to set the knock intensity and increase the compression ratio. A fixed percentage of iso-octane and heptane is placed in a test engine and the compression ratio

(CR) is increased continually until spontaneous combustion occurs, producing an engine knock. The compression ratio and the corresponding composition of the mixture are then recorded, and the test is repeated to obtain the calibration curve of compression ratio as a function of % iso-octane. After the calibration curve is obtained, the unknown is placed in the cylinder, and the compression ratio (CR) is increased until the set knock intensity is exceeded. The CR is then matched to the calibration curve to find the octane number.

The more compact the hydrocarbon molecule, the less likely it is to cause spontaneous combustion and engine knock. Consequently, it is desired to isomerize straight-chain hydrocarbon molecules into more compact molecules through a catalytic process called *reforming*.

In the United States, the higher the octane number, the greater the cost of a gallon (liter) of gasoline. However, because of government regulations, the cost of a gallon (liter) of gasoline in Jofostan is the same for all octane numbers.



The more compact the molecule, the greater the octane number.

Catalyst manufacture

One common reforming catalyst is platinum on alumina. Platinum on alumina (Al_2O_3) (see SEM photo in [Figure 10-19](#)) is a bifunctional catalyst that can be prepared by exposing alumina pellets to a chloroplatinic acid solution, drying, and then heating in air at 775–875 K for several hours. Next, the material is exposed to hydrogen at temperatures around 725–775 K to produce very small clusters of Pt on alumina. These clusters have sizes on the order of 10 Å, while the alumina pore sizes on which the Pt is deposited are on the order of 100–10,000 Å (i.e., 10–1000 nm).

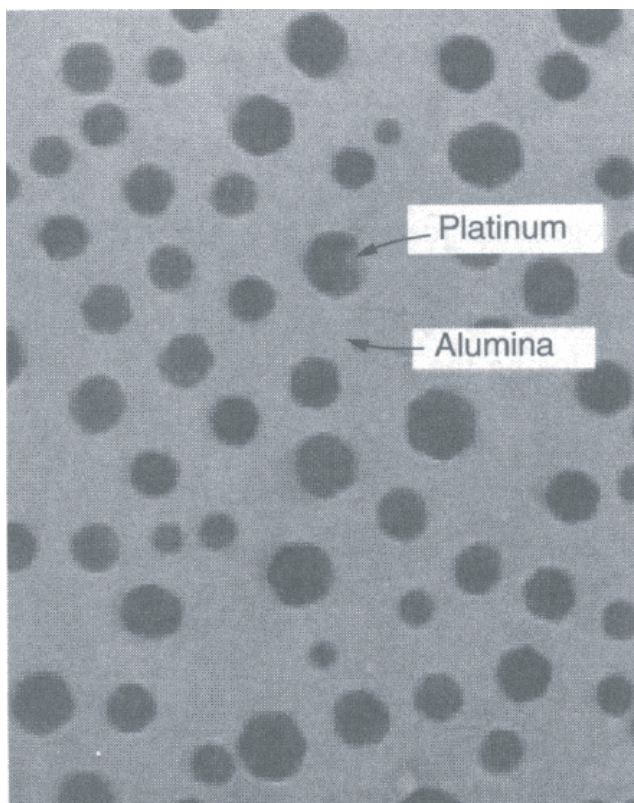
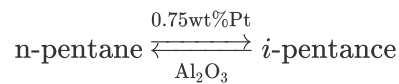


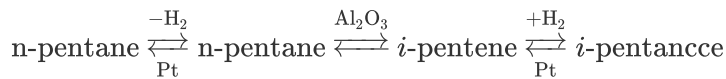
Figure 10-19 Platinum on alumina. (Masel, Richard. *Chemical Kinetics and Catalysis*, p. 700. © John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.)

Gasoline	
C ₅	10%
C ₆	10%
C ₇	20%
C ₈	25%
C ₉	20%
C ₁₀	10%
C ₁₁₋₁₂	5%

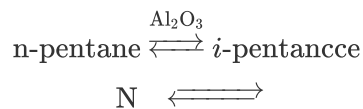
As an example of catalytic reforming, we shall consider the isomerization of *n*-pentane to *i*-pentane



Normal pentane has an octane number of 62, while *iso*-pentane, which is more compact, has an octane number of 90! The *n*-pentane adsorbs onto the platinum, where it is dehydrogenated to form *n*-pentene. The *n*-pentene desorbs from the platinum and adsorbs onto the alumina, where it is isomerized to *i*-pentene, which then desorbs and subsequently adsorbs onto platinum, where it is hydrogenated to form *i*-pentane. That is,



We shall focus on the isomerization step to develop the mechanism and the rate law

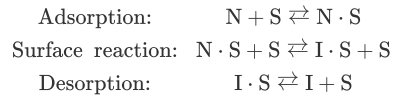


The procedure for formulating a mechanism, rate-limiting step, and corresponding rate law is given in [Table 10-4](#).

TABLE 10-4 ALGORITHM FOR DETERMINING THE REACTION MECHANISM AND RATE-LIMITING STEP

<p>Isomerization of <i>n</i>-pentene (N) to <i>i</i>-pentene (I) over alumina</p> $\text{N} \xrightleftharpoons[\text{Al}_2\text{O}_3]{} \text{I}$ <p>Reforming reaction to increase octane number of gasoline</p>
--

Step 1. *Select a mechanism.* (Let's choose a Dual-Site Mechanism)



Treat each reaction step as an elementary reaction when writing rate laws.

Step 2. *Assume a rate-limiting step.* We choose the surface reaction first, because more than 75% of all heterogeneous reactions that are not diffusion-limited are surface-reaction-limited. We note that the PSSH must be used when more than one step is rate limiting (see [Section 10.3.6](#)).

The rate law for the surface reaction step is

$$-r'_\text{N} = r_\text{S} = k_\text{S} \left(C_\text{v} C_{\text{N}\cdot\text{S}} - \frac{C_{\text{I}\cdot\text{S}} C_\text{v}}{K_\text{S}} \right) \quad (10-54)$$



Step 3. *Find the expression for concentration of the adsorbed species $C_{\text{i}\cdot\text{S}}$. Use the other steps that are not limiting to solve for $C_{\text{i}\cdot\text{S}}$ (e.g., $C_{\text{N}\cdot\text{S}}$ and $C_{\text{I}\cdot\text{S}}$).* For this reaction

$$\text{From } \frac{r_{\text{AD}}}{k_{\text{A}}} \simeq 0 : \quad C_{\text{N}\cdot\text{S}} = P_{\text{N}} K_{\text{N}} C_\text{v} \quad (10-55)$$

$$\text{From } \frac{r_{\text{D}}}{k_{\text{D}}} \simeq 0 : \quad C_{\text{I}\cdot\text{S}} = \frac{P_{\text{I}} C_\text{v}}{K_{\text{D}}} = K_{\text{I}} P_{\text{I}} C_\text{v}$$

Step 4. Write a site balance.

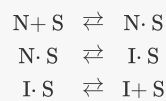
$$C_t = C_v + C_{N.S} + C_{I.S} \quad (10-56)$$

Step 5. Derive the rate law. Combine Steps 2, 3, and 4 to arrive at the rate law

$$-r'_N = r_S = \frac{\overbrace{k_S C_t^2 K_N}^k (P_N - K_P)}{(1 + K_N P_N + K_I P_I)^2} \quad (10-57)$$

Step 6. Compare with data. Compare the rate law derived in Step 5 with experimental data. If they agree, there is a good chance that you have found the correct mechanism and rate-limiting step. If your derived rate law (i.e., model) does not agree with the data

1. Assume a *different* rate-limiting step and repeat Steps 2–6.
2. If, after assuming that each step is rate-limiting, none of the derived rate laws agrees with the experimental data, then select a *different* mechanism (e.g., a single-site mechanism)



and then proceed through Steps 2–6.

The single-site mechanism turns out to be the correct one. For this mechanism, the rate law is

$$-r'_N = \frac{k(P_N - P_I/K_P)}{(1 + K_N P_N + K_I P_I)} \quad (10-58)$$

3. If two or more models agree, the statistical tests discussed in Chapter 7 (e.g., comparison of residuals) should be used to discriminate between them (see the Supplementary Reading).

An observation: We note that in Table 10-4 for the dual-site mechanism, the denominator of the rate law for $-r'_N$ is squared (i.e., in Step 5 $[1/()^2]$), while for a single-site mechanism, it is not squared (i.e., Step 6 $[1/()]$). This fact is useful when analyzing catalytic reactor data.

TABLE 10-5 IRREVERSIBLE SURFACE-REACTION-LIMITED RATE LAWS

Single site	
$A \cdot S \rightarrow B \cdot S$	$-r'_A = \frac{kP_A}{1+K_AP_A+K_BP_B} \quad (10-59)$
Dual site	
$A \cdot S + S \rightarrow B \cdot S + S$	$-r'_A = \frac{kP_A}{(1+K_AP_A+K_BP_B)^2} \quad (10-60)$
$A \cdot S + B \cdot S \rightarrow C \cdot S + S$	$-r'_A = \frac{kP_AP_B}{(1+K_AP_A+K_BP_B+K_CP_C)^2} \quad (10-61)$
Eley–Rideal	
$A \cdot S + B(g) \rightarrow C \cdot S$	$-r'_A = \frac{kP_AP_B}{1+K_AP_A+K_CP_C} \quad (10-62)$



We need a word of caution at this point. Just because the mechanism and rate-limiting step may fit the rate data does not imply that the mechanism is correct.¹⁴ Usually, spectroscopic measurements are needed to confirm a mechanism absolutely. However, the development of various mechanisms and rate-limiting steps can provide insight into the best way to correlate the data and develop a rate law.

¹⁴ R. I. Masel, *Principles of Adsorption and Reaction on Solid Surfaces*, New York: Wiley, 1996, p. 506, www.masel.com. This is a terrific book.

10.3.6 Rate Laws Derived from the Pseudo-Steady-State Hypothesis (PSSH)

In [Section 9.1](#) we discussed the PSSH, where the net rate of formation of *reactive intermediates* was assumed to be zero. An alternative way to derive a catalytic rate law rather than setting

$$\frac{r_{AD}}{k_A} \cong 0$$

is to assume that each species adsorbed on the surface is a *reactive intermediate*. Consequently, the net rate of formation of species *i* adsorbed on the surface will be zero

$$r_{i,S}^* = 0 \quad (10-63)$$

The PSSH is primarily used when more than one step is rate-limiting. The isomerization example shown in Table 10-4 is reworked using the PSSH in the Chapter 10 Expanded Material on the CRE Web site (http://www.umich.edu/~elements/6e/10chap/expanded_ch10_PSSH.pdf).

10.3.7 Temperature Dependence of the Rate Law

Consider a surface-reaction-limited irreversible isomerization



in which both A and B are adsorbed on the surface, and the rate law is

$$-r'_A = \frac{kP_A}{1 + K_A P_A + K_B P_B} \quad (10-64)$$

The specific reaction rate, k , will usually follow an Arrhenius temperature dependence and increase exponentially with temperature. However, the adsorption of all species on the surface is exothermic. Consequently, the higher the temperature, the smaller the adsorption equilibrium constant. That is, as the temperature increases, K_A and K_B decrease resulting in less coverage of the surface by A and B. Therefore, at high temperatures, the denominator of catalytic rate laws approaches 1. That is, at high temperatures (low coverage)

The rate law could then be approximated as

$$-r'_A \simeq kP_A \quad (10-65)$$

$$1 \gg (P_A K_A + P_B K_B)$$

Neglecting the adsorbed species at high temperatures

or for a reversible isomerization we would have

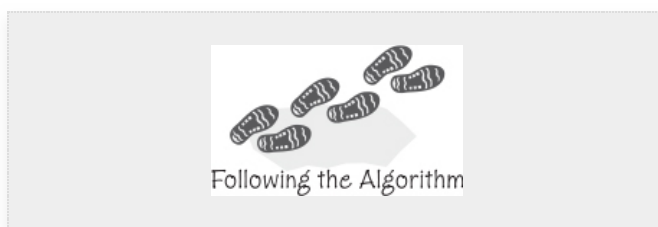
$$-r'_A \simeq k \left(P_A - \frac{P_B}{K_P} \right) \quad (10-66)$$

<u>Algorithm</u>
<i>Deduce</i>
Rate law
<i>Find</i>
Mechanism
<i>Evaluate</i>
Rate-law parameters
<i>Design</i>
PBR
CSTR

The algorithm we can use as a start in postulating a reaction mechanism and rate-limiting step is shown in [Table 10-4](#). Again, we can never really prove a mechanism to be correct by comparing the derived rate law with experimental data. Independent spectroscopic experiments are usually needed to confirm the mechanism. We can, however, prove that a proposed mechanism is *inconsistent* with the experimental data by following the algorithm in [Table 10-4](#). Rather than taking all the experimental data and then trying to build a model from the data, Box et al. describe techniques of sequential data collection and model building.¹⁵

¹⁵ G. E. P. Box, J. S. Hunter, and W. G. Hunter, *Statistics for Experimenters: Design, Innovation, and Discovery*, 2nd ed., Hoboken, New Jersey: Wiley, 2005.

10.4 HETEROGENEOUS DATA ANALYSIS FOR REACTOR DESIGN



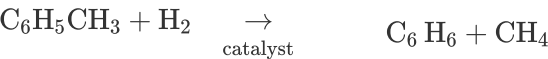
In this section, we focus on four operations that chemical reaction engineers need to be able to accomplish:

- 1. Developing an algebraic rate law consistent with experimental observations,
- 2. Analyzing the rate law in such a manner that the rate-law parameters (e.g., k , K_A) can readily be determined from the experimental data,
- 3. Finding a mechanism and rate-limiting step consistent with the experimental data, and
- 4. Designing a catalytic reactor to achieve a specified conversion

We shall use the hydrodemethylation of toluene to illustrate these four operations.

Hydrogen and toluene are reacted over a solid mineral catalyst containing clinoptilolite (a crystalline silica-alumina) to form methane and benzene¹⁶

¹⁶ J. Papp, D. Kallo, and G. Schay, *J. Catal.*, 23, 168.



We wish to design a packed-bed reactor and a “fluidized bed” CSTR to process a feed consisting of 30% toluene, 45% hydrogen, and 25% inerts. Toluene is fed at a rate of 50 mol/min at a temperature of 640=C and a pressure of 40 atm (4052 kPa). To design the PBR, we must first determine the rate law from the differential reactor data presented in [Table 10-6](#). In this table, we are given the rate of reaction of toluene as a function of the partial pressures of hydrogen (H_2), toluene (T), benzene (B), and methane (M). In the first two runs, methane was introduced into the feed together with hydrogen and toluene, while the other product, benzene, was fed to the reactor together with the reactants only in runs 3, 4, and 6. In runs 5 and 16, both methane and benzene were introduced in the feed. Because the conversion was less than 1% in the differential reactor, the partial pressures of the products, methane and benzene, formed in these runs were essentially zero, and the reaction rates were equivalent to initial rates of reaction.

TABLE 10-6 DATA FROM A DIFFERENTIAL REACTOR

--

$-r'_T \times 10^{10}$		Partial Pressure (atm)			
Ru	$\left(\frac{\text{g mol toluene}}{\text{g-cat}\cdot\text{s}} \right)$	Toluene (T), P_T	Hydrogen (H ₂), P_{H_2}	Methane (M), P_M	Benzene (B), P_B

Set A

1	71.0	1	1	1	0
---	------	---	---	---	---

2	71.3	1	1	4	0
---	------	---	---	---	---

Set B

3	41.6	1	1	0	1
---	------	---	---	---	---

4	19.7	1	1	0	4
---	------	---	---	---	---

5	42.0	1	1	1	1
---	------	---	---	---	---

6	17.1	1	1	0	5
---	------	---	---	---	---

Set C

7	71.8	1	1	0	0
---	------	---	---	---	---

8	142.0	1	2	0	0
---	-------	---	---	---	---

9	284.0	1	4	0	0
---	-------	---	---	---	---

Set D

10	47.0	0.5	1	0	0
----	------	-----	---	---	---

11	71.3	1	1	0	0
----	------	---	---	---	---

12	117.0	5	1	0	0
----	-------	---	---	---	---

13	127.0	10	1	0	0
----	-------	----	---	---	---

14	131.0	15	1	0	0
----	-------	----	---	---	---

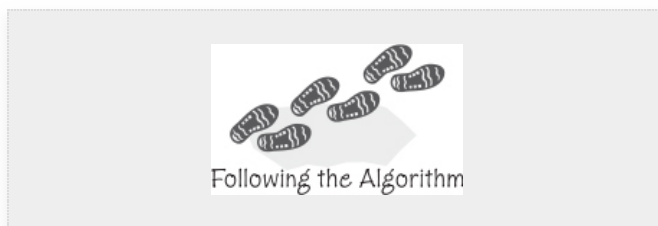
15	133.0	20	1	0	0
----	-------	----	---	---	---

16	41.8	1	1	1	1
----	------	---	---	---	---

Unscramble the data to find the rate law.

10.4.1 Deducing a Rate Law from the Experimental Data

To unscramble the data, let's first look at run 3. In run 3, there is no possibility of the reverse reaction taking place because the concentration of methane is zero, that is, $P_M = 0$, whereas in run 5 the reverse reaction could take place because all products are present. Comparing runs 3 and 5, we see that the initial rate is essentially the same for both runs, and we can assume that the reaction is virtually irreversible.

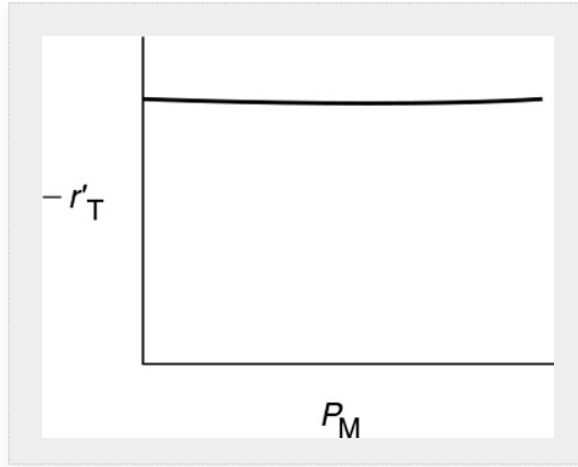


We now ask what qualitative conclusions can be drawn from the data about the dependence of the rate of disappearance of toluene, $-r'_T$, on the partial pressures of toluene, hydrogen, methane, and benzene.

1. *Dependence on the product methane.* If methane were adsorbed on the surface, the partial pressure of methane would appear in the denominator of the rate expression and the rate would vary inversely with methane concentration

$$-r'_T \sim \frac{[]}{1 + K_M P_M + \dots} \quad (10-67)$$

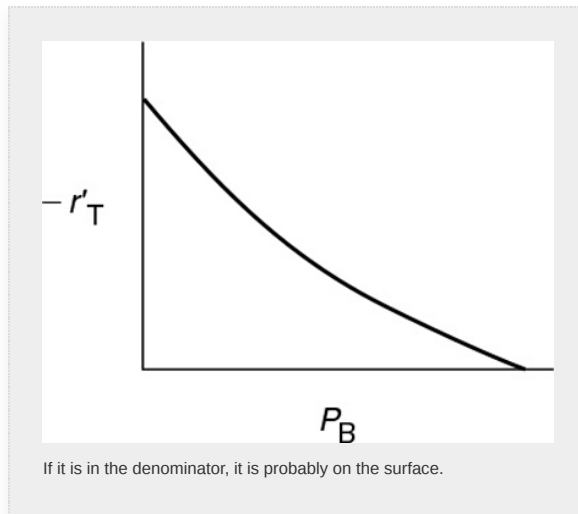
However, comparing runs 1 and 2 we observe that a fourfold increase in the pressure of methane has little effect on $-r'_T$. Consequently, we assume that methane is either very weakly adsorbed (i.e., $K_M P_M \ll 1$) or goes directly into the gas phase in a manner similar to propylene in the cumene decomposition previously discussed.



2. *Dependence on the product benzene.* In runs 3 and 4, we observe that, for fixed concentrations (partial pressures) of hydrogen and toluene, the rate decreases with increasing concentration of benzene. A rate expression in which the benzene partial pressure appears in the denominator could explain this dependency

$$-r'_T \sim \frac{1}{1+K_B P_B + \dots} \quad (10-68)$$

The type of dependence of on P_B given by Equation (10-68) suggests that benzene is adsorbed on the clinoptilolite surface.

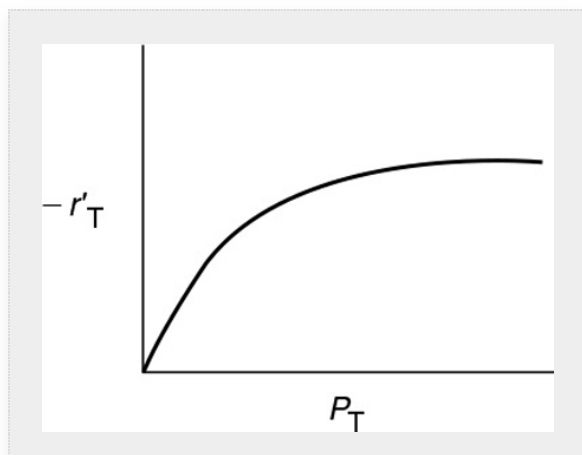


3. *Dependence on toluene.* At low concentrations of toluene (runs 10 and 11), the rate increases with increasing partial pressure of toluene, while at high toluene concentrations (runs 14 and 15), the rate is virtually independent of the toluene partial pressure. A form of the rate expression that would describe this behavior is

$$-r'_T \sim \frac{P_T}{1+K_T P_T + \dots} \quad (10-69)$$

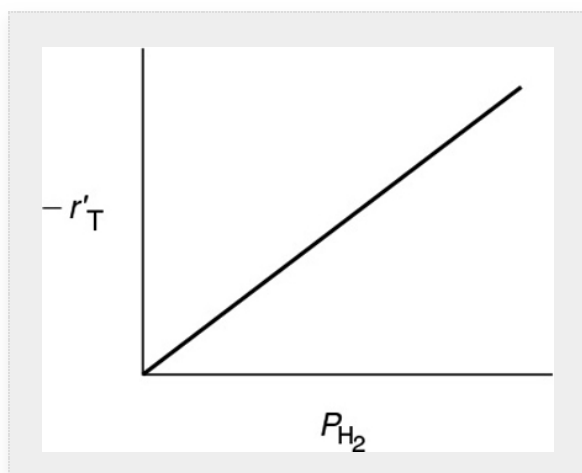
A combination of Equations (10-68) and (10-69) suggests that the rate law may be of the form

$$-r'_T \sim \frac{P_T}{1+K_T P_T + K_B P_B + \dots} \quad (10-70)$$



4. *Dependence on hydrogen.* When we compare runs 7, 8, and 9 in Table 10-6, we see that the rate increases linearly with increasing hydrogen concentration, and we conclude that the reaction is first order in H_2 . In light of this fact, hydrogen is either not adsorbed on the surface or its coverage of the surface is extremely low ($1 \gg K_{H_2} P_{H_2}$) for the pressures used. If H_2 were adsorbed, $-r'_T$ would have a dependence on P_{H_2} analogous to the dependence of $-r'_T$ on the partial pressure of toluene, P_T (see Equation (10-69)). For first-order dependence on H_2 ,

$$-r'_T \sim P_{H_2} \quad (10-71)$$



Deduced the rate law from data using our knowledge of catalysis

Combining Equations (10-67)–(10-71), we find that the rate law

$$-r'_T = \frac{k P_{H_2} P_T}{1 + K_B P_B + K_T P_T}$$

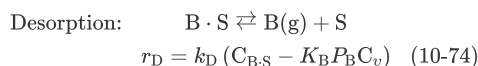
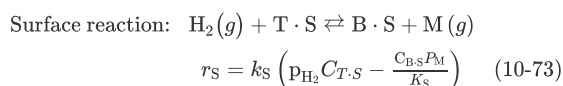
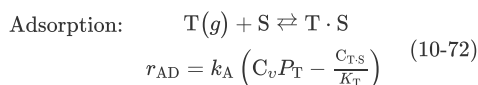
is in qualitative agreement with the data shown in Table 10-6.

10.4.2 Finding a Mechanism Consistent with Experimental Observations

We now propose a mechanism for the hydrodemethylation of toluene. Because the partial pressure of H_2 only appears in the numerator, we assume that the reaction follows an *Eley–Rideal mechanism*. Applying the Eley–Rideal mechanism, toluene is adsorbed on the surface and then reacts with hydrogen in the gas phase to produce benzene adsorbed on the surface and methane in the gas phase. Benzene is then desorbed from the surface. Because approximately 75%–80% of all heterogeneous reaction mechanisms are surface-reaction-limited rather than adsorption- or desorption-limited, we begin by assuming the reaction between adsorbed toluene and gaseous hydrogen to be reaction-rate-limited. Symbolically, this mechanism and associated rate laws for each elementary step are

Approximately 75% of all heterogeneous reaction mechanisms are surface-reaction-limited.

Proposed Mechanism



Eley–Rideal mechanism

The rate law for the surface reaction step is

$$r_S = k_S \left(P_{H_2} C_{T \cdot S} - \frac{C_{B \cdot S} P_M}{K_S} \right) \quad (10-73)$$

For surface-reaction-limited mechanisms we see that we need to replace $C_{T \cdot S}$ and $C_{B \cdot S}$ in Equation (10-73) by quantities that we can measure, for example, concentration or partial pressure.

For surface-reaction-limited mechanisms, we use the adsorption rate Equation (10-72) for toluene to obtain $C_{T,S}$ ¹⁷, that is,

¹⁷ See footnote 11 on page 466.

$$\frac{r_{AD}}{k_A} \approx 0$$

Then

$$C_{T,S} = K_T P_T C_v \quad (10-75)$$

and we use the desorption rate Equation (10-74) for benzene to obtain $C_{B,S}$:

$$\frac{r_D}{k_D} \approx 0$$

Then

$$C_{B,S} = K_B P_B C_v \quad (10-76)$$

The total concentration of sites is

$$C_t = C_v + C_{T,S} + C_{B,S} \quad (10-77)$$

Substituting Equations (10-75) and (10-76) into Equation (10-77) and rearranging, we obtain

$$C_v = \frac{C_t}{1 + K_T P_T + K_B P_B} \quad (10-78)$$

Perform a site balance to obtain C_v .

Next, substitute for $C_{T,S}$ and $C_{B,S}$, in terms of partial pressures and then substitute for in Equation (10-73) to obtain the rate law for the case when the reaction is surface-reaction-rate-limited

$$-r'_T = \frac{\overbrace{C_t k_S K_T}^k (P_{H_2} P_T - P_B P_M / K_P)}{1 + K_T P_T + K_B P_B} \quad (10-79)$$

We have shown by comparing runs 3 and 5 that we can neglect the reverse reaction, that is, the thermodynamic equilibrium constant K_p is very, very large. Consequently, we obtain

$$-r'_T = \frac{kP_{H_2}P_T}{1+K_BP_B+K_TP_T} \quad (10-80)$$

Rate law for Eley–Rideal surface-reaction-limited mechanism

Again we note that the adsorption equilibrium constant of a given species is exactly the reciprocal of the desorption equilibrium constant of that species.

10.4.3 Evaluation of the Rate-Law Parameters

In the original work on this reaction by Papp et al.,¹⁸ over 25 models were tested against experimental data, and it was concluded that the preceding mechanism and rate-limiting step (i.e., the surface reaction between adsorbed toluene and H_2 gas) is the correct one. Assuming that the reaction is essentially irreversible, the rate law for the reaction on clinoptilolite is

¹⁸ Ibid.

$$-r'_T = k \frac{P_{H_2}P_T}{1+K_BP_B+K_TP_T} \quad (10-80)$$

We now wish to determine how best to analyze the data to evaluate the rate-law parameters, k , K_T , and K_B . This analysis is referred to as *parameter estimation*.¹⁹ We will use nonlinear least squares which require initial estimates of the parameters. These estimates can be obtained from a linear least-squares analysis. To use linear least square, we now rearrange our rate law to obtain a linear relationship between our measured variables. For the rate law given by Equation (10-80), we see that if both sides of Equation (10-80) are divided by $P_{H_2}P_T$ and the equation is then inverted

¹⁹ See the Supplementary Reading for Chapter 10 on the CRE Web site (page 539) for a variety of techniques for estimating the rate-law parameters.

$$\frac{P_{H_2}P_T}{-r'_T} = \frac{1}{k} + \frac{K_BP_B}{k} + \frac{K_TP_T}{k} \quad (10-81)$$

Linearize the rate equation to extract the rate-law parameters.

The regression techniques described in [Chapter 7](#) could be used to determine the rate-law parameters by using the equation

$$Y_j = a_0 + a_1 X_{1j} + a_2 X_{2j}$$

A linear least-squares analysis of the data shown in [Table 10-6](#) is presented on the CRE Web site.

One can use the linearized least-squares analysis (PRS 7.3) to obtain initial estimates of the parameters k , K_T , K_B , in order to obtain convergence in nonlinear regression. However, in many cases it is possible to use a nonlinear regression analysis directly, as described in [Sections 7.5 and 7.6](#), and in [Example 10-1](#).

Example 10–1 Nonlinear Regression Analysis to Determine the Model Parameters k , K_B , and K_T and Site Concentration Ratio $C_{T,S}/C_{B,S}$

1. Use nonlinear regression, as discussed in Section 7.5, along with the data in Table 10-6, to find the best estimates of the rate-law parameters k , K_B , and K_T in Equation (10-80).
2. Write the rate law solely as a function of the partial pressures.
3. Find the ratio of the sites occupied by toluene, $C_{T,S}$, to those occupied by benzene, $C_{B,S}$, at 40% conversion of toluene.

Solution

The data from Table 10-6 were entered into the Polymath nonlinear least-squares program with the following modification. The rates of reaction in column 1 were multiplied by 10^{10} , so that each of the numbers in column 1 was entered directly (i.e., 71.0, 71.3, ...). The model equation was

$$\text{Rate} = \frac{kP_T P_{H_2}}{1 + K_B P_B + K_T P_T} \quad (\text{E10-1.1})$$

Living Example Problem

Following the step-by-step regression procedure in Chapter 7 and on the CRE Web site *Summary Notes*, we arrive at the following parameter values shown in Table E10-1.1 for this Living Example Problem (LEP). A tutorial is also given for LEP 10-1.

TABLE E10-1.1 PARAMETER VALUES

Source data points and calculated data points

	PT	PH2	PB	RATE	RATE calc	Delta RATE
1	1	1	0	71	71.0197	-0.0196996
2	1	1	0	71.3	71.0197	0.2803004
3	1	1	1	41.6	42.21931	-0.6193089
4	1	1	4	19.7	19.04705	0.6529537
5	1	1	1	42	42.21931	-0.2193089
6	1	1	5	17.1	16.10129	0.9987095
7	1	1	0	71.8	71.0197	0.7803004
8	1	2	0	142	142.0394	-0.0393992
9	1	4	0	284	284.0788	-0.0787985
10	0.5	1	0	47	47.64574	-0.6457351
11	1	1	0	71.3	71.0197	0.2803004
12	5	1	0	117	116.8977	0.102331
13	10	1	0	127	127.1662	-0.1661677
14	15	1	0	131	131.002	-0.0019833
15	20	1	0	133	133.008	-0.007997
16	1	1	1	41.8	42.21931	-0.4193089

Model: $\text{RATE} = k \cdot \text{PT} \cdot \text{PH}_2 / (1 + k_B \cdot \text{PB} + k_T \cdot \text{PT})$

Variable	Initial guess	Value	95% confidence
k	144.	144.7673	1.240307
k _B	1.4	1.390525	0.0457965
k _T	1.03	1.038411	0.0131585

Nonlinear regression settings
Max # iterations = 64

Precision

R ²	0.9999509
R ² adj	0.9999434
Rmsd	0.1128555
Variance	0.2508084

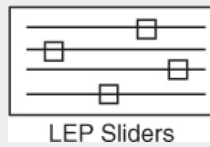
1. The best estimates are shown in the upper-right-hand box of Table E10-1.1.
2. Converting the rate law to kilograms of catalyst and minutes,

$$-r'_T = \frac{1.45 \times 10^{-8} P_T P_{H_2}}{1 + 1.39 P_B + 1.038 P_T} \frac{\text{mol T}}{\text{g-cat} \cdot \text{S}} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{60 \text{ s}}{\text{min}} \quad (\text{E10-1.2})$$

we have

$$-r'_T = \frac{8.7 \times 10^{-4} P_T P_{H_2}}{1 + 1.39 P_B + 1.038 P_T} \left(\frac{\text{mol T}}{\text{g-cat} \cdot \text{min}} \right) \quad (\text{E10-1.3})$$

Ratio of sites occupied by toluene to those occupied by benzene



3. After we have the adsorption constants, K_T and K_B , we can calculate the ratio of sites occupied by the various adsorbed species. For example, taking the ratio of Equation (10-75) to Equation (10-76), the ratio of toluene-occupied sites to benzene-occupied sites at 40% conversion is

$$\begin{aligned} \frac{C_{T,S}}{C_{B,S}} &= \frac{C_e K_T P_T}{C_e K_B P_B} = \frac{K_T P_T}{K_B P_B} = \frac{K_T P_{A0}(1-X)}{K_B P_{A0}X} \quad (\text{E10-1.4}) \\ &= \frac{K_T(1-X)}{K_B X} = \frac{1.038(1-0.4)}{1.39(0.4)} = 1.12 \end{aligned}$$

We see that at 40% conversion there are approximately 12% more sites occupied by toluene than by benzene. This fact is *common knowledge* to every chemical engineering student at Jofostan University, Riça, Jofostan.

Analysis: This example shows once again how to determine the values of rate-law parameters from experimental data using Polymath nonlinear regression. It also shows how to calculate the different fraction of sites, both vacant and occupied, as a function of conversion.

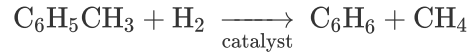
10.4.4 Reactor Design

Our next step is to express the partial pressures P_T , P_B , and P_{H_2} as a function of X , combine the partial pressures with the rate law, $-r'_A$, as a function of conversion, and carry out the integration of the packed-bed design equation

$$\frac{dX}{dW} = \frac{-r'_A}{F_{A0}} \quad (2-17)$$

Example 10–2 Catalytic Reactor Design

The hydrodemethylation of toluene is to be carried out in a PBR catalytic reactor.



The molar feed rate of toluene to the reactor is 50 mol/min, and the reactor inlet is at 40 atm and 640°C. The feed consists of 30% toluene, 45% hydrogen, and 25% inerts. Hydrogen is used in excess to help prevent coking. The pressure-drop parameter, α , is $9.8 \times 10^{-5} \text{ kg}^{-1}$.

1. Plot and analyze the conversion, the pressure ratio, p , and the partial pressures of toluene, hydrogen, and benzene as a function of PBR catalyst weight.
2. Determine the catalyst weight in a fluidized CSTR with a bulk density of 400 kg/m^3 (0.4 g/cm^3) to achieve 65% conversion.

Solution**1. PBR with pressure drop****1. Mole Balance:**

$$\frac{dF_T}{dW} = r'_T$$

$$\boxed{\frac{dX}{dW} = \frac{-r'_T}{F_{T0}}} \quad (\text{E10-2.1})$$

Balance on toluene (T), the limiting reactant

2. Rate Law: From Equation (E10-1.1) we have

$$\boxed{-r'_T = \frac{kP_{\text{H}_2}P_T}{1 + K_B P_B + K_T P_T}} \quad (\text{E10-2.2})$$

with $k = 0.00087 \text{ mol/atm}^2/\text{kg-cat/min}$, $K_B = 1.39 \text{ atm}^{-1}$, and $K_T = 1.038 \text{ atm}^{-1}$.

3. Stoichiometry:

$$\boxed{\begin{aligned} P_T &= C_T RT = C_{T0} RT_0 \left(\frac{1-X}{1+\varepsilon X} \right) P = P_{T0} \left(\frac{1-X}{1+\varepsilon X} \right) P \\ \varepsilon &= y_{T0} \delta = 0.3(0) = 0 \\ P &= \frac{P_0}{P_0} \\ P_T &= P_{T0}(1-X)p \\ P_{\text{H}_2} &= P_{T0}(\Theta_{\text{H}_2} - X)p \end{aligned}} \quad (\text{E10-2.3})$$

Relating Toluene (T) Benzene (B) Hydrogen (H₂)

$$\Theta_{H_2} = \frac{0.425}{0.30} = 1.5$$

$$P_{H_2} = P_{T0}(1.5 - X)P \quad (\text{E10-2.4})$$

$$P_B = P_{T0}X_P \quad (\text{E10-2.5})$$

Because $\varepsilon = 0$, we can use the integrated form of the pressure-drop term.

$$P = \frac{P_0}{P_0} = (1 - \alpha W)^{1/2} \quad (5-33)$$

P_0 = total pressure at the entrance

$$\alpha = 9.8 = 10^{-5} \text{ kg}^{-1}$$

Note that P_{T0} designates the inlet partial pressure of toluene. In this example, the inlet total pressure is designated P_0 to avoid any confusion. The inlet mole fraction of toluene is 0.3 (i.e., $y_{T0} = 0.3$), so that the inlet partial pressure of toluene is

$$P_{T0} = (0.3)(40) = 12 \text{ atm}$$

Pressure drop in PBRs is discussed in Section 5.5.

We now calculate the maximum catalyst weight we can have, such that the exiting pressure will not fall below atmospheric pressure (i.e., 1.0 atm) for the specified feed rate. This weight is calculated by substituting the entering pressure of 40 atm and the exiting pressure of 1 atm into Equation (5-33), that is,

$$p = \frac{P}{P_0} = (1 - \alpha W)^{1/2}$$

$$\frac{1}{40} = (1 - 9.8 \times 10^{-5} W)^{1/2}$$

$$W = 10197 \text{ kg}$$

Maximum catalyst weight for conditions given.

TABLE E10-2.1 POLYMATH PROGRAM AND OUTPUT

Differential equations

1 $d(X)/d(W) = -r_t/FTo$

Explicit equations

1 $FTo = 50$

2 $k = .00087$

3 $KT = 1.038$

4 $KB = 1.39$

5 $\alpha = 0.000098$

6 $Po = 40$

7 $PTo = 0.3*Po$

8 $p = (1-\alpha*W)^{0.5}$

9 $P = p*Po$

10 $PH2 = PTo*(1.5-X)*p$

11 $PB = PTo*X*p$

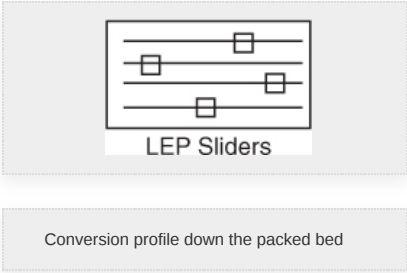
12 $PT = PTo*(1-X)*p$

13 $rt = -k*PT*PH2/(1+KB*PB+KT*PT)$

14 $RATE = -rt$

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	alpha	9.8E-05	9.8E-05
2	FTo	50.	50.
3	k	0.00087	0.00087
4	KB	1.39	1.39
5	KT	1.038	1.038
6	p	1.	0.1414214
7	P	40.	5.656854
8	PB	0	1.157913
9	PH2	18.	1.387671
10	Po	40.	40.
11	PTo	12.	0.5391433
12	PTo	12.	12.
13	RATE	0.0139655	0.0002054
14	rt	-0.0139655	-0.0002054
15	W	0	10000.
16	X	0	0.6823067



4. **Evaluate:** Consequently, we will set our final weight at 10000 kg and determine the conversion profile as a function of catalyst weight up to this value. Equations (E10-2.1)–(E10-2.5) are shown in the Polymath program in Table E10-2.1. The conversion is shown as a function of catalyst weight in Figure E10-2.1, and profiles of the partial pressures of toluene, hydrogen, and benzene are shown in Figure E10-2.2. We note that the pressure drop causes (cf. Equation E10-2.5) the partial pressure of benzene to go through a maximum as one traverses the reactor.

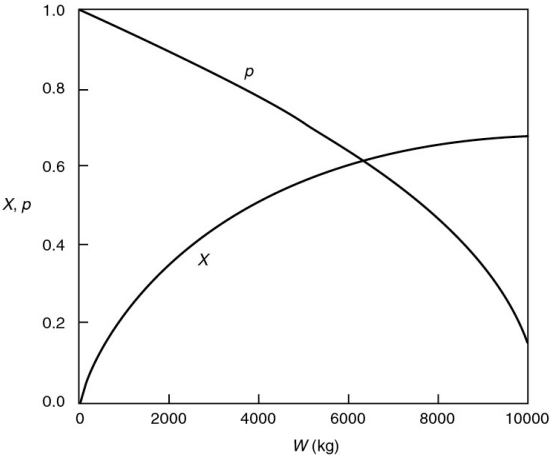
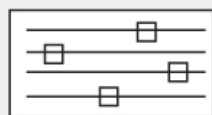


Figure E10-2.1 Conversion and pressure ratio profiles.



LEP Sliders

Note the partial pressure of benzene goes through a maximum. Why?

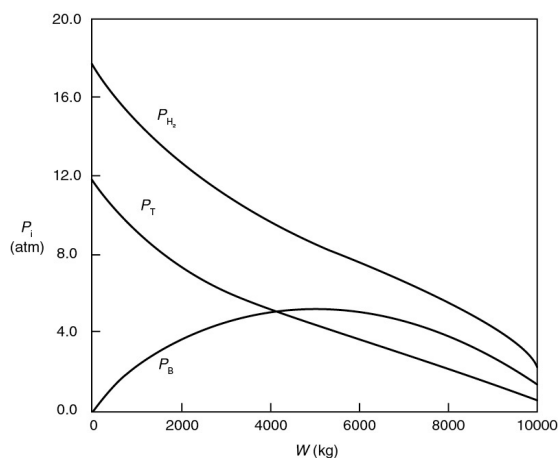


Figure E10-2.2 Partial pressure profiles.

If one had neglected ΔP it could have been very embarrassing.

See YouTube video, "Reaction Engineering Gone Wrong," accessible from the CRE Web site home page.

PBR Analysis: For the case of no pressure drop, the conversion that would have been achieved with 10000 kg of catalyst would have been 79%, compared with 68.2% when there is pressure drop in the reactor. To carry out this calculation, for the case of no pressure drop, we use the Polymath Living Example Program (**LEP**) on the CRE Web site and simply multiply the pressure-drop parameter by zero, that is, line (5) would read $\alpha = 0.000098 \cdot 0$. For the feed rate given, eliminating or minimizing pressure drop would increase the production of benzene by up to 61 million pounds per year! Finally, we note in [Figure E10-2.2](#) that the partial pressure of benzene (P_B) goes through a maximum. This maximum can be explained by recalling that P_B is just the product of the benzene mole fraction (y_B) times the total pressure (P) (i.e., $P_B = y_B P_T$). Near the middle to end of the bed, benzene is no longer being formed so that y_B stops increasing. However, because of the pressure drop, the total pressure decreases and, as a result, so does P_B .

2. “Fluidized” CSTR

We will now calculate the fluidized CSTR catalyst weight necessary to achieve the same (ca.) conversion as in the packed-bed reactor at the same operating conditions. The bulk density in the fluidized reactor is 0.4 g/cm^3 with $p = 1$. The design equation is

1. Mole Balance:

<u>In</u>	–	<u>Out</u>	+	<u>Gen</u>	=	<u>Accum</u>
F_T	–	F_T	+	$r'_T W$	=	0

Rearranging

$$W = \frac{F_{T0} - F_T}{-r'_T} = \frac{F_{T0} X}{-r'_T} \quad (\text{E10-2.6})$$

2. Rate Law and

3. Stoichiometry same as in part (a) PBR calculation.

4. Combine and Evaluate: Writing Equation (E10-2.2) in terms of conversion (E10-2.3) and then substituting $X = 0.65$ and $P_{T0} = 12 \text{ atm}$, we have

$$-r'_T = \frac{8.7 \times 10^{-4} P_T P_{H_2}}{1 + 1.39 P_B + 1.038 P_T} = \frac{8.7 \times 10^{-4} P_{T0}^2 (1-X)(1.5-X)}{1 + 1.39 P_{T0} X + 1.038 P_{T0} (1-X)} = 2.3 \times 10^{-3} \frac{\text{mol}}{\text{kg-cat-min}}$$

$$W = \frac{F_{T0} X}{-r'_T} = \frac{(50 \text{ mol T/min})(0.65)}{2.3 \times 10^{-3} \text{ mol T/kg cat-min}}$$

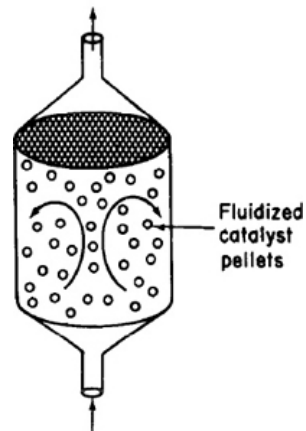
$W = 1.41 \times 10^4 \text{ kg of catalyst}$

The corresponding reactor volume is

$$V = \frac{W}{\rho_b} = \frac{1.41 \times 10^4 \text{ kg}}{400 \text{ kg/m}^3} = 35.25 \text{ m}^3$$

This volume would correspond to a cylindrical reactor 2 m in diameter and 10 m high.

Fluidized CSTR



Analysis: This example used real data and the CRE algorithm to design a PBR and CSTR. An important point is that it showed how one could be embarrassed by not including pressure drop in the design of a packed-bed reactor. We also note that for both the PBR and fluidized CSTR, the values of the catalyst weight and reactor volume are quite high, especially for the low feed rates given. *Consequently, the temperature of the reacting mixture should be increased to reduce the catalyst weight, provided that side reactions and catalyst decay do not become a problem at higher temperatures.*

How can the weight of catalyst be reduced?

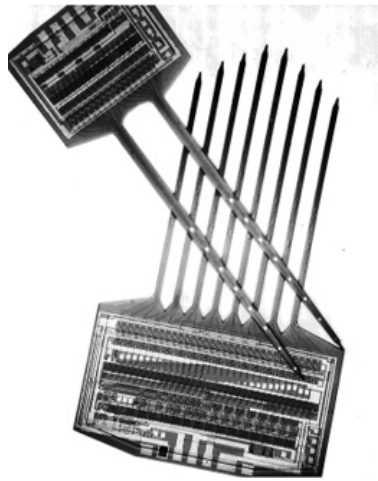
Raise the temperature?

Example 10-2 illustrated the major activities pertinent to catalytic reactor design described earlier in Figure 10-6. In this example, the rate law was extracted directly from the data and then a mechanism was found that was consistent with experimental observation. Conversely, developing a feasible mechanism may guide one in the synthesis of the rate law.

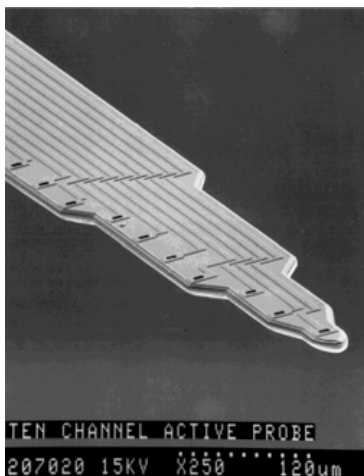
10.5 REACTION ENGINEERING IN MICROELECTRONIC FABRICATION

10.5.1 Overview

We now extend the principles of the preceding sections to one of the newer technologies in chemical engineering. Chemical engineers are now playing an important role in the electronics industry. Specifically, they are becoming more involved in the manufacture of electronic and photonic devices, recording materials, and especially microfluidics and medical lab-on-a-chip devices.



Surface reactions play an important role in the manufacture of microelectronic devices. One of the single most important developments of the twentieth century was the invention of the integrated circuit. Advances in the development of integrated circuitry have led to the production of circuits that can be placed on a single semiconductor chip the size of a pinhead and perform a wide variety of tasks by controlling the electron flow through a vast network of channels. These channels, which are made from semiconductors such as silicon, gallium arsenide, indium phosphide, and germanium, have led to the development of a multitude of novel microelectronic devices. Examples of microelectronic sensing devices manufactured using chemical reaction engineering principles are shown in the left-hand margin.



The manufacture of an integrated circuit requires the fabrication of a network of pathways for electrons. The principal reaction engineering steps of the fabrication process include depositing material on the surface of a material called a *substrate* (e.g., by chemical vapor deposition, abbreviated as CVD), changing the conductivity of regions of the surface (e.g., by boron doping or ion implantation), and removing unwanted material (e.g., by etching). By applying these steps systematically, miniature electronic circuits can be fabricated on very small semiconductor chips. The fabrication of microelectronic devices may include as few as 30 or as many as 200 individual steps to produce chips with up to 10^9 elements per chip. An abbreviated discussion of the steps involved to produce a typical metal-oxide semiconductor field-effect transition (MOSFET) is given in the *Additional Material* for this chapter on the Web site (http://umich.edu/~elements/6e/10chap/pdf/Steps_in_Microchip_Fabrication.pdf).

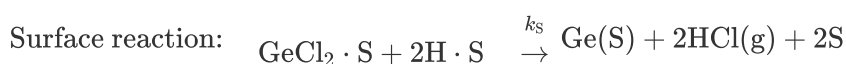
10.5.2 Chemical Vapor Deposition (CVD)

The mechanisms by which CVD occurs are very similar to those of heterogeneous catalysis discussed earlier in this chapter. The reactant(s) adsorbs on the surface and then reacts on the surface to form a new surface. This process may be followed by a desorption step, depending on the particular reaction.

Ge used in solar cells

The growth of a germanium epitaxial film as an interlayer between a gallium arsenide layer and a silicon layer has received attention in the microelectronics industry.²⁰ Epitaxial germanium is also an important material in the fabrication of tandem solar cells. The growth of germanium films can be accomplished by CVD. A proposed mechanism is

²⁰ H. Ishii and Y. Takahashi, *J. Electrochem. Soc.*, 135, p. 1539.



Mechanism

At first it may appear that a *site* has been lost when comparing the right- and left-hand sides of the surface reaction step. However, the newly formed germanium atom on the right-hand side is a site for the future adsorption of $\text{H}_2(\text{g})$ or $\text{GeCl}_2(\text{g})$, and there are three sites on both the right- and left-hand sides of the surface reaction step. These sites are shown schematically in Figure 10-20.

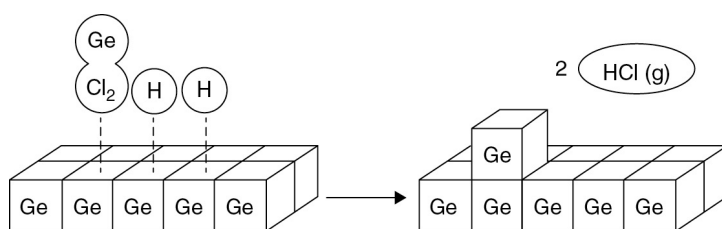


Figure 10-20 Manufacture of phthalic anhydride.

The surface reaction between adsorbed molecular hydrogen and germanium dichloride is believed to be rate-limiting. The reaction follows an elementary rate law with the rate being proportional to the fraction of the surface covered by GeCl_2 times the square of the fraction of the surface covered by molecular hydrogen.

Rate law for rate-limiting step

$$r''_{\text{Dep}} = k_S f_{\text{GeCl}_2} f_{\text{H}}^2 \quad (10-82)$$

where

r''_{Dep} = deposition rate per unit surface area, nm/s

k_S = surface specific reaction rate, nm/s

f_{GeCl_2} = fraction of the surface occupied by germanium dichloride

f_{H} = fraction of the surface covered by molecular hydrogen

The deposition rate (film growth rate) is usually expressed in nanometers per second and is easily converted to a molar rate ($\text{mol/m}^2 \cdot \text{s}$) by multiplying by the molar density of solid germanium (mol/m^3).

The difference between developing CVD rate laws and rate laws for catalysis is that the site concentration (e.g., C_v) is replaced by the fractional surface area coverage (e.g., the fraction of the surface that is vacant, f_v). The total fraction of surface available for adsorption should, of course, add up to 1.0.

Area balance

Fractional area balance:
$$f_v + f_{\text{GeCl}_2} + f_{\text{H}} = 1 \quad (10-83)$$

We will first focus our attention on the adsorption of GeCl_2 .

The rate of *jumping on* to the surface is proportional to the partial pressure of GeCl_2 , P_{GeCl_2} , and the fraction of the surface that is vacant, f_v and the rate of *jumping off* is proportional to fraction area covered with GeCl_2 . The net rate of GeCl_2 adsorption is

$$r_{\text{AD}} = k_A \left(f_v P_{\text{GeCl}_2} - \frac{f_{\text{GeCl}_2}}{K_A} \right) \quad (10-84)$$

Since the surface reaction is rate-limiting, in a manner analogous to catalysis reactions, we have for the adsorption of GeCl_2

Adsorption of GeCl_2 not rate-limiting

$$\frac{r_{\text{AD}}}{k_{\text{A}}} \approx 0$$

Solving Equation (10-84) for the fractional surface coverage of GeCl_2 gives

$$f_{\text{GeCl}_2} = f_{\text{v}} K_{\text{A}} P_{\text{GeCl}_2} \quad (10-85)$$

For the dissociative adsorption of hydrogen on the Ge surface, the equation analogous to Equation (10-84) is

$$r_{\text{ADH}_2} = k_{\text{H}} \left(P_{\text{H}_2} f_{\text{v}}^2 - \frac{f_{\text{H}}^2}{K_{\text{H}}} \right) \quad (10-86)$$

Since the surface reaction is rate-limiting

Adsorption of H_2 is not rate-limiting.

$$\frac{r_{\text{ADH}_2}}{k_{\text{H}}} \approx 0$$

Then

$$f_{\text{H}} = f_{\text{v}} \sqrt{K_{\text{H}} P_{\text{H}_2}} \quad (10-87)$$

Recalling the rate of deposition of germanium, we substitute for f_{GeCl_2} and f_{H} in Equation (10-82) to obtain

$$r''_{\text{Dep}} = f_{\text{v}}^3 k_{\text{S}} K_{\text{A}} P_{\text{GeCl}_2} K_{\text{H}} P_{\text{H}_2} \quad (10-88)$$

We solve for f_{v} in an identical manner to that for C_{v} in heterogeneous catalysis. Substituting Equations (10-85) and (10-87) into Equation (10-83) gives

$$f_{\text{v}} + f_{\text{v}} \sqrt{K_{\text{H}} P_{\text{H}_2}} + f_{\text{v}} K_{\text{A}} P_{\text{GeCl}_2} = 1$$

Rearranging yields

$$f_{\text{v}} = \frac{1}{1 + K_{\text{A}} P_{\text{GeCl}_2} + \sqrt{K_{\text{H}} P_{\text{H}_2}}} \quad (10-89)$$

Finally, substituting for f_{v} in Equation (10-88), we find that

$$r''_{\text{Dep}} = \frac{k_S K_H K_A P_{\text{GeCl}_2} P_{\text{H}_2}}{\left(1 + K_A P_{\text{GeCl}_2} + \sqrt{K_H P_{\text{H}_2}}\right)^3}$$

and lumping K_A , K_H , and k_S into a specific reaction rate k' yields

Rate of deposition of Ge

$$r''_{\text{Dep}} = \frac{k' P_{\text{GeCl}_2} P_{\text{H}_2}}{\left(1 + K_A P_{\text{GeCl}_2} + \sqrt{K_H P_{\text{H}_2}}\right)^3} \quad (10-90)$$

We now need to relate the partial pressure of GeCl_2 to the partial pressure of GeCl_4 in order to calculate the conversion of GeCl_4 . If we assume that the gas-phase reaction

Equilibrium in gas phase



is in equilibrium, we have

$$K_P = \frac{P_{\text{GeCl}_2} P_{\text{Cl}_2}}{P_{\text{GeCl}_4}}$$

$$P_{\text{GeCl}_2} = \frac{P_{\text{GeCl}_4}}{P_{\text{Cl}_2}} \cdot K_P$$

and if hydrogen is weakly adsorbed ($\sqrt{K_H P_{\text{H}_2}} < 1$), and letting $k = k' K_P$, we obtain the rate of deposition as

$$r''_{\text{Dep}} = \frac{k P_{\text{GeCl}_4} P_{\text{H}_2} P_{\text{Cl}_2}^2}{\left(P_{\text{Cl}_2} + K_A K_P P_{\text{GeCl}_4}\right)^3} \quad (10-91)$$

Rate of deposition of Ge when H_2 is weakly adsorbed

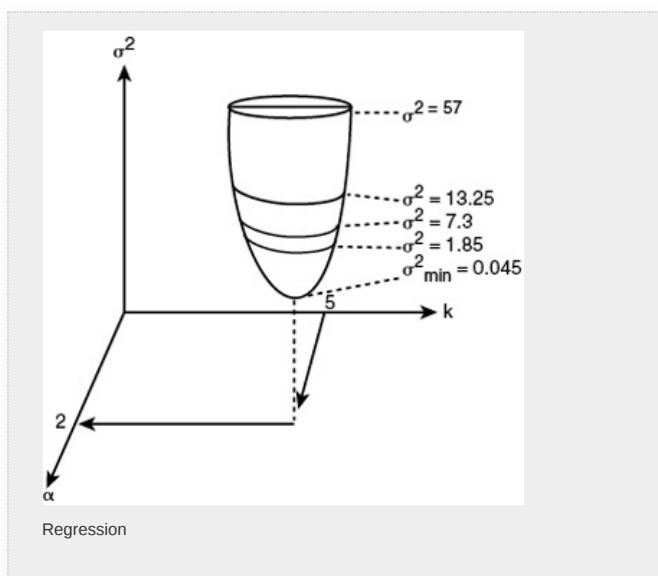
We now can use stoichiometry to express each of the species' partial pressures in terms of conversion and the entering partial pressure of GeCl_4 , $P_{\text{GeCl}_4,0}$, and then proceed to calculate the conversion.

It should be noted that it is possible that GeCl_2 may also be formed by the reaction of GeCl_4 and a Ge atom on the surface,

in which case a different rate law would result.

10.6 MODEL DISCRIMINATION

We have seen that for each mechanism and each rate-limiting step we can derive a rate law. Consequently, if we had *three* possible mechanisms and *three* rate-limiting steps for each mechanism, we would have *nine* possible rate laws to compare with the experimental data. We will use the regression techniques discussed in [Chapter 7](#) to identify which model equation best fits the data by choosing the one with the smaller sums of squares and/or carrying out an F-test. We could also compare the nonlinear regression residual plots for each model, which not only show the error associated with each data point but also show if the error is randomly distributed or if there is a trend in the error. If the error is randomly distributed, this result is an additional indication that the correct rate law has been chosen.



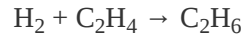
We need to raise a caution here about choosing the model with the smallest sums of squares. The caution is that the model parameter values that give the smallest sum must be realistic. In the case of heterogeneous catalysis, *all values of the adsorption equilibrium constants must be positive*. In addition, if the temperature dependence is given, because adsorption is exothermic, the adsorption equilibrium constant

must decrease with increasing temperature. To illustrate these principles, let's look at the following example.



Example 10–3 Hydrogenation of Ethylene to Ethane

The hydrogenation (H) of ethylene (E) to form ethane (EA),



is carried out over a cobalt molybdenum catalyst (*Collect. Czech. Chem. Commun.*, 51, 2760). Carry out a nonlinear regression analysis to determine which of the following rate laws best describes the data in [Table E10-3.1](#).

$$\begin{aligned} \text{(a)} \quad -r'_E &= \frac{kP_E P_H}{1 + K_{EA} P_{EA} + K_E P_E} & \text{(C)} \quad -r'_E &= \frac{kP_E P_E}{(1 + K_E P_E)^2} \\ \text{(b)} \quad -r'_E &= \frac{kP_E P_H}{1 + K_E P_E} & \text{(d)} \quad -r'_E &= kP_E^a P_H^b \end{aligned}$$

Procedure

- Enter data
- Enter model
- Make initial estimates of parameters
- Run regression
- Examine parameters and variance
- Observe error distribution
- Choose model

TABLE E10-3.1 DIFFERENTIAL REACTOR DATA

Run Number	Reaction Rate (mol/kg-cat. · s)	P_E (atm)	P_{EA} (atm)	P_H (atm)
1	1.04	1	1	1
2	3.13	1	1	3
3	5.21	1	1	5
4	3.82	3	1	3
5	4.19	5	1	3
6	2.391	0.5	1	3

7	3.867	0.5	0.5	5
8	2.199	0.5	3	3
9	0.75	0.5	5	1



Summary Notes

Solution

Polymath was chosen as the software package to solve this problem. The data in Table E10-3.1 were entered into the program. A screen-shot-by-screen-shot tutorial and set of instructions on how to carry out the regression is given on the CRE Web site, at the end of the *Summary Notes for Chapter 7* (<http://www.umich.edu/~elements/6e/07chap/summary.html>). After entering the data and following the step-by-step procedures, the results shown in Table E10-3.2 were obtained.

TABLE E10-3.2 RESULTS OF THE POLYMATH
NONLINEAR REGRESSION

Model (a)			Model (b)		
Model: RATE = $k^*P_E^*P_H/(1+K_EA^*P_{EA}+K_E^*P_E)$			Model: RATE = $k^*P_E^*P_H/(1+K_E^*P_E)$		
Variable	Value	95% confidence	Variable	Value	95% confidence
k	3.3478805	0.2922517	k	3.1867851	0.287998
K_{EA}	0.0428419	0.0636262	K_E	2.1013363	0.2638835
K_E	2.2110797	0.2392585			
Nonlinear regression settings Max # iterations = 64			Nonlinear regression settings Max # iterations = 64		
Precision R^2 = 0.998321 R^2_{adj} = 0.9977614 Rmsd = 0.0191217 Variance = 0.0049361			Precision R^2 = 0.9975978 R^2_{adj} = 0.9972547 Rmsd = 0.022872 Variance = 0.0060534		

Model (c)			Model (d)		
Model: RATE = $k^*P_E^*P_H/(1+K_E^*P_E)^2$			Model: RATE = $k^*P_E^*a^*P_H^b$		
Variable	Value	95% confidence	Variable	Value	95% confidence
k	2.0087761	0.2661838	k	0.8940237	0.2505474
K_E	0.3616652	0.0623045	a	0.2584412	0.0704628
			b	1.0615542	0.2041339
Nonlinear regression settings Max # iterations = 64			Nonlinear regression settings Max # iterations = 64		
Precision R^2 = 0.9752762 R^2_{adj} = 0.9717442 Rmsd = 0.0733772 Variance = 0.0623031			Precision R^2 = 0.9831504 R^2_{adj} = 0.9775338 Rmsd = 0.0605757 Variance = 0.0495372		

Model (a) Single site, surface-reaction, rate-limited with hydrogen weakly adsorbed



From Table E10-3.2 data, we can obtain

$$-r'_E = \frac{3.348 P_E P_H}{1 + 0.043 P_{EA} + 2.21 P_E} \quad (\text{E10-3.1})$$

We now examine the sums of squares (variance) and range of variables themselves. The sums of squares is reasonable and, in fact, the smallest of all the models at 0.0049. However, let's look at K_{EA} . We note that the value for the 95% confidence limit of ± 0.0636 is greater than the nominal value of $K_{EA} = 0.043 \text{ atm}^{-1}$ itself (i.e., $K_{EA} = 0.043 \pm 0.0636$). The 95% confidence limit means that if the experiment were run 100 times and then 95 times it would fall within the range $(-0.021) < K_{EA} < (0.1066)$. Because K_{EA} can never be

negative, we are going to reject this model. Consequently, we set $K_{EA} = 0$ and proceed to model (b).

Model (b) Single site, surface-reaction, rate-limited with ethane and hydrogen weakly adsorbed

From Table E10-3.2 we can obtain

$$-r'_E = \frac{3.187 P_E P_H}{1 + 2.1 P_E} \quad (\text{E10-3.2})$$

The value of the adsorption constant $K_E = 2.1 \text{ atm}^{-1}$ is reasonable and is not negative within the 95% confidence limit. Also, the variance is small at $\sigma_B^2 = 0.0061$.

Model (c) Dual site, surface-reaction, rate-limited with hydrogen and ethane weakly adsorbed From Table E10-3.2 we can obtain

$$-r'_E = \frac{2.0 P_E P_H}{(1 + 0.36 P_E)^2} \quad (\text{E10-3.3})$$

While K_E is small, it never goes negative within the 95% confidence interval. The variance of this model at $\sigma_B^2 = 0.0623$ is much larger than the other models. Comparing the variance of model (c) with model (b)

$$\frac{\sigma_C^2}{\sigma_B^2} = \frac{0.0623}{0.0061} = 10.2$$

We see that the σ_C^2 is an order of magnitude greater than σ_B^2 , and therefore we eliminate model (c).²¹

²¹ See G. F. Froment and K. B. Bischoff, *Chemical Reaction Analysis and Design*, 2nd ed. New York: Wiley, 1990, p. 96.

Model (d) Empirical

Similarly for the power-law model, we obtain from Table E10-3.2

$$-r'_E = 0.894 P_E^{0.26} P_H^{1.06} \quad (\text{E10-3.4})$$

As with model (c), the variance is quite large compared to model (b)

$$\frac{\sigma_D^2}{\sigma_B^2} = \frac{0.049}{0.0061} = 8.03$$

So we also eliminate model (d). For heterogeneous reactions, Langmuir-Hinshelwood rate laws are preferred over power-law models.



Analysis: *Choose the Best Model.* In this example, we were presented with four rate laws and were asked which law best fits the data. Because all the parameter values are realistic for **model (b)** and the sums of squares are significantly smaller for **model (b)** than for the other models, we choose **model (b)**. We note again that there is a caution we need to point out regarding the use of regression! One cannot simply carry out a regression and then choose the model with the lowest value of the sums of squares. If this were the case, we would have chosen **model (a)**, which had the smallest sums of squares of all the models with $\sigma^2 = 0.0049$. However, one must consider the physical realism of the parameters in the model. In **model (a)**, the 95% confidence interval was greater than the parameter itself, thereby yielding negative values of the parameter, K_{AE} , which is physically impossible.

10.7 CATALYST DEACTIVATION

In designing fixed and ideal fluidized bed catalytic reactors, we have assumed up to now that the activity of the catalyst remains constant throughout the catalyst's life. That is, the total concentration of active sites, C_t , accessible to the reaction does not change with time. Unfortunately, Mother Nature is not so kind as to allow this behavior to be the case in most industrially significant catalytic reactions. One of the most insidious problems in catalysis is the loss of catalytic activity that occurs as the reaction takes place on the catalyst. A wide variety of mechanisms have been proposed by Butt and Petersen, to explain and model catalyst deactivation.^{22,23,24}

²² J. B. Butt and E. E. Petersen, *Activation, Deactivation and Poisoning of Catalysts*, New York: Academic Press, 1988.

²³ D. T. Lynch and G. Emig, *Chem. Eng. Sci.*, 44(6), 1275–1280 (1989).

²⁴ R. Hughes, *Deactivation of Catalysts*, San Diego: Academic Press, 1984.

Catalytic deactivation adds another level of complexity to sorting out the reaction-rate law parameters and pathways. In addition, we need to make adjustments for the decay of the catalysts in the design of catalytic reactors. *However, please don't worry*, this adjustment is usually made by a quantitative specification of the catalyst's activity, $a(t)$. In analyzing reactions over decaying catalysts, we divide the reactions into two categories: *separable kinetics* and *non-separable kinetics*. In separable kinetics, we separate the rate law and activity

Separable kinetics: $-r'_A = a(\text{Past history}) \times -r'_A(\text{Fresh catalyst})$

When the kinetics and activity are *separable*, it is possible to study catalyst decay and reaction kinetics independently. However, nonseparability

Nonseparable kinetics: $-r'_A = -r'_A(\text{Past history, fresh catalyst})$

must be accounted for by assuming the existence of a nonideal surface or by describing deactivation by a mechanism composed of several elementary steps.^{23,24}

We shall consider only *separable kinetics* and define the activity of the catalyst at time t , $a(t)$, as the ratio of the rate of reaction on a catalyst that has been used for a time t to the rate of reaction on a fresh catalyst ($t = 0$):

$a(t)$: catalyst activity

$$a(t) = \frac{-r'_A(t)}{-r'_A(t=0)} \quad (10-92)$$

Because of the catalyst decay, the activity decreases with time and a typical curve of the activity as a function of time is shown in Figure 10-21.

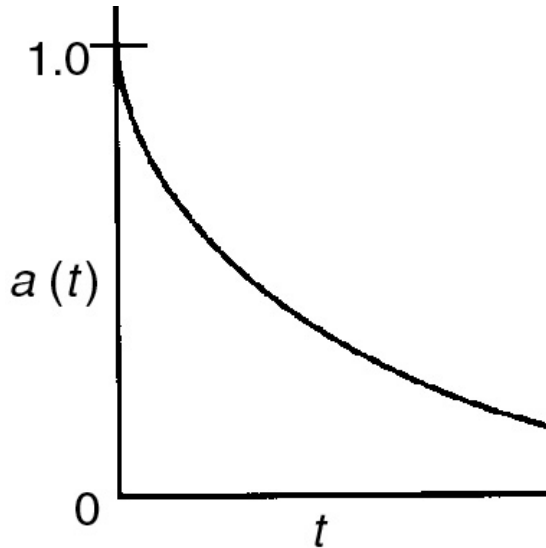


Figure 10-21 Activity as a function of time.

Combining Equations (10-92) and (3-2), the rate of disappearance of reactant A on a catalyst that has been utilized for a time t is

Reaction-rate law accounting for catalyst activity

$$-r'_A = a(t)k(T) f_n(C_A, C_B, \dots, C_P) \quad (10-93)$$

where $a(t)$ = catalytic activity, time-dependent

$k(T)$ = specific reaction rate, temperature-dependent

C_i = gas-phase concentration of reactants, products, or contaminant

The rate of catalyst decay, r_d , can be expressed in a rate law analogous to Equation (10-93)

$$r_d = -\frac{da}{dt} = p[a(t)]k_d(T) h(C_A, \dots, C_P) \quad (10-94)$$

Catalyst decay rate law

For example, $p[a(t)] = [a(t)]^2$

where $p[a(t)]$ is some function of the catalyst activity, k_d is the specific decay constant, and $h(C_i)$ is the functionality of rate of decay, r_d , on the species concentrations in the reacting mixture. For the cases presented in this chapter, this functionality either will be independent of concentration (i.e., $h = 1$) or as in the case of catalytic poisoning it could be a linear function of species concentration (i.e., $h = C_i$).

The functionality of the activity term, $p[a(t)]$, in the decay law can take a variety of forms. For example, for a first-order decay

$$p(a) = a \quad (10-95)$$

and for a second-order decay

$$p(a) = a^2 \quad (10-96)$$

The particular function, $p(a)$, will vary with the gas catalytic system being used and the reason or mechanism for catalytic decay.

10.7.1 Types of Catalyst Deactivation

There are three categories into which the loss of catalytic activity can traditionally be divided: *sintering* or *aging*, *fouling* or *coking*, and *poisoning*.

- Sintering
- Fouling
- Poisoning

10.7.1A Deactivation by Sintering (Aging)²⁵

²⁵ See G. C. Kuczynski, ed., *Sintering and Catalysis*, vol. 10 of *Materials Science Research*, New York: Plenum Press, 1975.

Sintering, also referred to as aging, is the loss of catalytic activity due to a loss of active surface area resulting from the

prolonged exposure to high gas-phase temperatures. The active surface area may be lost either by growth of the metals deposited on the support or by narrowing or closing of the pores inside the catalyst pellet. A change in the surface structure may also result from either surface recrystallization or the formation or elimination of surface defects (active sites). The reforming of heptane over platinum on alumina is an example of catalyst deactivation as a result of sintering.

Figure 10-22 shows the loss of surface area resulting from the flow of the solid porous catalyst support at high temperatures to cause pore closure. Figure 10-23 shows growth of small metal crystallites into larger particles where the interior atoms are not accessible to reactions thereby leading to a loss of metal surface area of the catalyst. Professor Abhaya Datye has recently identified that the dominant mechanism for this sintering of industrial catalysts involves the transport of mobile species, a process called Ostwald ripening.²⁶

²⁶ T. W. Hansen, A. T. Delariva, S. R. Challa, and A. K. Datye, "Sintering of Catalytic Nanoparticles: Particle Migration or Ostwald Ripening?" *Acc. Chem. Res.*, 46(8), 17-20–17-30 (2013).

Sintering is usually negligible at temperatures below 40% of the melting temperature of the solid.²⁷ However, sintering can occur at lower temperatures when mobile species are generated through a reaction of the solid with the gas phase, for example the formation of volatile PtO_2 due to reaction of Pt and O_2 .

²⁷ R. Hughes, *Deactivation of Catalysts*, San Diego: Academic Press, 1984.

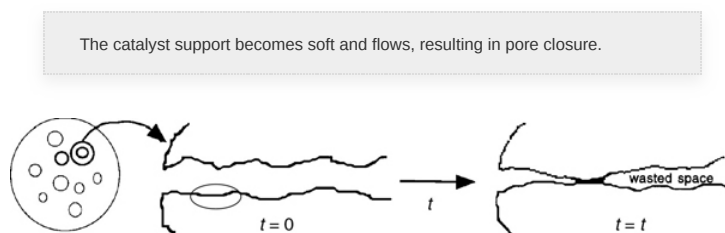


Figure 10-22 Decay by sintering: pore closure; loss of reactive surface area.

The catalyst support becomes soft and flows, resulting in pore closure.

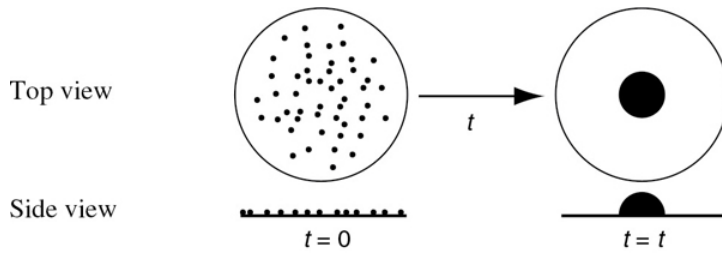


Figure 10-23 Decay by sintering: agglomeration of deposited metal sites; loss of reactive surface area.

The atoms move along the surface and agglomerate.

Deactivation by sintering may in some cases be a function of the mainstream gas concentration. Although other forms of the sintering decay rate laws exist, one of the most commonly used sintering decay laws is second order with respect to the present activity

$$r_d = k_d a^2 = -\frac{da}{dt} \quad (10-97)$$

Integrating, with $a = 1$ at time $t = 0$, for constant k_d during the time t yields

Sintering: second-order decay

$$a(t) = \frac{1}{1 + k_d t} \quad (10-98)$$

The amount of sintering is usually measured in terms of the active surface area of the catalyst S_a

$$S_a = \frac{S_{a0}}{1 + k_d t} \quad (10-99)$$

The sintering decay constant, k_d , follows the Arrhenius equation

$$k_d = k_d(T_0) \exp \left[\frac{E_d}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right] \quad (10-100)$$

Minimizing sintering

The decay activation energy, E_d , for the reforming of heptane on $\text{Pt}/\text{Al}_2\text{O}_3$ is on the order of 70 kcal/mol, which is rather high. As mentioned earlier, sintering can be reduced by keeping the temperature below 0.3–0.4 times the metal's melting point temperature, that is, ($T < 0.3 T_{\text{melting}}$).

For the case where the temperature varies during the reaction time t , Equations (10-93), (10-94), along with the energy balance must be solved simultaneously.

We will now stop and consider reactor design for a fluid–solid system with decaying catalyst. To analyze these reactors, we only add one step to our algorithm; that is, determine the catalyst decay law. The sequence is shown here.

The algorithm

Mole balance	→	Reaction-rate law	→	<i>Decay rate law</i>	→
Stoichiometry	→	Combine and solve	→	Numerical techniques	

Example 10–4 Calculating Conversion with Catalyst Decay in Batch Reactors

The first-order isomerization



is being carried out isothermally in a batch reactor on a catalyst that is decaying as a result of aging. Derive an equation for conversion as a function of time.

Solution

1. Mol Balance:

$$N_{A0} \frac{dX_d}{dt} = -r'_A W \quad (\text{E10-4.1})$$

where X_d is the conversion of A when the catalyst is decaying.

2. Reaction-Rate Law:

$$-r'_A = k' a(t) C_A \quad (\text{E10-4.2})$$

3. Decay Law: For second-order decay by sintering:

$$a(t) = \frac{1}{1 + k_d t} \quad (10-98)$$

One extra step (number 3) is added to the algorithm.



4. Stoichiometry:

$$C_A = C_{A0} (1 - X_d) = \frac{N_{A0}}{V} (1 - X_d) \quad (\text{E10-4.3})$$

5. Combining gives us

$$\frac{dX_d}{dt} = k' (1 - X_d) a \frac{W}{V} \quad (\text{E10-4.4})$$

Let $k = k'W/V$. Substituting for catalyst activity a , we have

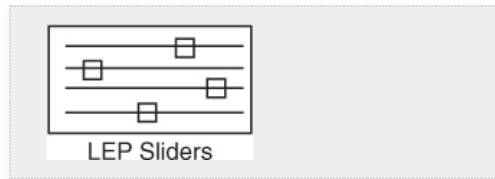
$$\frac{dX_d}{dt} = k(1 - X_d)a = k \frac{(1 - X_d)}{(1 + k_d t)} \quad (\text{E10-4.5})$$

where X_d is the conversion when there is decay. We want to compare the conversion with and without catalyst decay.

For no decay $k_d = 0$

$$\frac{dX}{dt} = k(1 - X)$$

The Polymath program and a comparison of the conversion with decay X_d and without decay X are shown below.



POLYMATH Report

Ordinary Differential Equations

Calculated values of DEQ variables

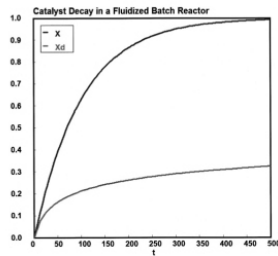
	Variable	Initial value	Final value
1	k	0.01	0.01
2	kd	0.1	0.1
3	t	0	500.
4	X	0	0.9932621
5	Xd	0	0.3250945

Differential equations

- 1 $d(X)/d(t) = k^*(1-X)$
- 2 $d(X_d)/d(t) = k^*(1-X_d)/(1+kd*t)$

Explicit equations

- 1 $k = 0.01$
- 2 $kd = 0.1$



Analytical Solution

One can also obtain an analytical solution for this reaction order with catalyst decay. Separating variables and integrating yields

$$\int_0^x \frac{dX_d}{1-X_d} = k \int_0^t \frac{dt}{1+k_d t} \quad (\text{E10-4.6})$$

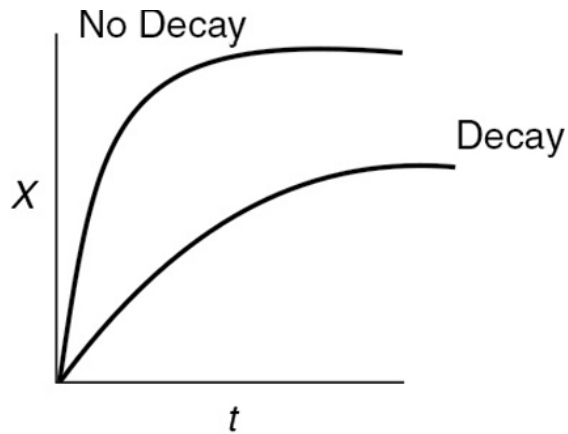
$$\ln \frac{1}{1-X_d} = \frac{k}{k_d} = \ln(1 + k_d t) \quad (\text{E10-4.7})$$

6. **Solving** for the conversion X_d at any time, t , in a decaying catalyst we find that

$$X_d = 1 - \frac{1}{(1+k_d t)^{k/k_d}} \quad (\text{E10-4.8})$$

the analytical solution **without decay**

$$\ln X = 1 - e^{-kt} = kt \quad (\text{E10-4.9})$$



Parameters

$$k = k_1 \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad k_d = k_{1d} \exp \left[\frac{E_d}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right) \right]$$

$$\begin{aligned} E &= 20000 \text{ cal/mol} & k_{1d} &= 0.1 \text{ s}^{-1} \\ k_1 &= 0.01 \text{ s}^{-1} & T_2 &= 300 \text{ K} \\ T_1 &= 300 \text{ K} & E_d &= 75000 \text{ cal/mol} \\ & & R &= 1.9787 \end{aligned}$$

Analysis: One observes that for long times the conversion in reactors with catalyst decay approaches a rather flat plateau and reaches conversion of about 30%. This is the conversion that will be achieved in a batch reactor for a first-order reaction when the catalyst decay law is second order. By comparison, we obtain virtually complete conversion in 500 seconds when there is no decay. The purpose of this example was to demonstrate the algorithm for isothermal catalytic reactor design for a decaying catalyst. In problem P10-1B(d), you are asked to sketch the temperature–time trajectories for various values of k and k_d .

10.7.1B Deactivation by Coking or Fouling

This mechanism of decay (see Figures 10-24, 10-25, and 10-26) is common to reactions involving hydrocarbons. It results from a carbonaceous (coke) material being deposited on the surface of a catalyst. The amount of coke on the surface after a time t has been found to obey the following empirical relationship

$$C_C = At^n \quad (10-101)$$

where C_C is the concentration of carbon on the surface (g/m^2) and n and A are empirical fouling parameters, which can be functions of the feed rate. This expression was originally developed by Voorhies and has been found to hold for a wide

variety of catalysts and feed streams. Representative values for Equation (10-101) for the cracking of a crude oil in fixed-bed of catalyst given

$$C_C = 0.52 t^{0.38}$$

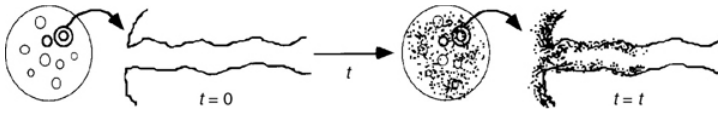


Figure 10-24 Schematic of decay by coking; loss of reactive surface area.

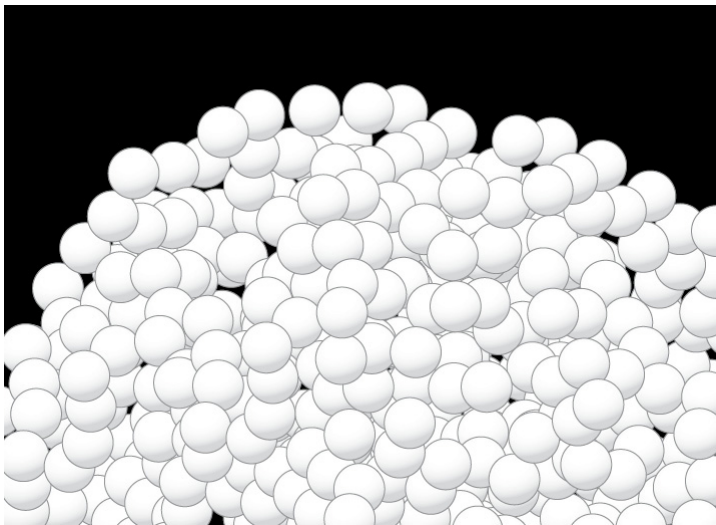


Figure 10-25 Catalyst decay fresh catalyst.

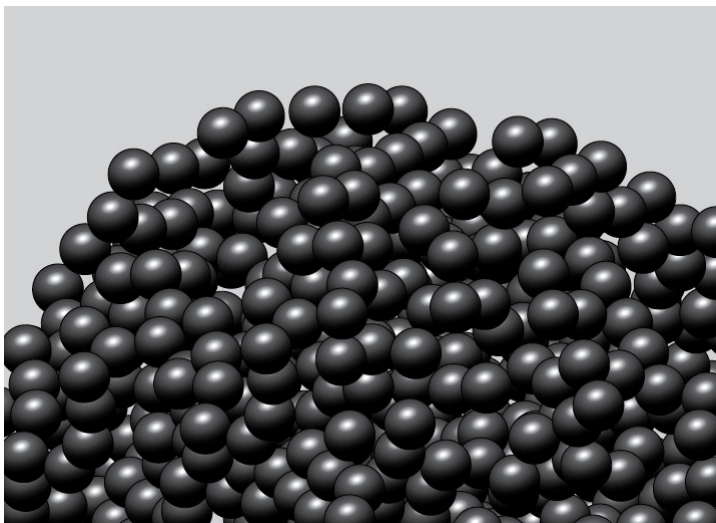


Figure 10-26 Catalyst decay spent catalyst.

Another relationship for the weight percent coke for the cracking of East Texas light gas oil is^{28,29}

²⁸ A. Voorhies, *Ind. Eng. Chem.*, 37, 318.

²⁹ C. O. Prater and R. M. Lago, *Adv. Catal.*, 8, 293.

$$\% \text{coke} = 0.47 \sqrt{t \text{ (min)}}$$

Different functionalities between the activity and amount of coke on the surface have been observed. One commonly used form is

$$a = \frac{1}{k_{\text{Ck}} C_{\text{C}}^p + 1} \quad (10-102)$$

or, in terms of time, we combine Equations (10-101) and (10-102)

$$a = \frac{1}{k_{\text{Ck}} A p t^{np} + 1} = \frac{1}{1 + k' t^m} \quad (10-103)$$

For light Texas gas oil being cracked at 750°F over a synthetic catalyst for short times, the decay law is

$$a = \frac{1}{1 + 7.6 t^{1/2}} \quad (10-104)$$

where t is in seconds.

Activity for deactivation by coking

Other commonly used forms are

$$a = e^{-\alpha_1 C_{\text{C}}} \quad (10-105)$$

and

$$a = \frac{1}{1 + \alpha_2 C_{\text{C}}} \quad (10-106)$$

A dimensionless fouling correlation has been developed by Pacheco and Petersen.³⁰

³⁰ M. A. Pacheco and E. E. Petersen, *J. Catal.*, 86, 75.

Minimizing coking

When possible, coking can be reduced by running at elevated pressures (2000–3000 kPa) and hydrogen-rich streams. A number of other techniques for minimizing fouling are discussed by Bartholomew.³¹ Catalysts deactivated by coking can usually be regenerated by burning off the carbon.

³¹ R. J. Farrauto and C. H. Bartholomew, *Fundamentals of Industrial Catalytic Processes*, 2nd ed. New York: Blackie Academic and Professional, 2006. This book is one of the most definitive resources on catalyst decay.

10.7.1C Deactivation by Poisoning

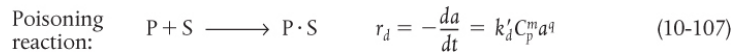
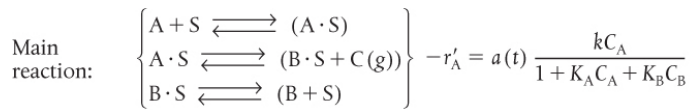
Deactivation by this mechanism occurs when the poisoning molecules become irreversibly chemisorbed to active sites, thereby reducing the number of sites available for the main reaction. The poisoning molecule, P, may be a reactant and/or a product in the main reaction, or it may be an impurity in the feed stream.

Side Note. One of the most significant examples of catalyst poisoning occurred at the gasoline pump. Oil companies found that adding lead to the gasoline increased the octane number. The television commercials said, "We are going to enhance your gasoline, *but it's going to cost you* for the added tetra-ethyl lead." So, for many years they used tetra-ethyl lead as an anti-knock component. As awareness grew about NO, HC, and CO emission from the engine, it was decided to add a catalytic afterburner in the exhaust system to reduce these emissions. Unfortunately, it was found that the lead in the gasoline poisoned the reactive catalytic sites. So, the television commercials now said, "We are going to take the lead out of gasoline but to receive the same level of performance as without lead, *but it's going to cost you* because of the added refining costs to raise the octane number." *#Seriously?* Do you think that, financially, consumers would have been better off if they never put the lead in the gasoline in the first place?

It's going to cost you. #Really?

10.7.1D Poison in the Feed

Many petroleum feed stocks contain trace impurities such as sulfur, lead, and other components that are too costly to remove, yet poison the catalyst slowly over time. For the case of an impurity, P, in the feed stream, such as sulfur, for example, in the reaction sequence



the surface sites would change with time as shown in [Figure 10-27](#).

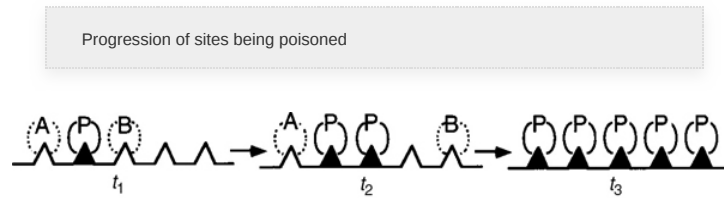


Figure 10-27 Decay by poisoning.

If we assume the rate of depletion of the poison from the reactant gas stream onto the catalyst sites, r_p , is proportional to the number of sites that are unpoisoned ($C_{t0} - C_{p \cdot s}$) and the concentration of poison in the gas phase is C_p then

Total site balance at time t $C_t = C_{t0} - C_{p \cdot s}$

$$r_{p \cdot s} = k_d (C_{t0} - C_{p \cdot s}) C_p$$

where $C_{p \cdot s}$ is the concentration of poisoned sites and C_{t0} is the total number of sites initially available. Because every molecule that is adsorbed from the gas phase onto a site is assumed to poison the site, this rate is also equal to the rate of removal of total active sites (C_t) from the surface

$$-\frac{dC_t}{dt} = \frac{dC_{p \cdot s}}{dt} = r_{p \cdot s} = k_d (C_{t0} - C_{p \cdot s}) C_p$$

Dividing through by C_{t0} and letting f be the fraction of the total number of sites that have been poisoned yields

$$\frac{df}{dt} = k_d (1 - f) C_p \quad (10-108)$$

The fraction of sites available for adsorption ($1 - f$) is essentially the activity $a(t)$. Consequently, [Equation \(10-108\)](#) becomes

$$\boxed{-\frac{da}{dt} = a(t)k_d C_p} \quad (10-109)$$

A number of examples of catalysts with their corresponding catalyst poisons are given by Farrauto and Bartholomew.³²

³² Ibid.

10.7.2 Decay in Packed-Bed Reactors

In packed-bed reactors where the poison is removed from the gas phase by being adsorbed on the specific catalytic sites, the deactivation process can move through the packed bed as a wave front. Here, at the start of the operation, only those sites near the entrance to the reactor will be deactivated because the poison (which is usually present in trace amounts) is removed from the gas phase by the adsorption; consequently, the catalyst sites farther down the reactor will not be affected. However, as time continues, the sites near the entrance of the reactor become saturated, and the poison must travel farther downstream before being adsorbed (removed) from the gas phase and attaching to a site to deactivate it. [Figure 10-28](#) shows the corresponding activity profile for this type of poisoning process. We see in [Figure 10-28](#) that by time t_4 the entire bed has become deactivated. The corresponding overall conversion at the exit of the reactor might vary with time as shown in [Figure 10-29](#). The partial differential equations that describe the movement of the reaction front shown in [Figure 10-28](#) are derived and solved in an example on the CRE Web site, at the very end of the *Summary Notes for Chapter 10* (<http://www.umich.edu/~elements/6e/10chap/summary-example3.html>).

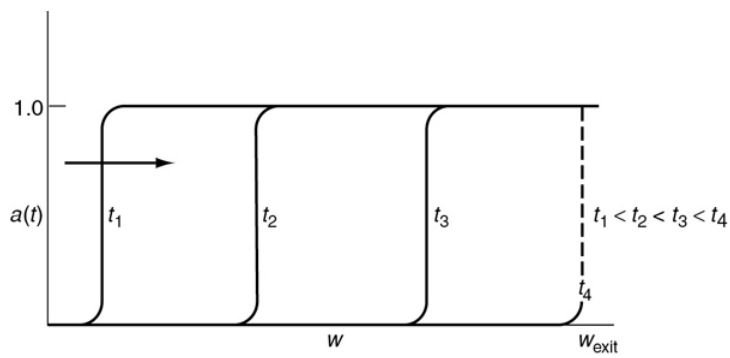


Figure 10-28 Movement of activity front in a packed bed.

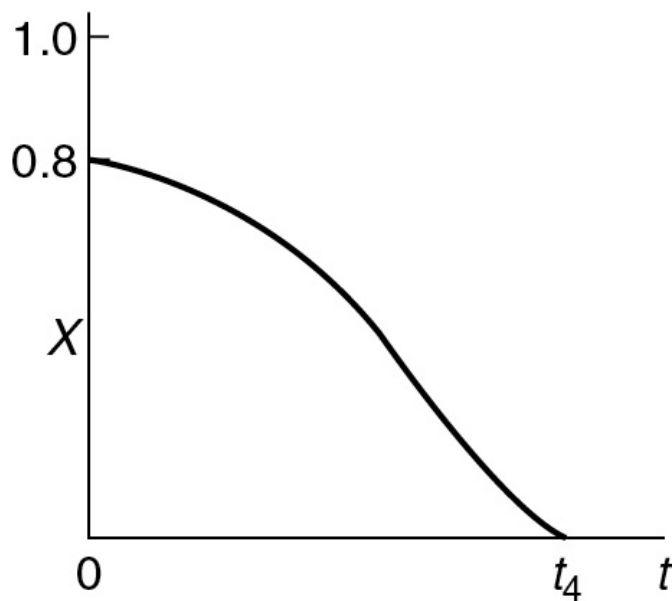


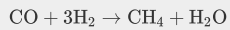
Figure 10-29 Exit conversion as a function of time.

10.7.2A Poisoning by Either Reactants or Products

For the case where the main reactant also acts as a poison, the rate laws are



An example where one of the reactants acts as a poison is in the reaction of CO and H₂ over ruthenium to form methane, with



$$\begin{aligned} -r_{\text{CO}} &= k a(t) C_{\text{CO}} \\ -\frac{da}{dt} &= r_d = k'_d a(t) C_{\text{CO}} \end{aligned}$$

Similar rate laws can be written for the case when the product B acts as a poison.

For *separable deactivation kinetics* resulting from contacting a poison at a constant concentration and no spatial variation

Separable deactivation kinetics

$$-\frac{da}{dt} = r_d = k'_d C_{p_0}^n a^n(t) = k_d a^n \quad (10-110)$$

where $k_d = k'_d C_{p_0}^n$. The solution to this equation for the case of first-order decay, $n = 1$

$$-\frac{da}{dt} = k_d a \quad (10-111)$$

is

$$a = e^{-k_d t} \quad (10-112)$$

10.7.2B Empirical Decay Laws

Table 10-7 gives a number of empirical decay laws along with the reaction systems to which they apply.

Key resource for catalyst deactivation

One should also see *Fundamentals of Industrial Catalytic Processes*, by Farrauto and Bartholomew, which contains rate laws similar to those in Table 10-7, and also gives a comprehensive treatment of catalyst deactivation.³³

³³ Ibid.

Examples of reactions with decaying catalysts and their decay laws

TABLE 10-7 DECAY RATE LAWS

Functional Form of Activity	Decay Reaction Order	Differential Form	Integral Form	Form Examples
Linear	0	$-\frac{da}{dt} = \beta_0$	$a = 1 - \beta_0 t$	Conversion of <i>para</i> -hydrogen on tungsten when poisoned with oxygen ^a
Exponential	1	$-\frac{da}{dt} = \beta_1 a$	$a = e^{-\beta_1 t}$	Ethylene hydrogenation on Cu poisoned with CO ^{b, c} Paraffin dehydrogenation on Cr? Al ₂ O ₃ ^c Cracking of gas oil ^d Vinyl chloride monomer formation ^e

Source: J. B. Butt, *Chemical Reactor Engineering—Washington, Advances in Chemistry Series 109*, Washington, D.C.: American Chemical Society, 1972, p. 259. Also see CES 23, 881(1968).

We will now consider three reaction systems that can be used to help offset systems with decaying catalyst. We will classify these systems as those having slow, moderate, and rapid losses of catalytic activity. To offset the decline in chemical reactivity of decaying catalysts in continuous-flow reactors, the following three methods are commonly used:

Matching the reactor type with speed of catalyst decay

- Slow decay – *Temperature–Time Trajectories* (10.8.1)
- Moderate decay – *Moving-Bed Reactors* (10.8.2)
- Rapid decay – *Straight-Through Transport Reactors* (10.8.3)

10.8.1 Temperature–Time Trajectories

In many large-scale reactors, such as those used for hydrotreating, and reaction systems where deactivation by poisoning occurs, the catalyst decay is relatively slow. In these continuous-flow systems, constant conversion is usually necessary in order that subsequent processing steps (e.g., separation) are not upset. One way to maintain a constant conversion with a decaying catalyst in a packed or fluidized bed is to increase the reaction rate by steadily increasing the feed temperature to the reactor. Operation of a “fluidized” bed in this manner is shown in [Figure 10-30](#).

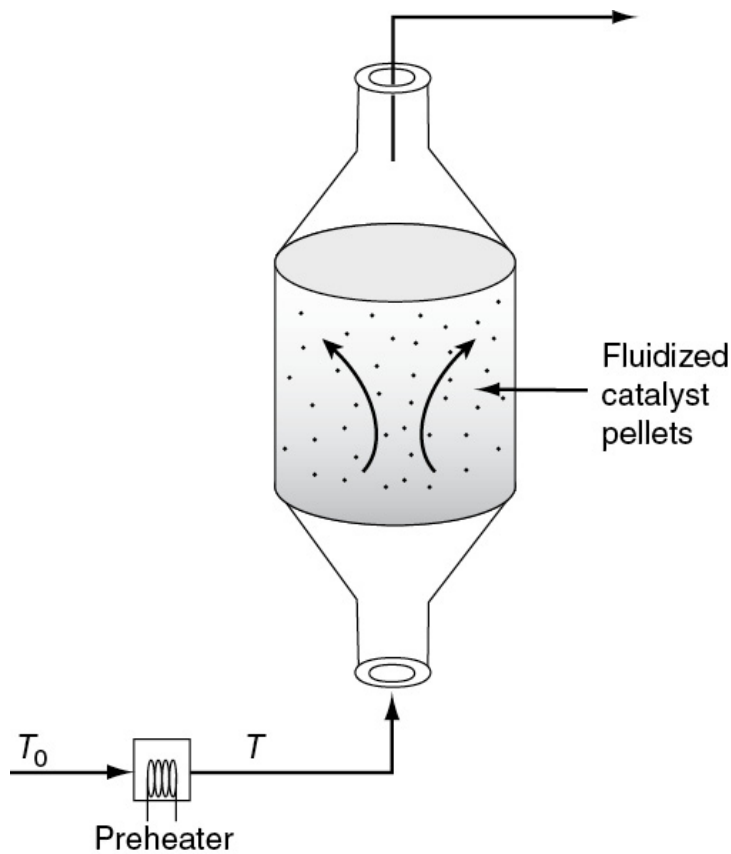


Figure 10-30 Reactor with preheater to continually increase feed temperature.

We are going to increase the feed temperature, T , in such a manner that the reaction rate remains constant with time:

$$-r'_A(t=0, T_0) = -r'_A(t, T) = a(t, T) [-r'_A(t=0, T)]$$

We will use a first-order reaction to illustrate the salient points. For a first-order reaction with decay we have

$$k(T_0)C_A = a(t, T)k(T)C_A$$

Slow rate of catalyst decay

We will neglect any variations in concentration so that the product of the activity (a) and specific reaction rate (k) is constant and equal to the specific reaction rate, k_0 at time $t = 0$ and temperature T_0 ; that is

$$\boxed{k(T)a(t, T) = k_0} \quad (10-113)$$

Note that for any power-law model, the reactant concentration dependence cancels out.

The goal is to find *how* the temperature should be increased with time (i.e., the temperature–time trajectory) to maintain constant conversion by keeping the rate $-r'_A$, constant. Using the Arrhenius equation to substitute for k in terms of the activation energy, E_A , gives

$$k_0 e^{(E_A/R)(1/T_0 - 1/T)} a = k_0 \quad (10-114)$$

Solving for $1/T$ yields

Gradually raising the temperature can help offset effects of catalyst decay.

$$\boxed{\frac{1}{T} = \frac{R}{E_A} \ln a + \frac{1}{T_0}} \quad (10-115)$$

The decay law also follows an Arrhenius-type temperature dependence

$$-\frac{da}{dt} = k_{d0} e^{(E_d/R)(1/T_0 - 1/T)} a^n \quad (10-116)$$

where k_{d0} = decay constant at temperature T_0 , S^{-1}

E_A = activation energy for the main reaction (e.g., $A \rightarrow B$), kJ/mol

E_d = activation energy for catalyst decay, kJ/mol

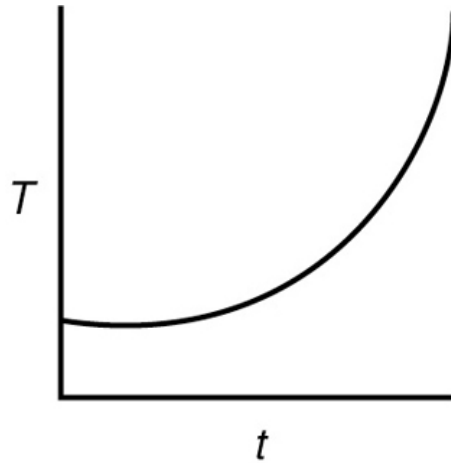
Substituting Equation (10-115) into (10-116) and rearranging yields

$$\boxed{-\frac{da}{dt} = k_{d0} \exp\left(-\frac{E_d}{E_A} \ln a\right) a^n = k_{d0} a^{(n - E_d/E_A)}} \quad (10-117)$$

Integrating with $a = 1$ at $t = 0$ for the case $n = (1 - E_d/E_A)$, we obtain

$$t = \frac{1 - a^{1 - n + E_d/E_A}}{k_{d0}(1 - n + E_d/E_A)} \quad (10-118)$$

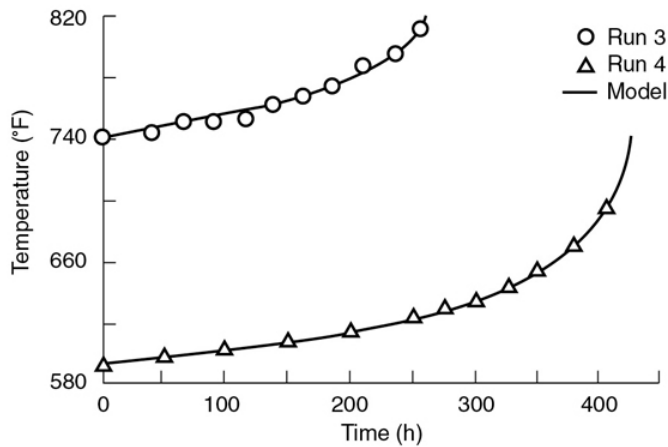
Solving Equation (10-114) for a and substituting in (10-118) gives



$$t = \frac{1 - \exp\left[\frac{E_A - nE_A + E_d}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right]}{k_{d0}(1 - n + E_d/E_A)} \quad (10-119)$$

Equation (10-119) tells us how the temperature of the catalytic reactor should be increased with time in order for the reaction rate and conversion to remain constant. However one would first want to solve this equation for temperature, T , as a function of time, t , in order to correctly operate the preheater shown in Figure 10-30.

In many industrial reactions, the decay rate law changes as temperature increases. In hydrocracking, the temperature–time trajectories are divided into three regimes. Initially, there is fouling of the acidic sites of the catalyst followed by a linear regime due to slow coking and, finally, accelerated coking characterized by an exponential increase in temperature. The temperature–time trajectory for a deactivating hydrocracking catalyst is shown in Figure 10-31.



Run	E_A (cal/mol)	A (h^{-1})	E_d (cal/mol)	A_d (h^{-1})
3	30.0	0.52×10^{12}	42.145	1.54×10^{11}
4	30.0	0.52×10^{12}	37.581	2.08×10^{11}

Figure 10-31 Temperature–time trajectories for deactivating hydrocracking catalyst, runs 3 and 4. (Krishnaswamy, S., and J. R. Kittrell. Analysis of Temperature–Time Data for Deactivating Catalysts. *Industry and Engineering Chemistry Process Design and Development*, 1979, 18(3), 399–403. Copyright © 1979, American Chemical Society. Reprinted by permission.)

COMPARISON OF MODEL WITH INDUSTRIAL DATA

For a first-order decay, Krishnaswamy and Kittrell's expression, Equation (10-119), for the temperature–time trajectory reduces to

$$t = \frac{E_A}{k_{d0} E_d} \left[1 - e^{(E_d/R)(1/T - 1/T_0)} \right] \quad (10-120)$$

Comparing theory and experiment

One observes the model compares favorably with the experimental data.

10.8.2 Moving-Bed Reactors

Reaction systems with relatively rapid catalyst decay require the continual regeneration and/or replacement of the catalyst.

Two types of reactors currently in commercial use that accommodate production with decaying catalysts are the moving-bed for moderate decay and straight-through transport reactor for rapid decay. A schematic diagram of a moving-bed reactor (used for catalytic cracking) is shown in Figure 10-32.

The freshly regenerated catalyst enters the top of the reactor and then moves through the reactor as a compact packed bed. The catalyst is coked continually as it moves through the reactor until it exits the reactor into the kiln, where air is used to burn off the carbon. The regenerated catalyst is lifted from the kiln by an airstream and then fed into a separator before it is returned to the reactor. The catalyst pellets are typically between one-quarter and one-eighth inch in diameter.

The Chemical Safety Board video on the *Process Safety Across the Chemical Engineering Curriculum* Web site ([http://umich.edu/~safeche/assets/pdf/courses/Problems/CRE/344ReactionEngrModule\(3\)PS-Exxon.pdf](http://umich.edu/~safeche/assets/pdf/courses/Problems/CRE/344ReactionEngrModule(3)PS-Exxon.pdf)) shows an animation of the moving-bed reactor at the ExxonMobil Torrance, California refinery.

The reactant feed stream enters at the top of the reactor and flows rapidly through the reactor relative to the flow of the catalyst through the reactor (Figure 10-33). If the feed rates of the catalyst and the reactants do not vary with

Moving-bed reactor, used for reactions with moderate rate of catalyst decay

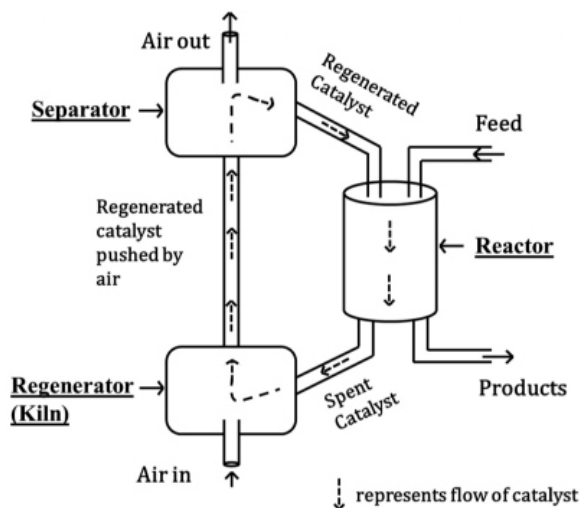


Figure 10-32 Catalytic cracking unit with catalytic regeneration.

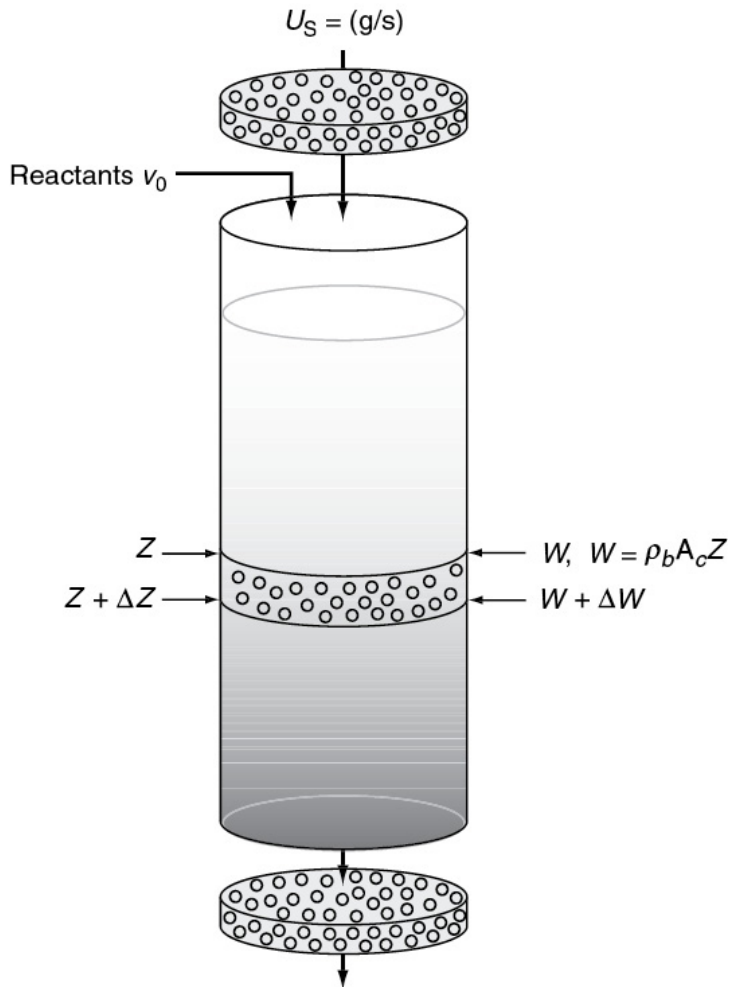


Figure 10-33 Moving-bed reactor schematic. The value of the catalyst contained in a reactor of this type is approximately \$1 million.

time, the reactor operates at steady state; that is, conditions at any point in the reactor do not change with time. The mole balance on reactant A over ΔW is

$$\begin{bmatrix} \text{Molar} \\ \text{flow} \\ \text{rate of A in} \end{bmatrix} - \begin{bmatrix} \text{Molar} \\ \text{flow} \\ \text{rate of A out} \end{bmatrix} + \begin{bmatrix} \text{Molar} \\ \text{rate of} \\ \text{generation of A} \end{bmatrix} = \begin{bmatrix} \text{Molar} \\ \text{rate of} \\ \text{accumulation of A} \end{bmatrix}$$

$$F_A(W) - F_A(W + \Delta W) + r'_A \Delta W = 0 \quad (10-121)$$

Dividing by ΔW , letting ΔW approach zero, and expressing the flow rate in terms of conversion gives

Mole Balance

$$F_{A0} \frac{dX}{dW} = -r'_A \quad (2-17)$$

The rate of reaction at any time t is

$$-r'_A = a(t) [-r'_A(t=0)] = a(t=0) = a(t) [k \text{ fn } (C_A, C_B, \dots, C_P)] \quad (10-93)$$

The activity, as before, is a function of the time the catalyst has been in contact with the reacting gas stream. The decay rate law is

Decay Law

$$-\frac{da}{dt} = k_d a^n \quad (10-110)$$

We now need to relate the contact time to the weight of the catalyst. Consider a point z in the reactor, where the reactant gas has passed cocurrently through a catalyst weight W . Because the solid catalyst is moving through the bed at a rate U_s (mass per unit time), the time t that the catalyst has been in contact with the gas when the catalyst reaches a point z is

$$t = \frac{W}{U_s} \quad (10-122)$$

If we now differentiate Equation (10-122)

$$dt = \frac{dW}{U_s} \quad (10-123)$$

and combine it with the decay rate law, we obtain

$$-\frac{da}{dW} = \frac{k_d}{U_s} a^n \quad (10-124)$$

The activity equation is combined with the mole balance

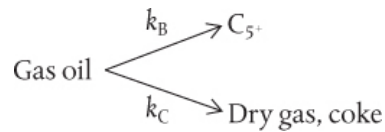
The design equation for moving-bed reactors

$$\boxed{\frac{dX}{dW} = \frac{a[-r'_A(t=0)]}{F_{A0}}} \quad (10-125)$$

these two coupled differential equations (i.e., Equations (10-124) and (10-125)) are numerically solved simultaneously with an ODE solver, for example, Polymath.

Example 10–5 Catalytic Cracking in a Moving-Bed Reactor

The catalytic cracking of a gas-oil charge, A, to form C_5+ (B) and to form coke and dry gas (C) is to be carried out in a screw-type conveyor, moving-bed reactor at 900°F:



This cracking of gas oil can also be written as



While pure hydrocarbons are known to crack according to a first-order rate law, the fact that the gas-oil exhibits a wide spectrum of cracking rates gives rise to the fact that the lumped cracking rate is well represented by a second-order rate law with the following specific reaction rate:³⁴

³⁴ Estimated from V. W. Weekman and D. M. Nace, *AIChE J.*, 16, 397 (1970).

$$-r'_A = 600 \frac{(\text{dm})^6}{(\text{kg cat})(\text{mol})(\text{min})} C_A^2$$

The catalytic deactivation is independent of gas-phase concentration and follows a first-order decay rate law, with a decay constant, k_d of 0.72 reciprocal minutes. The feed stream is diluted with nitrogen so that as a first approximation, volume changes can be neglected with reaction. The reactor contains 22 kg of catalyst that moves through the reactor at a rate of 10 kg/min. The gas-oil is fed at a rate of 30 mol/min at a concentration of 0.075 mol/dm³.

Determine the conversion that can be achieved in this reactor.[†]

[†] AWFOS–S. Be sure to see the animation of a moving-bed reactor and description of the ExxonMobil

Torrance, California accident
([http://umich.edu/~safeche/assets/pdf/courses/Problems/CRE/344ReactionEngrModule\(3\)PS-Exxon.pdf](http://umich.edu/~safeche/assets/pdf/courses/Problems/CRE/344ReactionEngrModule(3)PS-Exxon.pdf)).

Solution

1. Mole Balance:

$$F_{A0} \frac{dX}{dW} = a (-r'_A) \quad (\text{E10-5.1})$$

2. Rate Law:

$$-r'_A = kC_A^2 \quad (\text{E10-5.2})$$

3. Decay Law. First-order decay:

$$-\frac{da}{dt} = k_d a$$

Moving beds: moderate rate of catalyst decay

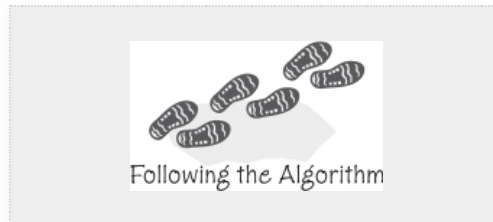
Using Equation (10-124), we obtain

$$-\frac{da}{dW} = \frac{k_d}{U_s} a \quad (\text{E10-5.3})$$

Integrating

$$a = e^{-(k_d/U_s)W} \quad (\text{E10-5.4})$$

4. Stoichiometry. If $v \approx v_0$, then



$$C_A = C_{A0} (1 - X) \quad (\text{E10-5.5})$$

5. Combining we have

$$\frac{dX}{dW} = a \frac{kC_{A0}^2(1-X)^2}{F_{A0}} \quad (\text{E10-5.6})$$

$$a = e^{-(k_d/U_s)W}$$

The polymath program is shown below along with a conversion profile.

POLYMATH Report

Ordinary Differential Equations

Calculated values of DEQ variables

Variable	Initial value	Final value
1 a	1.	0.2051528
2 Ca	0.075	0.033453
3 Cao	0.075	0.075
4 Fao	30.	30.
5 k	600.	600.
6 kd	0.72	0.72
7 raprime	-3.375	-0.6714636
8 Us	10.	10.
9 W	0	22.
10 X	0	0.5539595

Differential equations

1 $d(a)/d(W) = -kd \cdot a / U_s$

2 $d(X)/d(W) = a \cdot (-raprime) / Fao$

3 $a' = (-raprime) / Fao$

Explicit equations

1 $U_s = 10$

2 $kd = 0.72$

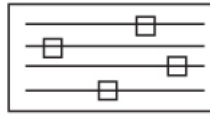
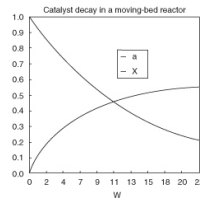
3 $Fao = 30$

4 $Cao = 0.075$

5 $Ca = Cao \cdot (1 - X)$

6 $k = 600$

7 $raprime = -k \cdot Ca^2$

**LEP Sliders**

Explore this problem using Wolfram or Python and then use Polymath to change the decay law and make two observations.

For the simple rate law and activity law given here, we also could have solved this problem analytically as shown below.

6. Separating and integrating yields (E10-5.7)

$$F_{A0} \frac{dX}{dW} = e^{-(k_d/U_s)W} k C_{A0}^2 (1 - X)^2$$

$$\frac{F_{A0}}{k C_{A0}^2} \int_0^X \frac{dX}{(1-X)^2} = \int_0^W e^{-(k_d/U_s)W} dW \quad (\text{E10-5.7})$$

$$\frac{X}{1-X} = \frac{k C_{A0}^2 U_s}{F_{A0} k_d} (1 - e^{-k_d W / U_s}) \quad (\text{E10-5.8})$$

7. Numerical evaluation:

$$\frac{X}{1-X} = \frac{0.6 \text{ dm}^6}{\text{mol} \cdot \text{g} \cdot \text{cat} \cdot \text{min}} \times \frac{(0.075 \text{ mol} / \text{dm}^3)^2}{30 \text{ mol} / \text{min}} \frac{10000 \text{ g cat} / \text{min}}{0.72 \text{ min}^{-1}} \times \left(1 - \exp \left[\frac{(-0.72 \text{ min}^{-1})(22 \text{ g})}{10 \text{ kg} / \text{min}} \right] \right)$$

$$\frac{X}{1-X} = 1.24$$

$$X = 55\%$$

If there were no catalyst decay, the conversion would be

$$\frac{X}{1-X} = \frac{k C_{A0}^2}{F_{A0}} W$$

$$600 \left(\frac{\text{dm}^6}{(\text{kg cat})(\text{mol})(\text{min})} \times \frac{(0.075 \text{ mol} / \text{dm}^3)^2}{(30 \text{ mol} / \text{min})} (22 \text{ kg cat}) \right)$$

$$= 2.47$$

$$X = 71\%$$

Analysis: The purpose of this example was to show step-by-step how to apply the algorithm to a moving-bed reactor that has been used to reduce the effects of catalyst decay that would occur in a PBR. *#Splaining.* You would have some explaining to do if your company was expecting 71% conversion and you only observed 55%.

We will now rearrange Equation (E10-5.8) to a form more commonly found in the literature. Let λ be a dimensionless decay time

$$\lambda = k_d t = \frac{k_d W}{U_s} \quad (10-126)$$

and Da_2 be the Damköhler number for a second-order reaction (*a reaction rate divided by a transport rate*) for a packed-bed reactor

$$Da_2 = \frac{(kC_{A0}^2)(W)}{F_{A0}} = \frac{kC_{A0}W}{v_0} \quad (10-127)$$

Through a series of manipulations we arrive at the equation for the conversion in a *moving bed* where a second-order reaction is taking place³⁵

³⁵ Ibid.

Second-order reaction in a moving-bed reactor

$$X = \frac{Da_2(1-e^{-\lambda})}{\lambda + Da_2(1-e^{-\lambda})} \quad (10-128)$$

Similar equations are given or can easily be obtained for other reaction orders or decay laws.

10.8.3 Straight-Through Transport Reactors (STTR)

This reactor is used for reaction systems in which the catalyst deactivates very rapidly. Commercially, the STTR is used in the production of gasoline from the cracking of heavier petroleum fractions where coking of the catalyst pellets occurs very rapidly. In the STTR, the catalyst pellets and the reactant feed enter together and are transported very rapidly through

the reactor. The bulk density of the catalyst particle in the STTR is significantly smaller than in moving-bed reactors, and the particles are carried through at the same velocity as the gas velocity. In some places the STTR is also referred to as a circulating fluidized bed (CFB). A schematic diagram is shown in [Figure 10-34](#).

A mole balance on the reactant A over the differential reactor volume

$$\Delta V = A_C \Delta z$$

is

$$F_A|_z - F_A|_{z+\Delta z} + r_A A_C \Delta z = 0$$

STTR: Used when catalyst decay (usually coking) is very rapid

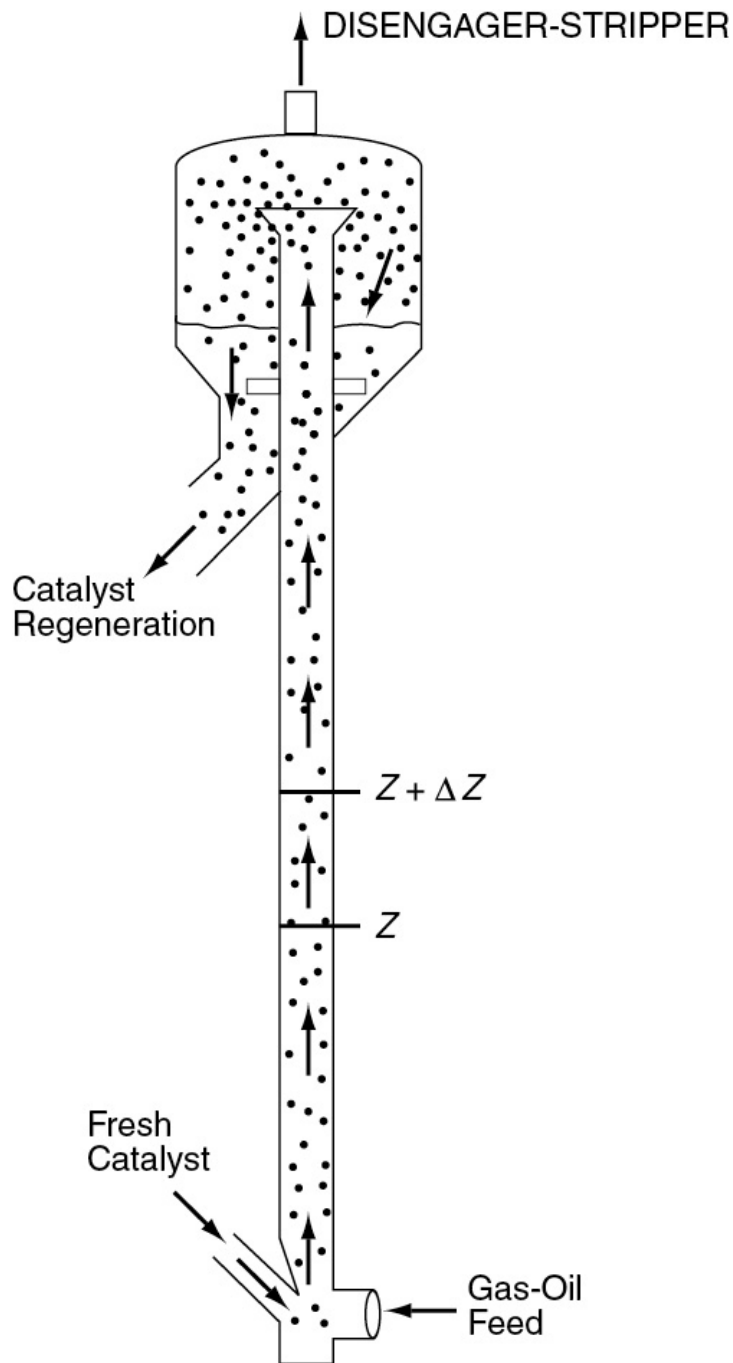


Figure 10-34 Straight-through transport reactor.

Dividing by Δz and taking the limit as $\Delta z \rightarrow 0$, letting ρ_b be the bulk density of the suspended catalyst and recalling that $r_A = \rho_B r'_A$, we obtain

$$\frac{dF_A}{dz} = r_A A_C = r'_A \rho_B A_C \quad (10-129)$$

In terms of conversion [$F_A = F_{A0}(-X)$] and catalyst activity [$-r'_A = -r'_A(t=0)a(t)$], the reactor mole balance is written as

$$\frac{dX}{dz} = \left(\frac{\rho_B A_C}{F_{A0}} \right) [-r'_A(t=0)] a(t) \quad (10-130)$$

For a catalyst particle traveling through the reactor with a particle velocity U_p , the time the catalyst pellet has been in the reactor when it reaches a height z is just

$$t = \frac{z}{U_p} \quad (10-131)$$

Substituting for time t in terms of distance z (i.e., $a(t) = a(z/U_p)$), the mole balance now becomes

$$\frac{dX}{dz} = \frac{\rho_B A_C [-r'_A(t=0)] a(z/U_p)}{F_{A0}}$$

The entering molar flow rate, F_{A0} , can be expressed in terms of the gas velocity U_0 , C_{A0} , and A_C

$$F_{A0} = U_0 A_C C_{A0}$$

Substituting for F_{A0} , we have

$$\boxed{\frac{dX}{dz} = \frac{\rho_B a(z/U_p) [-r'_A(t=0)]}{C_{A0} U_0}} \quad (10-132)$$

Equation (10-132) describes how the conversion varies as we move up the reactor.

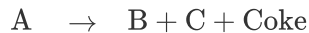
Example 10–6 Decay in a Straight-Through Transport Reactor

The vapor-phase cracking of a gas-oil is to be carried out in a straight-through transport reactor (STTR) that is 10-m high and 1.5 m in diameter. Gas-oil is a mixture of normal and branched paraffins (C_{12} – C_{40}), naphthenes, and aromatics, all of which will be lumped as a single species, A. We shall lump the primary hydrocarbon products according to distillate temperature into two respective groups, dry gas (C_1 – C_4) species B and gasoline (C_5 – C_{14}) species C. The reaction

A typical cost of the catalyst in the reactor system is \$1 million.



can be written symbolically as



Both B and C are adsorbed on the surface. The rate law for a gas-oil cracking reaction on fresh catalyst can be approximated by

$$-r'_A = \frac{k' P_A}{1 + K_A P_A + K_B P_B + K_C P_C}$$

with $k' = 0.0014$ kmol/kg-cat·s·atm, $K_A = 0.05$ atm $^{-1}$, $K_B = 0.15$ atm $^{-1}$, and $K_C = 0.1$ atm $^{-1}$. The catalyst decays by the deposition of coke, which is produced in most cracking reactions along with the reaction products. The decay law is

$$a = \frac{1}{1 + At^{1/2}} \quad \text{with } A = 7.6 \text{ s}^{-1/2}$$

Pure gas-oil enters at a pressure of 12 atm and a temperature of 400°C. The bulk density of catalyst in the STTR is 80 kg-cat/m 3 .

Plot the activity, $a(z)$, and conversion, $X(z)$, of gas-oil up the 10-m reactor for entering gas velocity $U_0 = 2.5$

m/s.

Solution

Mole Balance:

$$F_{A0} \frac{dX}{dz} = -r_A A_C$$

$$\boxed{\frac{dX}{dz} = \frac{-r_A}{U_0 C_{A0}}} \quad (\text{E10-6.1})$$

The height of the catalyst particle at time “ t ” after entering the STTR is



$$z = \int_0^t U_p dt$$

Differentiating, we can find a relation between the time the catalyst particle has been in the STTR and reached a height z , which we can use to find the activity a .

$$\boxed{\frac{dt}{dz} = \frac{1}{U}}$$

Rate Law:

$$-r_A = \rho_B (-r'_A) \quad (\text{E10-6.2})$$

$$-r_A = a [-r'_A (t = 0)] \quad (\text{E10-6.3})$$

On fresh catalyst

$$-r'_A (t = 0) = k' \frac{P_A}{1 + K_A P_A + K_B P_B + K_C + P_C} \quad (\text{E10-6.4})$$

We assume the solid particles travel up the reactor at the same velocity as the gas, that is, $U_p = U_g = U_c$

Combining Equations (E10-6.2)–(E10-6.4) gives

$$-r'_A = a \left(\rho_B k' \frac{P_A}{1 + K_A P_A + K_B P_B + K_C P_C} \right) \quad (\text{E10-6.5})$$

Decay Law. Assuming that the catalyst particle and gas travel up the reactor at the velocity $U_P = U_g$, we obtain the contact time with the catalyst at a height z to be

$$t = \frac{z}{U_g} \quad (\text{E10-6.6})$$

$$a = \frac{1}{1 + A \left(\frac{z}{U_g} \right)^{1/2}} \quad (\text{E10-6.7})$$

where

$$U_g = v/A_C = v_0 (1 + \varepsilon X) / A_C \text{ and } A_C = \pi D^{2/4}$$

Stoichiometry (gas-phase isothermal and no pressure drop):

$$P_A = P_{A0} \frac{1-X}{1+\varepsilon X} \quad (\text{E10-6.8})$$

$$P_B = \frac{P_{A0} X}{1+\varepsilon X} \quad (\text{E10-6.9})$$

$$P_C = P_B \quad (\text{E10-6.10})$$

Parameter Evaluation:

$$\varepsilon = y_{A0} \delta = (1 + 1 - 1) = 1$$

$$U_g = U_0 (1 + \varepsilon X)$$

$$C_{A0} = \frac{P_{A0}}{RT_0} = \frac{12 \text{ atm}}{(0.082 \text{ m}^3 \cdot \text{atm} / \text{kmol} \cdot \text{K})(673 \text{ K})} = 0.22 \frac{\text{kmol}}{\text{m}^3}$$

Equations (E10-6.1), (E10-6.5), (E10-6.7), and (E10-6.8)–(E10-6.10) are now combined and solved using an ODE solver. The Polymath program is shown in Table E10-6.1, and the computer output is shown in Figure E10-6.1.

TABLE E10-6.1 EQUATIONS FOR THE STTR:
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Calculated values of DEQ variables

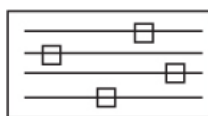
	Variable	Initial value	Final value
1	A	7.6	7.6
2	a	1.	0.078026
3	Cao	0.2174465	0.2174465
4	D	1.5	1.5
5	eps	1.	1.
6	Ka	0.05	0.05
7	Kb	0.15	0.15
8	Kc	0.1	0.1
9	kprime	0.0014	0.0014
10	Pa	12.	2.503813
11	Pao	12.	12.
12	Pb	0	4.748094
13	Pc	0	4.748094
14	R	0.082	0.082
15	ra	-0.84	-0.0094631
16	raprime	-0.0105	-0.0001183
17	rho	80.	80.
18	T	673.	673.
19	U	2.5	4.136843
20	Uo	2.5	2.5
21	vo	4.417875	4.417875
22	X	0	0.6547373
23	z	0	10.

Differential equations

$$1 \quad d(X)/d(z) = -ra/Uo/Cao$$

Explicit equations

$$\begin{aligned} 1 \quad & Ka = 0.05 \\ 2 \quad & Kb = 0.15 \\ 3 \quad & Pao = 12 \\ 4 \quad & eps = 1 \\ 5 \quad & A = 7.6 \\ 6 \quad & R = 0.082 \\ 7 \quad & T = 400 + 273 \\ 8 \quad & rho = 80 \\ 9 \quad & kprime = 0.0014 \\ 10 \quad & D = 1.5 \\ 11 \quad & Uo = 2.5 \\ 12 \quad & Kc = 0.1 \\ 13 \quad & U = Uo * (1 + eps * X) \\ 14 \quad & Pa = Pao * (1 - X) / (1 + eps * X) \\ 15 \quad & Pb = Pao * X / (1 + eps * X) \\ 16 \quad & vo = Uo * 3.1416 * D^2 / 4 \\ 17 \quad & Cao = Pao / R / T \\ 18 \quad & Pc = Pb \\ 19 \quad & a = 1 / (1 + A * (z/U)^{0.5}) \\ 20 \quad & raprime = a * (-kprime * Pa / (1 + Ka * Pa + Kb * Pb + Kc * Pc)) \\ 21 \quad & ra = rho * raprime \end{aligned}$$



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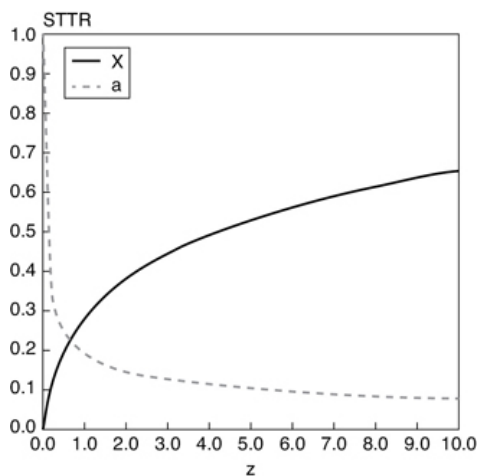


Figure E10-6.1 Activity and conversion profiles.

Use Wolfram to learn how the conversion and activity profiles shown above in [Figure E10-6.1](#) change as you vary the parameters.

Analysis: In this example we applied the algorithm to a STTR in which the gas velocity and, hence, particle velocity increases as we move through the reactor. The decay is quite rapid and the activity is only 15% of its initial value at $z = 3$ m into the reactor and the conversion begins to plateau at $z = 6$ m at 60%

conversion. If there were no catalyst decay ($a = 1$), the conversion would have been 97% at $z = 6$ m.

10.9 AND NOW... A WORD FROM OUR SPONSOR—SAFETY 10 (AWFOS—S10 EXXON MOBIL TORRANCE REFINERY EXPLOSION INVOLVING A STRAIGHT—THROUGH TRANSPORT REACTOR [STTR])

This incident and video can be found on the *Process Safety Across the Chemical Engineering Curriculum* Web site and it is highly recommended to view the video first. On Monday February 18, 2015 an explosion occurred at ExxonMobil's Torrance California refinery's electrostatic precipitator unit, a pollution control device associated with the fluid catalytic cracking (FCC) unit. While the explosion occurred in the precipitator, the pre-initiating events took place in the catalyst regeneration unit attached to a STTR, as shown in [Figure 10-35](#). In this incident, the spent catalyst from the STTR is covered with carbon compounds that are burned off in a regenerator. On a routine maintenance shut down, catalyst particles got lodged in the regenerator door allowing flammable vapor to flow out of the regeneration unit and proceed downstream to an electrostatic precipitator (ESP) where it found a spark and exploded.

Watch the Video: (<https://www.csb.gov/exxonmobil-refinery-explosion-/>)

Incident Report Available At::

(https://www.csb.gov/assets/1/20/exxonmobil_report_for_public_release.pdf?15813)

CSB Incident Report No. 2015-02-I CA ExxonMobil Torrance Refinery, February 18, 2015. If you need more detailed information that can be found in the video, review pages 1–22 of this report.

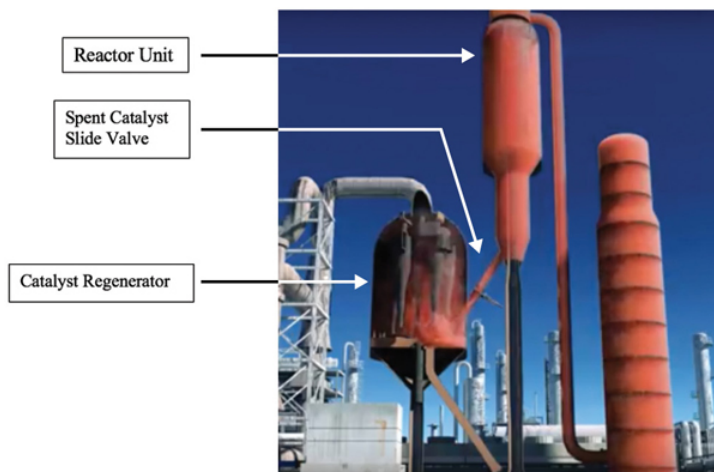


Figure 10-35 A STTR and regeneration unit.

Figure 14-8 in Chapter 14 shows a schematic for the removal of coke from a catalyst pellet. The time necessary to completely burn the coke off the pellet is

$$t = \frac{\rho_C R_0^2 \phi_C}{6D_c C_{A0}}$$

as described by the shrinking core model in Section 14.6, read to learn about Coke Regeneration.

It is important that chemical engineers have an understanding of what the accident was, why it happened, and how it could have been prevented in order ensure similar accidents may be prevented. Applying a safety algorithm to the incident will help achieve this goal. In order to become familiar with a strategy for accident awareness and prevention, view the Chemical Safety Board video on the explosion and fill out the incident report as shown below.

Safety Analysis of the Incident

Activity: The activity in this incident is the maintenance operation of a fluid catalytic cracking (FCC) unit at a refinery.

Hazard: The hazard in this incident is the flammability of light hydrocarbons.

Incident: The incident here is leakage of light hydrocarbons through the reactor into air-side of the unit and finally into the

electrostatic precipitator where they found a source of ignition and exploded.

Initiating Event: The initiating event was the lowering of pressure of steam in the reactor which allowed light hydrocarbons to flow back into the reactor and move toward the air-side through the regenerator, as well as the failure of the Spent Catalyst Slide Valve to completely seal the regenerator from the reactor.

Preventative Actions and Safeguards: Some preventive actions or safeguards include strict inspection to control use of old equipment that may have undergone erosion due to use beyond their life, reevaluation of operating procedure, and safe operating limits during Safe Park, extensive consideration of all possible failure scenarios. Other considerations include use of an alternative technology that avoids a possible ignition source (use of scrubber instead of ESP) when flammable substances are involved, regular inspection of plant equipment to determine their fitness, installation of gas detectors in the regenerator to detect presence of flammable gases that may flow to the ESP.

Contingency Plan/Mitigating Actions: Immediate shutdown of electrostatic precipitator or the FCC unit when a part of the plant is being opened, replaced, and so on, or when a safety critical safeguard, such as the barrier of catalyst, could not be established.

Lessons Learned: The lessons learned from this incident are that safe operating limits must be defined for all operations and process conditions must be verified to ensure that the process is safe. The equipment critical for safety must be maintained regularly to ensure that it performs its function and an assessment of various possible hazards must be made while changing practices, and they must be done only in consultation with experts from different fields.

A BowTie diagram for this incident is shown in Figure 10-36.

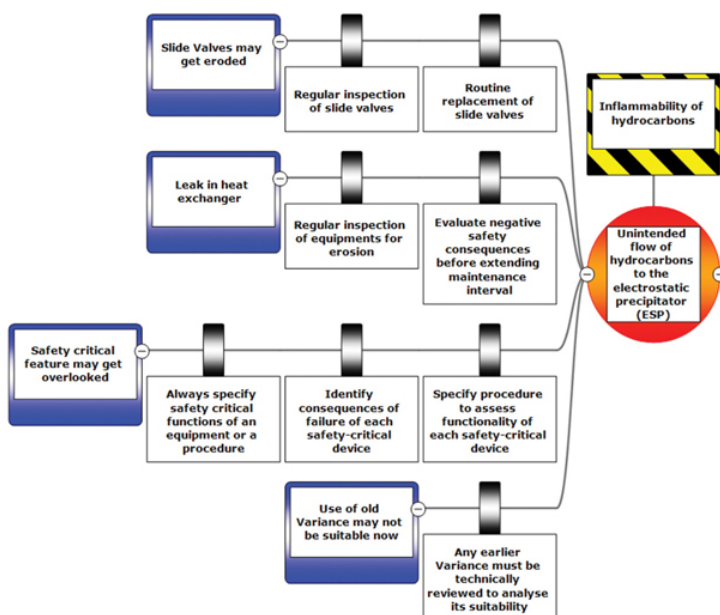


Figure 10-36 BowTie Diagram.

Review the ExxonMobil Safety Module

([http://umich.edu/~safeche/assets/pdf/courses/Problems/CRE/344ReactionEngrModule\(3\)PS20419-Exxon.pdf](http://umich.edu/~safeche/assets/pdf/courses/Problems/CRE/344ReactionEngrModule(3)PS20419-Exxon.pdf)) and the Catalyst Regeneration Web site.

In order to get the above BowTie diagram on one page, we had to divide it at the initiating event.

Closure. After reading this chapter, the reader should be able to discuss the steps in a heterogeneous reaction (adsorption, surface reaction, and desorption) and describe what is meant by a rate-limiting step. The differences between molecular adsorption and dissociated adsorption should be explained by the reader, as should the different types of surface reactions (single site, dual site, and Eley–Rideal). Given heterogeneous reaction-rate data, the reader should be able to analyze the data and develop a rate law for Langmuir–Hinshelwood kinetics. The reader should also be able to discriminate between rate laws to find which rate law best fits the data. After evaluating the rate-law parameters, the reader can proceed to the design of PBRs and fluidized CSTRs.

Applications of CRE in the electronics industry were discussed and readers should be able to describe the analogy between Langmuir–Hinshelwood kinetics and chemical vapor deposition (CVD), and to derive a rate law for CVD mechanisms.

Because of the high temperatures and harsh environment, catalysts do not always maintain their original activity and the catalysts decay during the course of the reaction. The reader should be able to discuss the three basic types of catalyst decay (sintering, coking or fouling, and poisoning). In addition, the reader should be able to suggest reactors (e.g., moving bed) to use to offset catalyst decay and should be able to carry out calculations to predict the conversion.

SUMMARY

1. Types of adsorption:

1. Chemisorption
2. Physical adsorption

2. The **Langmuir isotherm** relating the concentration of species A on the surface to the partial pressure of A in the gas phase is

$$C_{A.S} = \frac{K_A C_A P_A}{1 + K_A P_A} \quad (\text{S10-1})$$

3. The sequence of steps for the solid-catalyzed isomerization



is:

1. **Mass transfer of A** from the bulk fluid to the external surface of the pellet
2. **Diffusion of A** into the interior of the pellet
3. **Adsorption of A** onto the catalytic surface
4. **Surface reaction of A** to form **B**
5. **Desorption of B** from the surface
6. **Diffusion of B** from the pellet interior to the external surface
7. **Mass transfer of B** away from the solid surface to the bulk fluid

4. Assuming that mass transfer is not rate-limiting, the rate of adsorption is

$$r_{AD} = k_A \left(C_v P_A - \frac{C_{A.S}}{K_A} \right) \quad (\text{S10-3})$$

The rate of surface reaction is

$$r_s = k_s \left(C_{A.S} - \frac{C_{B.S}}{K_s} \right) \quad (\text{S10-4})$$

The rate of desorption is

$$r_D = k_D (C_{B.S} - K_B P_B C_v) \quad (\text{S10-5})$$

At steady state

$$-r'_A = r_{AD} = r_s = r_D \quad (\text{S10-6})$$

If there are no inhibitors present, the total concentration of sites is (S10-7)

$$C_t = C_v + C_{A.S} + C_{B.S} \quad (\text{S10-7})$$

5. If we assume that the surface reaction is rate-limiting, we set

$$\frac{r_{AD}}{k_A} \simeq 0 \quad \frac{r_D}{k_D} \simeq 0$$

and solve for $C_A \cdot S$ and $C_B \cdot S$ in terms of P_A and P_B . After substitution of these quantities in Equation (S10-4), the concentration of vacant sites is eliminated with the aid of Equation (S10-7)

$$-r'_A = r_s = \frac{\overbrace{C_1 k_s K_A}^k (P_A - P_B / K_P)}{1 + K_A P_A + K_B P_B} \quad (\text{S10-8})$$

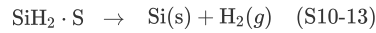
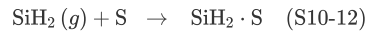
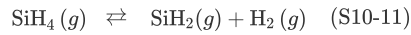
Recall that the equilibrium constant for desorption of species B is the reciprocal of the equilibrium constant for the adsorption of species B

$$K_B = \frac{1}{K_{DB}} \quad (\text{S10-9})$$

and the thermodynamic equilibrium constant, K_P , is

$$K_P = K_A K_S / K_B \quad (\text{S10-10})$$

6. Chemical vapor deposition (CVD)



$$r_{\text{Dep}} = \frac{k P_{\text{SiH}_4}}{P_{\text{H}_2} + K_P P_{\text{SiH}_4}} \quad (\text{S10-14})$$

7. Catalyst deactivation. The catalyst activity is defined as

$$a(t) = \frac{-r'_A(t)}{-r'_A(t=0)} \quad (\text{S10-15})$$

The rate of reaction at any time t is

$$-r'_A = a(t) k(T) f_n(C_A, C_B, \dots, C_P) \quad (\text{S10-16})$$

The rate of catalyst decay is

$$r_d = -\frac{da}{dt} = p[a(t)] k_d(T) g(C_A, C_B, \dots, C_P) \quad (\text{S10-17})$$

For first-order decay

$$p(a) = a \quad (\text{S10-18})$$

For second-order decay

$$p(a) = a^2 \quad (\text{S10-19})$$

8. For slow catalyst decay, the idea of a **temperature–time trajectory** is to increase the temperature in such a way that the rate of reaction remains constant.

9. The coupled differential equations to be solved for a **moving-bed reactor** are

$$F_{A0} \frac{dX}{dW} = a(-r'_A) \quad (\text{S10-20})$$

For n th-order activity decay and m order in a gas-phase concentration of species i in a moving bed where the solids move up with the velocity U_s

$$-\frac{da}{dW} = \frac{k_d a^n C_i^m}{U_s} \quad (\text{S10-21})$$

$$t = \frac{W}{U_s} \quad (\text{S10-22})$$

10. The coupled equations to be solved in a **straight-through transport reactor** are

$$\frac{dX}{dz} = \frac{a(t)[-r'_A(t=0)]}{U_0} \frac{\rho_{bc}}{C_{A0}} \quad (\text{S10-23})$$

$$U = U_0 (1 + \varepsilon X) \frac{T}{T_0} \quad (\text{S10-24})$$

$$t = \frac{z}{U_p} \quad (\text{S10-25})$$

where U_p is the particle velocity up the STTR. For coking

$$a(t) = \frac{1}{1 + \Delta t^{1/2}} \quad (\text{S10-26})$$

For the case when there is no slip between the catalyst particles and the gas velocity (S10-27)

$$U_p = U \quad (\text{S10-27})$$

ODE SOLVER ALGORITHM

The isomerization $A \rightarrow B$ is carried out over a decaying catalyst in a *moving-bed reactor* with pressure drop. Pure A enters the reactor and the catalyst flows through the reactor at a rate of 2.0 kg/s.

$$\begin{aligned} \frac{dX}{dW} &= \frac{-r'_A}{F_{A0}} & k &= 0.1 \text{ mol / (kg-cat} \cdot \text{s} \cdot \text{atm)} \\ r'_A &= \frac{-akP_A}{1 + K_A P_A} & K_A &= 1.5 \text{ atm}^{-1} \\ \frac{da}{dW} &= \frac{-k_d 2P_B}{U_s} & k_d &= \frac{0.75}{\text{s} \cdot \text{atm}} \\ P_A &= P_{A0}(1 - X)P & F_{A0} &= 10 \text{ mol/s} \\ P_B &= P_{A0}X_p & P_{A0} &= 20 \text{ atm} \\ \frac{dp}{dW} &= \frac{\alpha}{2p} & U_s &= 2.0 \text{ kg-cat/s} \\ \alpha &= 0.0019 \text{ kg}^{-1} & W_f &= 500 \text{ kg-cat} \end{aligned}$$

LEP Explore this problem using Python and/or Wolfram on the CRE Web site.

CRE WEB SITE MATERIALS ([HTTP://WWW.UMICH.EDU/~ELEMENTS/6E/10CHAP/OBJ.HTML#/\)](http://www.umich.edu/~elements/6e/10chap/obj.html#/)

Useful Links

Living
Example
Problems

Extra Help

Additional
Materials

Professional
Reference
Shelf

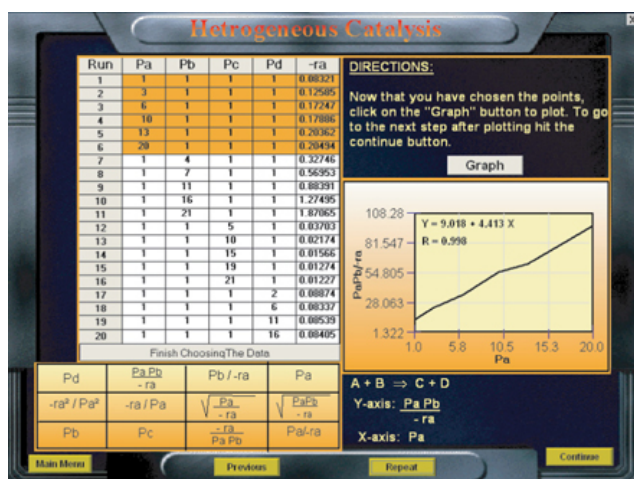
Computer
Simulation
Problem
Statements

Evaluation

Self Tests

Clicker
Questions

Interactive Computer Games



Heterogeneous Catalysis

(<http://umich.edu/%7Eelements/6e/icm/hetcat.html>)

After Reading Each Page in This Book, Ask Yourself a Question About What You Read

QUESTIONS, SIMULATIONS, AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$A = \bullet B = \blacksquare C = \blacklozenge D = \blacklozenge\blacklozenge$$




Homework Problems

Questions

Q10-1_A QBR (*Question Before Reading*). The rate laws for heterogeneous reactions usually have concentration terms in both the numerator and denominator. How can this function come about?

Q10-2_A i>clicker. Go to the Web site (http://www.umich.edu/~elements/6e/10chap/iclicker_ch10_q1.html) and view at least five i>clicker questions. Choose one that could be used as is, or a variation thereof, to be included on the next exam. You also could consider the opposite case: explaining why the question should *not* be on the next exam. In either case, explain your reasoning.

Q10-3_A Read over the problems at the end of this chapter. Make up an original problem that uses the concepts presented in this chapter. See Problem P5-1_A for guidelines. To obtain a solution:

1. Create your data and reaction.
2. Use a real reaction and real data.
The journals listed at the end of Chapter 1 may be useful for part (b).
3. Choose an FAQ from Chapter 10 and explain why it was most helpful.
4. Listen to the audios  on the *Summary Notes*, pick one, and explain why it was most helpful.

Q10-4_B For the decomposition of cumene discussed in this chapter, if an adsorbing inert is present, how would you compare the initial rate as a function of total pressure when desorption is the RLS, as shown in Figure 10-18?

Q10-5_A Choose five Chapter 10 i>clicker questions, pick the one that was the most challenging, and explain why.

Q10-6_A Revisit Example 10-4. What if you were asked to sketch or explain the difference in the temperature–time trajectories and to find the catalyst lifetimes (say $a = 0.1$) for first- and for second-order decay when E_A

$= 35 \text{ kcal/mol}$, $E_d = 10 \text{ kcal/mol}$, $k_{d0} = 0.01 \text{ day}^{-1}$, and $T_0 = 400 \text{ K}$? What would you say? Describe how the trajectory of the catalyst lifetime would change if $E_A = 10 \text{ kcal/mol}$ and $E_d = 35 \text{ kcal/mol}$? At what values of k_{d0} and ratios of E_d to E_A would temperature–time trajectories not be effective? Describe what your temperature–time trajectory would look like if $n = 1 + E_d/E_A$?

Q10-7_A Write a question for this problem that involves critical thinking and explain why it involves critical thinking.

Q10-8_A Go to the LearnChemE screencast link for Chapter 10 (<http://www.umich.edu/~elements/6e/10chap/learn-cheme-videos.html>). View one or more of the screencast 5- to 6-minute videos.

1. List two items you learned from Professor Dave's Lecture.
2. List four similarities between the Ely–Rideal mechanisms and the Langmuir–Hinshelwood screen-cast.
3. Write a two-sentence evaluation of the videos you viewed.

Q10-9_A AWFOS–S10 View the CSB video ([http://umich.edu/~safeche/assets/pdf/courses/Problems/CRE/344Reaction-EngrModule\(3\)PS-Exxon.pdf](http://umich.edu/~safeche/assets/pdf/courses/Problems/CRE/344Reaction-EngrModule(3)PS-Exxon.pdf)). After watching the Chemical Safety Board video, what points do you feel should have been emphasized more in the *Safety Analysis of the Incident* algorithm and the *BowTie Diagram*? Write three or so sentences describing your takeaway lesson from this incident.

Computer Simulations and Experiments

P10-1_B

1. Example 10-1: Nonlinear Regression to Determine Model

Parameters and Site Concentration Ratio = C_{T-S}/C_{B-S}

Wolfram and Python

1. Find the critical value of K_B at which fraction of vacant sites starts to increase with conversion for the initial settings. Repeat for K_T . Vary only one parameter at a time.
 2. Find the value K_B where the curve for $\left(\frac{C_{B-S}}{C_t}\right)$ versus conversion X changes from convex to concave and explain why this shape change occurs.
 3. Write a set of conclusions for your experiments (i) and (ii).
2. Example 10-2: Catalytic Reactor Design

Wolfram and Python

1. Describe how the partial pressure profiles change as you vary the sliders for α , K_T , and k .

- What if the molar flow rate were reduced by 50%; how would X and p change?
- After reviewing *Generating Ideas and Solutions* on the Web site ([http://www.umich.edu/~elements/6e/toc/SCPS,3rdEdBook\(Ch07\).pdf](http://www.umich.edu/~elements/6e/toc/SCPS,3rdEdBook(Ch07).pdf)), choose one of the brainstorming techniques (e.g., lateral thinking) to suggest two questions that should be included in this problem.
- Write two conclusions from your experiments with the sliders in this example.

Polymath

- What catalyst weight would be required for 60% conversion?
- Which parameter will you vary so that $P_B = P_{H_2}$ at the middle of the reactor (i.e., $W = 5000$ kg).

3. Example 10-3: Hydrogenation Ethylene to Ethane

- Use **Polymath** to learn how your answers would change if the following data for run 10 were incorporated in your regression table.

$$-r'_E = 0.8 \text{ mol/kg-cat} \cdot \text{s}, P_E = 0.5 \text{ atm}, P_{EA} = 15 \text{ atm}, P_H = 2 \text{ atm}$$

- How do the rate laws (e) and (f)

$$(e) -r'_E = \frac{kP_E P_H}{(1 + K_A P_{EA} + K_E P_E)^2} \quad (f) -r'_E = \frac{kP_H P_H}{1 + K_A P_{EA}}$$

compare with the nonlinear analysis with the other rate laws used to model the data?

4. Example 10-4: Calculating Conversion with Catalyst Decay in Batch Reactors

Wolfram and Python

- What is the maximum conversion that can be achieved if there is no catalyst decay?
- Vary k and k_d and describe what you find. Can you explain why there is no effect of catalyst decay on conversion at a high value of k ?
- Vary E and k_d and then write a few sentences and three conclusions describing the results of your experiments.
- Explain why conversion with catalyst decay increases with increasing E_d and decreases with increasing E .

Polymath

- Vary the ratio of (k/k_d) and describe what you find.
- Repeat this example (i.e., the plotting of X vs. t) for a second-order reaction with $(C_{A0} = 1 \text{ mol/dm}^3)$ and first-order decay, and describe the differences from the base case.
- Repeat this example for a first-order reaction and first-order decay and describe the differences from the base case.
- Repeat this example for a second-order reaction $(C_{A0} = 1 \text{ mol/dm}^3)$ and a second-order decay and describe the differences from the base case.

5. Example 10-5: Catalytic Cracking in a Moving-Bed Reactor

Wolfram and Python

1. Suppose k_d and U_S are at their maximum values. What could you do to increase conversion?
2. Vary the parameters and write a set of conclusions.

Polymath

3. Use Polymath to learn what the conversion would be if there is no catalyst decay.
4. What if the solids and reactants entered from opposite ends of the reactor? How would your answers change?
5. What if the decay in the moving bed were second order? By how much must the catalyst charge, U_S , be increased to obtain the same conversion?
6. What if $\varepsilon = 2$ (e.g., $A \rightarrow 3B$) instead of zero. How would the results be affected?

6. Example 10-6: Decay in a Straight-Through Transport Reactor

Wolfram and Python

1. What happens to a and X when T is varied?
2. What happens to a and X when U_0 is varied?
3. Vary the parameters and write a set of conclusions.

Polymath

4. What if you varied the parameters P_{A0} , U_g , A , and k' in the STTR? What parameter has the greatest effect on either increasing or decreasing the conversion?
5. Ask questions such as: What is the effect of varying the ratio of k to U_g or of k to A on the conversion? Make a plot of conversion versus distance as U_g is varied between 0.5 and 50 m/s.
6. Sketch the activity and conversion profiles for $U_g = 0.025, 0.25, 2.5$, and 25 m/s.
7. What gas velocity do you suggest operating at?
8. What is the corresponding entering volumetric flow rate?
9. What concerns do you have operating at the velocity you selected? Would you like to choose another velocity? If so, what is it? Which parameter will you vary so that conversion increases but activity decreases? Explain, if you can, this unusual behavior.

Interactive Computer Game

P10-2A Download the Interactive Computer Games (ICG)

from the CRE Web site

(<http://www.umich.edu/~elements/6e/icm/install.html>).

Play the game and then record your performance number for the game, which indicates your mastery of the material. Your professor has the key to decode your performance number. (This ICG is a little longer than the other ICGs.)

ICG Heterogeneous Catalysis Performance #

PROBLEMS

P10-3_A t-Butyl alcohol (TBA) is an important octane enhancer that is used to replace lead additives in gasoline (*Ind. Eng. Chem. Res.*, 27, 2224 (1988)). TBA was produced by the liquid-phase hydration (W) of isobutene (I) over an Amberlyst-15 catalyst. The system is normally a multiphase mixture of hydrocarbon, water, and solid catalysts. However, the use of cosolvents or excess TBA can achieve reasonable miscibility.

The reaction mechanism is believed to be



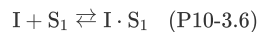
Derive a rate law assuming:

1. The surface reaction is rate-limiting.
2. The adsorption of isobutene is limiting.
3. The reaction follows Eley–Rideal kinetics



and the surface reaction is limiting.

4. Isobutene (I) and water (W) are adsorbed on different sites.

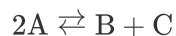


TBA is *not* on the surface, and the surface reaction is rate-limiting.

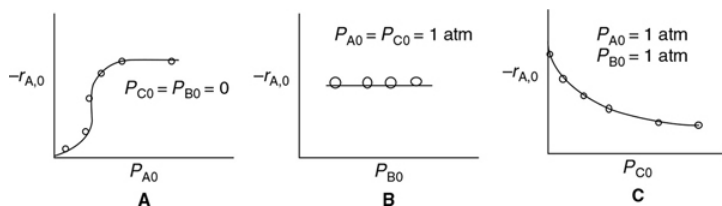
$$\left(Ans : r'_{TBA} = -r'_1 = \frac{k[C_1 C_W - C_{TBA}/K_c]}{(1 + K_W C_W)(1 + K_1 C_1)} \right)$$

5. What generalization can you make by comparing the rate laws derived in parts (a) through (d)?

P10-4_B OEQ (Old Exam Question). Consider the catalytic reaction as a function of the initial partial pressures



The rate of disappearance of species A was obtained in a differential reactor and is shown below.



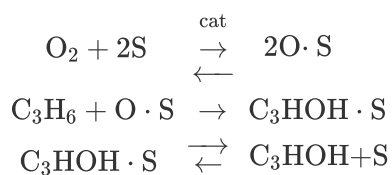
1. What species are on the surface?
2. What does Figure B tell you about the reversibility and what's adsorbed on the surface?
3. Derive the rate law and suggest a rate-limiting step consistent with the above figures.
4. How would you plot your data to linearize the initial rate data in Figure A?
5. Assuming pure A is fed, and the adsorption constants for A and C are $K_A = 0.5 \text{ atm}^{-1}$ and $K_C = 0.25 \text{ atm}^{-1}$ respectively, at what conversion are the number of sites with A adsorbed on the surface and C adsorbed on the surface equal? (Ans: $X = 0.66$)

P10-5A The rate law for the hydrogenation (H) of ethylene (E) to form ethane (A) over a cobalt-molybdenum catalyst (*Collection Czech. Chem. Commun.*, 51, 2760 (1988)) is

$$-r'_E = \frac{kP_E P_H}{1 + K_E P_E}$$

1. Suggest a mechanism and rate-limiting step consistent with the above rate law.
2. What was the most difficult part in finding the mechanism?

P10-6B The formation of propenol on a catalytic surface is believed to proceed by the following mechanism



Suggest a rate-limiting step and derive a rate law.

P10-7B **OEQ (Old Exam Question).** The dehydration of *n*-butyl alcohol (butanol) over an alumina-silica catalyst was investigated by J. F. Maurer (Ph.D. thesis, University of Michigan). The data in [Figure P10-7B](#) were obtained at 750°F in a modified differential reactor. The feed consisted of pure butanol.

1. Suggest a mechanism and rate-limiting step that are consistent with the experimental data.
2. Evaluate the rate-law parameters.

- At the point where the initial rate is a maximum, what is the fraction of vacant sites? What is the fraction of occupied sites by both A and B? % vacant = 0.41
- What generalizations can you make from studying this problem?
- Write a question that requires critical thinking and then explain why your question requires critical thinking. *Hint:* See Preface Section G.
- Apply to this problem one or more of the six ideas discussed in Table P-4 in the Complete Preface-Introduction on the Web site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>).

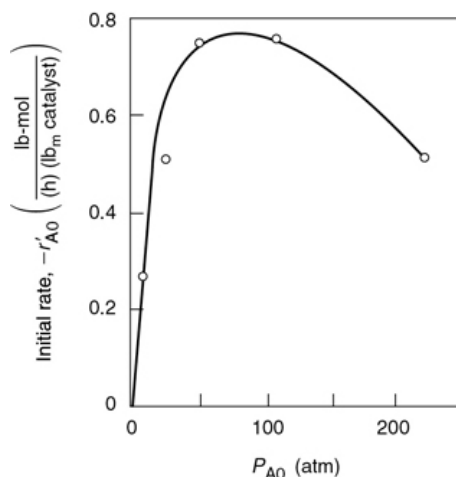


Figure P10-7B Initial reaction rate as function of initial partial pressure of butanol.

P10-8B *OEQ (Old Exam Question)*. The catalytic dehydration of methanol (ME) to form dimethyl ether (DME) and water was carried out over an ion exchange catalyst (K. Klusacek, *Collection Czech. Chem. Commun.*, 49, 170 (1984)). The packed bed was initially filled with nitrogen, and at $t = 0$. The N_2 feed is switched to pure methanol vapor entering the reactor at 413 K, 100 kPa, and $0.2 \text{ cm}^3/\text{s}$. The following partial pressures were recorded at the exit to the differential reactor containing 1.0 g of catalyst in 4.5 cm^3 of reactor volume.

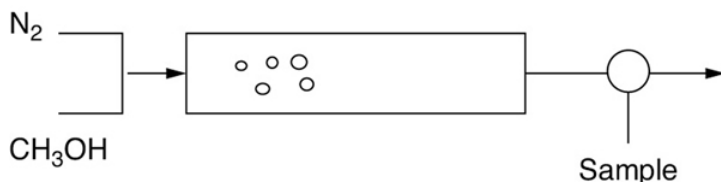


TABLE P10-8_B PARTIAL PRESSURE OF H₂, ME, AND DME
EXITING THE REACTOR AFTER TIME

$t(\text{s})$							
0 10 50 100 150 200 300							
P_{N_2} (kPa)	100	50	10	2	0	0	0
P_{ME} (kPa)	0	2	15	23	25	26	26
$P_{\text{H}_2\text{O}}$ (kPa)	0	10	15	30	35	37	37
P_{DME} (kPa)	0	38	60	45	40	37	37

Use parts (a) through (f) to lead you to suggest a mechanism, rate-limiting step, and rate law consistent with this data.

1. Using the data above, sketch the exit concentrations as a function of time.
2. Which species took longer than others to exit the reactor in the gas phase? What could have caused this difference in exit times?
3. What species are adsorbed on the surface?
4. Are any species not adsorbed on the surface? If so, which ones?
5. Which set of figures in Figure P10-8_B correctly describes the functionality of the chemical reaction rate with the partial pressure P_{W} , P_{DME} , and P_{ME} ?
6. Derive a rate law for the catalytic dehydration of methanol. Dimethyl Ether $2\text{ME} \rightarrow \text{DME} + \text{W}$.

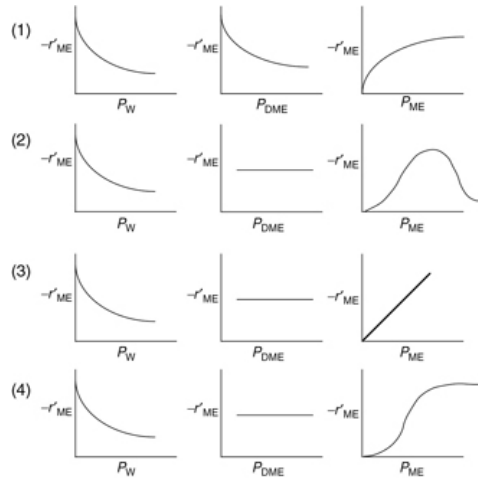


Figure P10-8B Rate data.

P10-9B In 1981, the U.S. government put forth the following plan for automobile manufacturers to reduce emissions from automobiles over the next few years.

Year				
	1981	1993	2010	
Hydrocarbons	0.41	0.25	0.125	
CO	3.4	3.4	1.7	
NO	1.0	0.4	0.2	

All values are in grams per mile. An automobile emitting 3.74 lb_m of CO and 0.37 lb_m of NO on a journey of 1000 miles would meet the current government requirements.



To remove oxides of nitrogen (assumed to be NO) from automobile exhaust, a scheme has been proposed that uses unburned carbon monoxide (CO) in the exhaust to reduce the NO over a solid catalyst, according to the reaction



Experimental data for a particular solid catalyst indicate that the reaction rate can be well represented over a large range of temperatures by

$$-r'_N = \frac{kP_N P_C}{(1 + K_1 P_N + K_2 P_C)^2} \quad (\text{P10-9.1})$$

where P_N = gas-phase partial pressure of NO

P_C = gas-phase partial pressure of CO

k, K_1, K_2 = coefficients depending only on temperature

1. Propose an adsorption–surface reaction–desorption mechanism and rate-limiting step that are consistent with the experimentally observed rate law. Do you need to assume any species are weakly adsorbed to get agreement with Equation (P10-9.1)?
2. A certain engineer thinks that it would be desirable to operate with a very large stoichiometric excess of CO to minimize catalytic reactor volume. Do you agree or disagree? Explain.
3. What would be the relevance of the problem if everyone were driving a hybrid by 2018? A driverless car by 2020?

P10-10_B OEQ (Old Exam Question). Methyl ethyl ketone (MEK) is an important industrial solvent that can be produced from the dehydrogenation of butan-2-ol

(Bu) over a zinc oxide catalyst (*Ind. Eng. Chem. Res.*, 27, 2050 (1988)):



The following data giving the reaction rate for MEK were obtained in a differential reactor at 490°C.

P_{Bu} (atm)	2	0.1	0.5	1	2	1
P_{MEK} (atm)	5	0	2	1	0	0
P_{H_2} (atm)	0	0	1	1	0	10
r'_{MEK} (mol/h · g – cat)	0.04	0.04	0.06	0.06	0.04	0.05
	4	0	9	0	3	9

1. Suggest a rate law consistent with the experimental data.
2. Suggest a reaction mechanism and rate-limiting step consistent with the rate law. *Hint:* Some species might be weakly adsorbed.
3. Apply to this problem one or more of the six ideas discussed in Table P-4 in the Complete preface-introduction on the Web site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>).
4. Plot conversion (up to 90%) and reaction rate as a function of catalyst weight for an entering molar flow rate of pure butan-2-ol of 10 mol/min at an entering pressure $P_0 = 10$ atm up to a catalyst weight $W_{\text{max}} = 23$ kg.
5. Write a question that requires critical thinking and then explain why your question requires critical thinking. *Hint:* See Preface Section G.
6. Repeat part (d), accounting for pressure drop and $\alpha = 0.03 \text{ kg}^{-1}$. Plot p and X as a function of catalyst weight down the reactor.

P10-11B Cyclohexanol was passed over a catalyst to form water and cyclohexene:



It is suspected that the reaction may involve a dual-site mechanism, but it is not known for certain. It is believed that the adsorption equilibrium constant for

cyclohexanol is around 1.0 and is roughly one or two orders of magnitude greater than the adsorption equilibrium constants for the other compounds. Using the data in Table P10-11_B

TABLE P10-11_B DATA FOR CATALYTIC FORMATION OF CYCLOHEXENE

n	R u (mol/dm ³ · s) × 10 ⁵	Reaction Rate	Partial Pressure of Cyclohexanol (atm)	Partial Pressure of Cyclohexene (atm)	Partial Pressure of Steam (H ₂ O) (atm)
1	3.3		1	1	1
2	1.05		5	1	1
3	0.565		10	1	1
4	1.826		2	5	1
5	1.49		2	10	1
6	1.36		3	0	5
7	1.08		3	0	10
8	0.862		1	10	10
9	0		0	5	8
10	1.37		3	3	3

1. Suggest a rate law and mechanism consistent with the data given here.
2. Determine the values of the rate-law parameters. (*Ind. Eng. Chem. Res.*, 32, 2626–2632.)
3. Why do you think estimates of the rate-law parameters were given?
4. For an entering molar flow rate of cyclohexanol of 10 mol/s at a partial pressure of 15 atm, what catalyst weight is necessary to achieve 85% conversion when the bulk density is 1500 gm/dm³?

P10-12_B OEQ (Old Exam Question). Experimental data for the gas-phase catalytic reaction



is shown below. The limiting step in the reaction is known to be irreversible, so that the overall reaction is

irreversible. The reaction was carried out in a differential reactor to which A, B, and C were all fed.

Run Number	P_A (atm)	P_B (atm)	P_C (atm)	Reaction rate (mol)/(g-cat · s)
1	1	1	2	0.114
2	1	10	2	1.140
3	10	1	2	0.180
4	1	20	2	2.273
5	1	20	10	0.926
6	20	1	2	0.186
7	0.1	1	2	0.0243

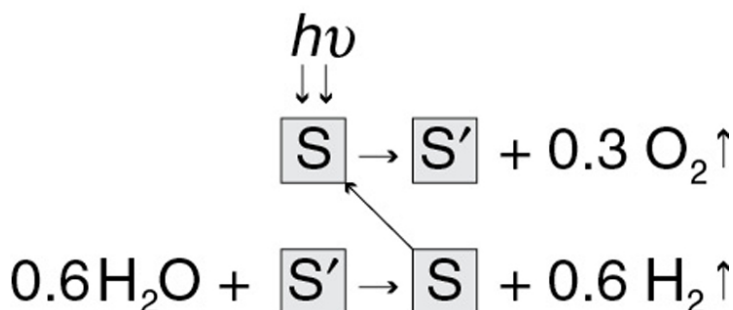
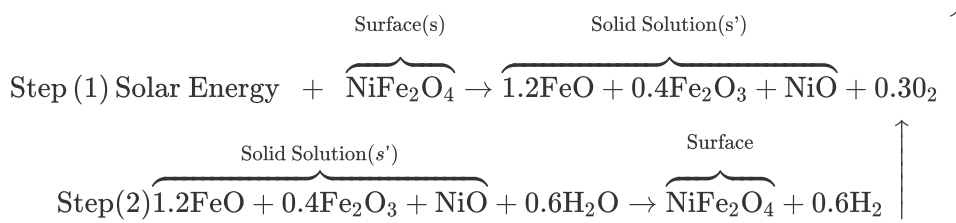
1. Suggest a rate law consistent with the experimental data. *Hint:* Sketch $(-r'_A)$ as a function of P_A , as a function of P_B , and as a function of P_C .
2. From your rate expression, which species can you conclude are adsorbed on the surface?
3. Suggest a rate law and then show that your mechanism is constant with the rate law in part (a).
4. For an entering partial pressure of A of 2 atm in a PBR, what is the ratio of A to C sites at 80% conversion of A?
5. At what conversion are the number of A and C sites equal? (**Ans:** $X = 0.235$)
6. What reactor volume is necessary to achieve 90% conversion of A for a stoichiometric feed and flow of A 2 mol/s? (**Ans:** $W = 8.9$ g-cat)

If necessary, feel free to use none, any, or all of the following parameter values:

$$k = 2.5 \frac{\text{mol}}{\text{atm}^2 \text{g-cat} \cdot \text{s}}, K_A = 4 \text{ atm}^{-1}, K_C = 13 \text{ atm}^{-1}, K_I = 10 \text{ atm}^{-1}$$

P10-13_B Solar Energy Capture: Water Splitting.

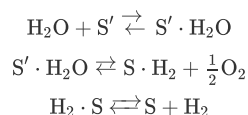
Hydrogen and O_2 can be combined in fuel cells to generate electricity. Solar energy can be used to split water to generate the raw reactants H_2 and O_2 for fuel cells. One method of solar thermal reduction is with NiFe_2O_4 in the sequence



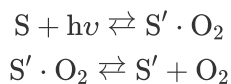
We note NiFe_2O_4 is regenerated in this process.³⁶

³⁶ J. R. Scheffe, J. Li, and A. W. Weimer, "A spinel ferrite/hercynite water-splitting redox cycle," *Int. J. Hydrogen Energy*, 35, 3333–3340 (2010).

1. Derive a rate law for Step (2), assuming that water adsorbs on the solid solution as a single-site mechanism and that the reaction is irreversible.
2. Repeat (a) when the reaction is reversible and the solid solution adsorption site for water (S') is different than the NiFe_2O_4 site for the adsorption of H_2 , (S).



3. How would your rate law change if we included the effect of $h\nu$ in Step 1?



P10-14_A Vanadium oxides are of interest for various sensor applications, owing to the sharp metal–insulator transitions they undergo as a function of temperature, pressure, or stress. Vanadium triisopropoxide (VTIPO) was used to grow vanadium oxide films by *chemical vapor deposition* (*J. Electrochem. Soc.*, 136, 897 (1989)). The deposition rate as a function of VTIPO pressure for two different temperatures follows.

$T = 120^{\circ}\text{C}$:

Growth Rate ($\mu\text{m/h}$)	0.0 04	0.0 15	0.02 5	0.0 4	0.06 8	0.0 8	0.09 5	0. 1
VTIPO Pressure (torr)	0.1	0.2	0.3	0.5	0.8	1.0	1.5	2. 0

$T = 200^{\circ}\text{C}$:

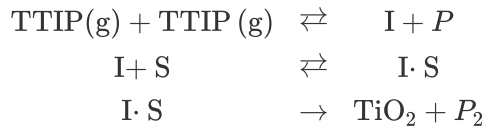
Growth Rate ($\mu\text{m/h}$)	0.028	0.45	1.8	2.8	7.2
VTIPO Pressure (torr)	0.05	0.2	0.4	0.5	0.8

In light of the material presented in this chapter, analyze the data and describe your results. Specify where additional data should be taken.

P10-15_A OEQ (Old Exam Question). Titanium dioxide is a wide-bandgap semiconductor that is showing promise as an insulating dielectric in VLSI capacitors and for use in solar cells. Thin films of TiO_2 are to be prepared by *chemical vapor deposition* from gaseous titanium tetraisopropoxide (TTIP). The overall reaction is



The reaction mechanism in a CVD reactor is believed to be (K. L. Sieferring and G. L. Griffin, *J. Electrochem. Soc.*, 137, 814 (1990))



where I is an active intermediate and P₁ is one set of reaction products (e.g., H₂O, C₃H₆), and P₂ is another set. Assuming the homogeneous gas-phase reaction for TTIP is in equilibrium, derive a rate law for the deposition of TiO₂. The experimental results show that at 200=C the reaction is second order at low partial pressures of TTIP and zero order at high partial pressures, while at 300=C the reaction is second order in TTIP over the entire pressure range. Discuss these results in light of the rate law you derived.

P10-16B The dehydrogenation of methylcyclohexane (M) to produce toluene (T) was carried out over a 0.3% Pt/ catalyst in a differential catalytic reactor. The reaction is carried out in the presence of hydrogen (H₂) to avoid coking (*J. Phys. Chem.*, 64, 1559 (1960)).

- Describe how you would determine the model parameters for each of the following rate laws.

$$\begin{array}{ll}
 (1) -r'_M = kP_M^\alpha P_{H_2}^\beta & (3) -r'_M = \frac{kP_M P_{H_2}}{(1 + K_M P_M)^2} \\
 (2) -r'_M = \frac{kP_M}{1 + K_M P_M} & (4) -r'_M = \frac{kP_M P_{H_2}}{1 + K_M P_M + K_{H_2} P_{H_2}}
 \end{array}$$

Use the data in Table P10-16B below.

- Which rate law best describes the data? *Hint:* Neither K_{H_2} or K_M can take on negative values.
- Where would you place additional data points?
- Suggest a mechanism and rate-limiting step consistent with the rate law you have chosen.

TABLE P10-16B DEHYDROGENATION OF METHYLCYCLOHEXANE

$P_{H_2} \text{ (atm)} P_M \text{ (atm)} r'_T \left(\frac{\text{mol toluene}}{\text{s} \cdot \text{kg-cat}} \right)$		
1	1	1.2
1.5	1	1.25
0.5	1	1.30
0.5	0.5	1.1
1	0.25	0.92

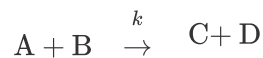
0.5	0.1	0.64
3	3	1.27
1	4	1.28
3	2	1.25
4	1	1.30
0.5	0.25	0.94
2	0.05	0.41

P10-17_A OEQ (Old Exam Question). Sketch *qualitatively* the reactant, product, and activity profiles as a function of length at various times for a *packed-bed reactor* for each of the following cases. In addition, sketch the effluent concentration of A as a function of time. The reaction is a simple isomerization:



1. Rate law: $-r'_A = kaC_A$
Decay law: $r_d = k_d a C_A$
Case I: $k_d \ll k$, Case II: $k_d = k$, Case III: $k_d \gg k$
2. $-r'_A = kaC_A$ and $r_d = k_d a^2$
3. $-r'_A = kaC_A$ and $r_d = k_d a C_B$
4. Sketch similar profiles for the rate laws in parts (a) and (c) in a *moving-bed reactor* with the solids entering at the same end of the reactor as the reactant.
5. Repeat part (d) for the case where the solids and the reactant enter at opposite ends.

P10-18_B The elementary irreversible gas-phase catalytic reaction



is to be carried out in a moving-bed reactor at constant temperature. The reactor contains 5 kg of catalyst. The feed is stoichiometric in A and B. The entering concentration of A is 0.2 mol/dm^3 . The catalyst decay law is zero order with $k_D = 0.2 \text{ s}^{-1}$ and $k = 1.0$

$\text{dm}^6/(\text{mol} \cdot \text{kg-cat} \cdot \text{s})$ and the volumetric flow rate is $v_0 = 1 \text{ dm}^3/\text{s}$.

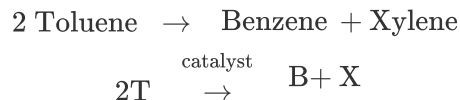
1. What conversion will be achieved for a catalyst feed rate of 0.5 kg/s?
(Ans: $X = 0.2$)
2. Sketch the catalyst activity as a function of catalyst weight (i.e., distance) down the reactor length for a catalyst feed rate of 0.5 kg/s.
3. What is the maximum conversion that could be achieved (i.e., at an infinite catalyst loading rate)?
4. What catalyst loading rate is necessary to achieve 40% conversion?
(Ans: $U_S = 1.5 \text{ kg/s}$)
5. At what catalyst loading rate (kg/s) will the catalyst activity be exactly zero at the exit of the reactor?
6. What does an activity of zero mean? Can catalyst activity be less than zero?
7. How would your answer in part (a) change if the catalyst and reactant were fed at opposite ends? Compare with part (a).
8. Now consider the reaction to be zero order with
 $k = 0.2 \text{ mol/kg-cat} \cdot \text{min}$.

The economics:

1. The product sells for \$160 per gram mole.
2. The cost of operating the bed is \$10 per kilogram of catalyst exiting the bed.

What is the feed rate of solids (kg/min) that will give the maximum profit? (Ans: $U_S = 4 \text{ kg/min}$.) Note: For the purpose of this calculation, ignore all other costs, such as the cost of the reactant, the cost to the company of providing free lunches to workers, and so on.

P10-19_B OEQ (Old Exam Question). With the increasing demand for xylene in the petrochemical industry, the production of xylene from toluene disproportionation has gained attention in recent years (*Ind. Eng. Chem. Res.*, 26, 1854 (1987)). This reaction,



was studied over a hydrogen mordenite catalyst that decays with time. As a first approximation, assume that the catalyst follows second-order decay

$$r_d = k_d a^2$$

and the rate law for low conversions is

$$-r'_T = k_T P_T a$$

with $k_T = 20 \text{ g mol/h} \cdot \text{kg-cat} \cdot \text{atm}$ and $k_d = 1.6 \text{ h}^{-1}$ at 735 K.

1. Compare the conversion–time curves in a batch reactor containing 5 kg-cat at different initial partial pressures (1 atm, 10 atm, etc.). The reaction volume containing pure toluene initially is 1 dm^3 and the temperature is 735 K.
2. What conversion can be achieved in a *moving-bed reactor* containing 50 kg of catalyst with a catalyst feed rate of 2 kg/h? Toluene is fed at a pressure of 2 atm and a rate of 10 mol/min.
3. Explore the effect of catalyst feed rate on conversion.
4. Suppose that $E_T = 25 \text{ kcal/mol}$ and $E_d = 10 \text{ kcal/mol}$. What would the temperature–time trajectory look like for a CSTR? What if $E_T = 10 \text{ kcal/mol}$ and $E_d = 25 \text{ kcal/mol}$?
5. The decay law more closely follows the equation

$$r_d = k_d P_T^2 a^2$$

with $k_d = 0.2 \text{ atm}^{-1}$. Redo parts (b) and (c) for these conditions.

P10-20A The vapor-phase cracking of gas-oil in Example 10-6 is carried out over a different catalyst, for which the rate law is

$$-r'_A = k' P_A^2 \quad \text{with } k' = 5 \times 10^{-5} \frac{\text{kmol}}{\text{kg-cat} \cdot \text{s} \cdot \text{atm}^2}$$

1. Assuming that you can vary the entering pressure and gas velocity, what operating conditions would you recommend?
2. What could go wrong with the conditions you chose?
Now assume the decay law is

$$-\frac{da}{dt} = k_D a C_{\text{coke}} \quad \text{with } k_D = 100 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \text{ at } 400^\circ\text{C}$$

where the concentration, C_{coke} , in mol/dm^3 , can be determined from a stoichiometric table.

3. For a temperature of 400°C and a reactor height of 15 m, what gas velocity do you recommend? Explain. What is the corresponding conversion?
4. The reaction is now to be carried in an STTR 15 m high and 1.5 m in diameter. The gas velocity is 2.5 m/s. You can operate in the temperature range between 100°C and 500°C . What temperature do you choose, and what is the corresponding conversion?
5. What would the temperature–time trajectory look like for a CSTR?

Additional information:

$$E_R = 3000 \text{ cal/mol}$$

$$E_D = 15000 \text{ cal/mol}$$

P10-21C When the impurity cumene hydroperoxide is present in trace amounts in a cumene feed stream, it can deactivate the silica-alumina catalyst over which cumene is being cracked to form benzene and

propylene. The following data were taken at 1 atm and 420°C in a differential reactor. The feed consists of cumene and a trace (0.08 mol %) of cumene hydroperoxide (CHP).

Benzene in Exit Stream (mol %)	2	1.	1.	1.	0.	0.	0.	0.
	62	62	32	06	85	56	37	24
t (s)	0	50	10	15	20	30	40	50
			0	0	0	0	0	0

1. Determine the order of decay and the decay constant. (**Ans:** $k_d = 4.27 \times 10^{-3} \text{ s}^{-1}$)
2. As a first approximation (actually a rather good one), we shall neglect the denominator of the catalytic rate law and consider the reaction to be first order in cumene. Given that the specific reaction rate with respect to cumene is $k = 3.8 \times 10^3 \text{ mol/kg fresh cat} \cdot \text{s} \cdot \text{atm}$, the molar flow rate of cumene (99.92% cumene, 0.08% CHP) is 200 mol/min, the entering concentration is 0.06 kmol/m^3 , the catalyst weight is 100 kg, and the velocity of solids is 1.0 kg/min, what conversion of cumene will be achieved in a *moving-bed reactor*?

P10-22C The decomposition of spartanol to wulfrene and CO_2 is often carried out at high temperatures (*J. Theor. Exp.*, 15, 15 (2014)). Consequently, the denominator of the catalytic rate law is easily approximated as unity, and the reaction is first order with an activation energy of 150 kJ/mol. Fortunately, the reaction is irreversible. Unfortunately, the catalyst over which the reaction occurs decays with time on stream. The following conversion–time data were obtained in a differential reactor:

For $T = 500 \text{ K}$:

t (days)	0	20	40	60	80	120
X %	1	0.7	0.56	0.45	0.38	0.29

For $T = 550 \text{ K}$:

t (days)	0	5	10	15	20	30	40

X %	2	1.2	0.89	0.69	0.57	0.42	0.33
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1. If the initial temperature of the catalyst is 480 K, determine the *temperature–time trajectory* to maintain a constant conversion.
2. What is the catalyst lifetime?

P10-23B The hydrogenation of ethylbenzene to ethylcyclohexane over a nickel–mordenite catalyst is zero order in both reactants up to an ethylbenzene conversion of 75% (*Ind. Eng. Chem. Res.*, 28 (3), 260 (1989)). At 553 K, $k = 5.8 \text{ mol ethylbenzene}/(\text{dm}^3 \text{ of catalyst} \cdot \text{h})$. When a 100-ppm thiophene concentration entered the system, the ethylbenzene conversion began to drop.

Time (h)	0	1	2	4	6	8	12
Conversion	0.92	0.82	0.75	0.50	0.30	0.21	0.10

The reaction was carried out at 3 MPa and a molar ratio of $\text{H}_2/\text{ETB} = 10$. Discuss the catalyst decay. Be quantitative where possible.

SUPPLEMENTARY READING

1. A terrific discussion of heterogeneous catalytic mechanisms and rate-controlling steps may or may not be found in

THORNTON W. BURGESS, *The Adventures of Grandfather Frog*. New York: Dover Publications, Inc., 1915.

R. I. MASEL, *Principles of Adsorption and Reaction on Solid Surfaces*. New York: Wiley, 1996. A great reference.

G. A. SOMORJAI, *Introduction to Surface Chemistry and Catalysis*. New York: Wiley, 1994.

2. A truly excellent discussion of the types and rates of adsorption together with techniques used in measuring catalytic surface areas is presented in

R. I. MASEL, *Principles of Adsorption and Reaction on Solid Surfaces*. New York: Wiley, 1996.

3. Techniques for discriminating between mechanisms and models can be found in

G. E. P. BOX, J. S. HUNTER, and W. G. HUNTER, *Statistics for Experimenters: Design, Innovation, and Discovery*, 2nd ed. Hoboken, NJ: Wiley, 2005.

4. Examples of applications of catalytic principles to microelectronic manufacturing can be found in

JOHN B. BUTT, *Reaction Kinetics and Reactor Design. Second Edition, Revised and Expanded*. New York: Marcel Dekker, Inc., 1999.

D. M. DOBKIN AND M. K. ZURAW, *Principles of Chemical Vapor Deposition*. The Netherlands: Kluwer Academic Publishers, 2003.

11. *Nonisothermal Reactor Design: The Steady-State Energy Balance and Adiabatic PFR Applications*

If you can't stand the *heat*, get out of the kitchen.

—Harry S Truman

Overview. Because most reactions are not carried out isothermally, we now focus our attention on heat effects in chemical reactors. The basic CRE algorithm of *mole balance, rate law, stoichiometry, combine, and evaluate* used in Chapters 1–10 for isothermal reactor design is still valid for the design of nonisothermal reactors and we only need to add one more step, the *energy balance* to solve nonisothermal problems. The major difference lies in the method of evaluating the combined mole balances, rate law, and stoichiometry when temperature varies along the length of a PFR or when heat is removed from a CSTR.

This chapter is arranged as follows:

- Section 11.1 shows why we need the energy balance and how it will be used to solve reactor design problems.
- Section 11.2 develops the energy balance to a point where it can be applied to different types of reactors. It then gives the end result, relating temperature and conversion or reaction rate for the main types of reactors we have been studying.
- Section 11.3 develops the user-friendly energy balances for reactors.
- Section 11.4 discusses the adiabatic operation of reactors.
- Section 11.5 shows how to determine the adiabatic equilibrium conversion and how to carry out interstage cooling.
- Section 11.6 shows how to find the optimum inlet temperature to achieve the maximum conversion for adiabatic operation.
- Section 11.7 closes the chapter with some thoughts on the type of critical thinking questions you could ask about the safety of your system.

11.1 RATIONALE

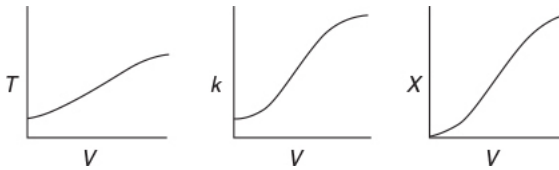
To identify the additional information necessary to design nonisothermal reactors, we consider the following example, in which a highly exothermic reaction is carried out adiabatically in a plug-flow reactor.

Example 11-1 What Additional Information Is Required?

The first-order liquid-phase reaction



is carried out in a PFR. The reaction is exothermic and the reactor is operated adiabatically. As a result, the temperature will increase with conversion down the length of the reactor. Because T varies along the length of the reactor, k will also vary, which was not the case for isothermal plug-flow reactors.



Describe how to calculate the PFR reactor volume necessary for 70% conversion and plot the corresponding profiles for X and T .

Solution

The same CRE algorithm can be applied to nonisothermal reactions as to isothermal reactions by adding one more step, **the energy balance**.

1. Mole Balance (design equation):

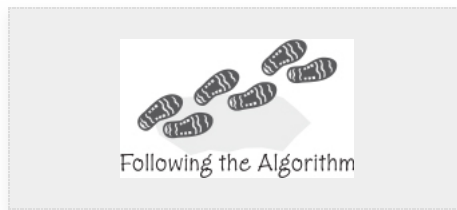
$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} \quad (\text{E11-1.1})$$

2. Rate Law:

$$-r_A = kC_A \quad (\text{E11-1.2})$$

Recalling the Arrhenius equation,

$$k = k_1 \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (\text{E11-1.3})$$



we know that k is a function of temperature, T .

3. Stoichiometry (liquid phase): $v = v_0$

$$C_A = C_{A0}(1-X) \quad (\text{E11-1.4})$$

4. Combining:

$$-r_A = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] C_{A0}(1-X) \quad (\text{E11-1.5})$$

Combining Equations (E11-1.1), (E11-1.2), and (E11-1.4), and canceling the entering concentration, C_{A0} , yields

$$\frac{dX}{dV} = \frac{k(1-X)}{v_0} \quad (\text{E11-1.6})$$

Combining Equations (E11-1.3) and (E11-1.6) gives us

$$\frac{dX}{dV} = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] \frac{1-X}{v_0} \quad (\text{E11-1.7})$$

Why we need the energy balance

Oops! We see that we need another relationship relating X and T or T and V to solve this equation. *The energy balance will provide us with this relationship.*

So we add another step to our algorithm; this step is the **energy balance**.

5. Energy Balance:

In this step, we will find the appropriate energy balance to relate temperature and conversion or reaction rate. For example, if the reaction is *adiabatic*, we will show that for equal heat capacities, C_{PA} and C_{PB} , and a constant heat of reaction, ΔH_{Rx}° , the temperature-conversion relationship for an adiabatic reaction (cf. Table 11-1) can be written in a form such as

$$T = T_0 + \frac{-\Delta H_{Rx}^\circ}{C_{PA}} X \quad (\text{E11-1.8})$$

T_0 =Entering CPB Temperature

ΔH_{Rx}° =Heat of Reaction

C_{PA} =Heat Capacity of species A

We now have all the equations we need to solve for the conversion and temperature profiles. We simply type Equations (E11-1.7) and (E11-1.8) along with the parameters into Polymath, Wolfram, Python, or MATLAB; click the RUN button; and then carry out the calculation to a volume where 70% conversion is obtained.

Analysis: The purpose of this example was to demonstrate that for nonisothermal chemical reactions we need another step in our CRE algorithm, **the energy balance**. The energy balance allows us to solve for the reaction temperature, which is necessary in evaluating the specific reaction-rate constant $k(T)$.

11.2 THE ENERGY BALANCE

11.2.1 First Law of Thermodynamics

The goal of this section is to use the energy balance to develop user-friendly relationships with temperature that can be easily applied to chemical reactors. We begin with the application of the first law of thermodynamics, first to a closed system and then to an open system. A system is any bounded portion of the universe, moving or stationary, which is chosen for the application of the various thermodynamic equations. For a closed system, no mass crosses the system boundaries and the change in total energy of the system, $d\hat{E}$, is equal to the *heat flow to the system* δQ , minus the *work done by the system on the surroundings*, δW . For a closed system, the energy balance is

$$d\hat{E} = \delta Q - \delta W \quad (11-1)$$

Closed system

The δ s signify that δQ and δW are not exact differentials of a state function.

The *continuous-flow reactors* we have been discussing are *open systems* in which mass crosses the system boundary. We shall carry out an energy balance on the open system shown in [Figure 11-1](#). For an open system in which some of the energy exchange is brought about by the flow of mass across the system boundaries, the energy balance for the case of *only one* species entering and leaving becomes

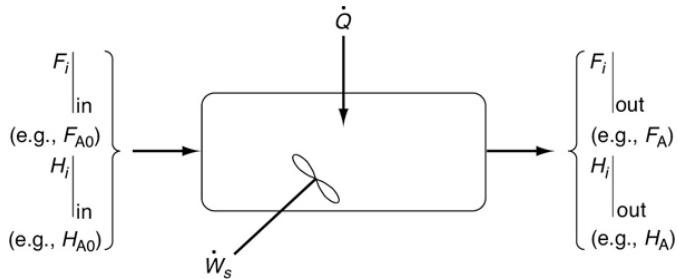


Figure 11-1 Energy balance on a well-mixed open system: schematic.

$$\begin{array}{ccccccc}
 \left[\begin{array}{c} \text{Rate of} \\ \text{accumulation} \\ \text{of energy} \\ \text{within the} \\ \text{system} \end{array} \right] & = & \left[\begin{array}{c} \text{Rate of flow} \\ \text{of heat to} \\ \text{the system} \\ \text{from the} \\ \text{surroundings} \end{array} \right] & - & \left[\begin{array}{c} \text{Rate of work} \\ \text{done by} \\ \text{the system} \\ \text{on the} \\ \text{surroundings} \end{array} \right] & + & \left[\begin{array}{c} \text{Rate of energy} \\ \text{added to the} \\ \text{system by mass} \\ \text{flow into the} \\ \text{system} \end{array} \right] & - & \left[\begin{array}{c} \text{Rate} \\ \text{energy l} \\ \text{the system} \\ \text{flow o} \\ \text{the sy} \end{array} \right] \\
 \frac{d\hat{E}_{sys}}{dt} & = & \dot{Q} & - & \dot{W} & + & F_{in}E_{in} & - & F_{out}E_{out} \\
 (\text{J/s}) & = & (\text{J/s}) & - & (\text{J/s}) & + & (\text{J/s}) & - & (\text{J/s})
 \end{array}$$

Energy balance on an open system

Typical units for each term in Equation (11-2) are (Joule/s).

(Joule bio: <http://www.corrosion-doctors.org/Biographies/JouleBio.htm>.)

We will assume that the contents of the system volume are well mixed, an assumption that we could relax but that would require a couple of pages of text to develop, and the end result would be the same! The unsteady-state energy balance for an open well-mixed system that now has n species, each entering and leaving the system at their respective molar flow rate F_i (moles of i per time) and with their respective energy E_i (Joules per mole of i), is

$$\frac{d\hat{E}_{sys}}{dt} = \dot{Q} - \dot{W} + \sum_{i=1}^n E_i F_i \Big|_{in} - \sum_{i=1}^n E_i F_i \Big|_{out} \quad (11-3)$$

The starting point

We will now discuss each of the terms in Equation (11-3).

11.2.2 Evaluating the Work Term

It is customary to separate the work term, \dot{W} , into *flow work* and *other work*, \dot{W}_s . The term \dot{W}_s , often referred to as the *shaft work*, could be produced from such things as a stirrer in a CSTR or a turbine in a PFR. *Flow work* is work that is necessary to get the mass *into* and *out of* the system. For example, when shear stresses are absent, we write

$$\dot{W} = \overbrace{-\sum_{i=1}^n F_i P \tilde{V}_i \Big|_{in} + \sum_{i=1}^n F_i P \tilde{V}_i \Big|_{out}}^{\text{[Rate of flow work]}} + \dot{W}_s \quad (11-4)$$

Flow work and shaft work

where P is the pressure (Pa) [$1 \text{ Pa} = 1 \text{ Newton/m}^2 = 1 \text{ kg}\cdot\text{m/s}^2/\text{m}^2$] and is \tilde{V}_i the specific molar volume of species i (m^3/mol of i).

Let's look at the units of the flow-work term, which is

$$F_i \cdot P \cdot \tilde{V}_i$$

where F_i is in mol/s, P is in Pa ($1 \text{ Pa} = 1 \text{ Newton/m}^2$), and \tilde{V}_i is in (m^3/mol). Multiplying the units of each term in $(F_i P \tilde{V}_i)$ through, we obtain the units of flow work, that is,

$$F_i \cdot P \cdot \tilde{V}_i \left[= \right] \frac{\text{mol}}{\text{s}} \cdot \frac{\text{Newton}}{\text{m}^2} \cdot \frac{\text{m}^3}{\text{mol}} = (\text{Newton} \cdot \text{m}) \cdot \frac{1}{\text{s}} = \text{Joules/s} = \text{Watts}$$

We see that the units for flow work are consistent with the other terms in Equation (11-3), that is, (J/s)

(<http://www.corrosion-doctors.org/Biographies/WattBio.htm>).

In most instances, the flow-work term is combined with those terms in the energy balance that represent the energy exchange by mass flow across the system boundaries. Substituting Equation (11-4) into (11-3) and grouping terms, we have

$$\frac{d\hat{E}_{\text{sys}}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^n F_i (E_i + P\tilde{V}_i) \Big|_{\text{in}} - \sum_{i=1}^n F_i (E_i + P\tilde{V}_i) \Big|_{\text{out}} \quad (11-5)$$

ConventionHeat Added

$$\dot{Q} = + -10 \text{ J/s}$$

Heat Removed

$$\dot{Q} = + -10 \text{ J/s}$$

Work Done by System

$$\dot{W}_s = + -10 \text{ J/s}$$

Work Done on System

$$\dot{W}_s = + -10 \text{ J/s}$$

The energy E_i is the sum of the internal energy (U_i), the kinetic energy ($u_i^2/2$), the potential energy (gz_i), and any other energies, such as electric or magnetic energy or light

$$E_i = U_i + \frac{u_i^2}{2} + gz_i + \text{other} \quad (11-6)$$

In almost all chemical reactor situations, the kinetic, potential, and “other” energy terms are negligible in comparison with the

enthalpy, heat transfer, and work terms in the energy balance, and hence will be omitted, in which case

$$E_i = U_i \quad (11-7)$$

We recall that the enthalpy, H_i (J/mol), is defined in terms of the internal energy U_i (J/mol), and the product $P\tilde{V}_i$ (1 Pa · m³/mol = 1 J/mol):

$$H_i = U_i + P\tilde{V}_i \quad (11-8)$$

Enthalpy

Typical units of H_i are

$$(H_i) = \frac{\text{J}}{\text{mol } i} \text{ or } \frac{\text{Btu}}{\text{lb-mol } i} \text{ or } \frac{\text{cal}}{\text{mol } i}$$

Enthalpy carried into (or out of) the system can be expressed as the sum of the internal energy carried into (or out of) the system by mass flow plus the flow work:

$$F_i H_i = F_i (U_i + P\tilde{V}_i)$$

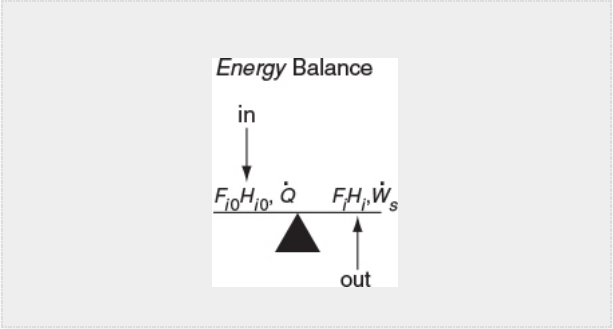
Combining Equations (11-5), (11-7), and (11-8), we can now write the energy balance in the form

$$\frac{d\hat{E}_{\text{sys}}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^n F_i H_i \Big|_{\text{in}} - \sum_{i=1}^n F_i H_i \Big|_{\text{out}}$$

The energy of the system at any instant in time, \hat{E}_{sys} , is the sum of the products of the number of moles of each species in the system multiplied by their respective energies. The derivative of the E_{sys} term wrt time will be discussed in more detail when unsteady-state reactor operation is considered in [Chapter 13](#).

We shall let the subscript “0” represent the inlet conditions. The conditions at the outlet of the chosen system volume will be represented by the unsubscripted variables.

$$\dot{Q} - \dot{W}_s + \sum_{i=1}^n F_{i0} H_{i0} - \sum_{i=1}^n F_i H_i = \frac{d\hat{E}_{\text{sys}}}{dt} \quad (11-9)$$



In [Section 11.1](#), we discussed that in order to solve reaction engineering problems with heat effects, we needed to relate temperature, conversion, and rate of reaction. The energy balance as given in [Equation \(11-9\)](#) is the most convenient starting point as we proceed to develop this relationship.

11.2.3 Overview of Energy Balances

What is the plan? In the following pages, we manipulate [Equation \(11-9\)](#) in order to apply it to each of the reactor types we have been discussing: BR, PFR, PBR, and CSTR. The end result of the application of the energy balance to each type of reactor is shown in [Table 11-1](#). These equations can be used in **Step 5** of the algorithm discussed in [Example 11-1](#). The equations in [Table 11-1](#) relate temperature to conversion and to molar flow rates, and to the system parameters, such as the product of overall heat transfer coefficient, U , and heat exchange surface area, a , that is, Ua , with the corresponding ambient temperature, T_a , and the heat of reaction, ΔH_{Rx} .

Examples of How to Use [Table 11-1](#). We now couple the *energy balance* equations in [Table 11-1](#) with the appropriate reactor *mole balance*, *rate law*, and *stoichiometry algorithm* to solve reaction engineering problems with heat effects.

[Table 11-1](#) gives the user-friendly reaction energy balances

End results of manipulating the energy balance ([Sections 11.2.4](#), [12.1](#), and [12.3](#))

TABLE 11-1 ENERGY BALANCES OF COMMON REACTORS

--

1. **Adiabatic** ($\dot{Q} \equiv 0$) CSTR, PFR, Batch, or PBR. The relationship between conversion calculated from the energy balance, X_{EB} , and temperature for $\dot{W}_s=0$, constant C_{p_i} , and $\Delta C_p = 0$, is

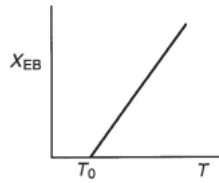
Conversion in terms of temperature

$$X_{EB} = \frac{\sum \Theta_i C_{p_i} (T - T_0)}{-\Delta H_{Rx}^0} \quad (\text{T11-1.A})$$

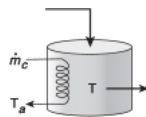
Temperature in terms of conversion calculated from the energy balance

$$T = T_0 + \frac{(-\Delta H_{Rx}^0) X_{EB}}{\sum \Theta_i C_{p_i}} \quad (\text{T11-1.B})$$

For an exothermic reaction $(-\Delta H_{Rx}) > 0$

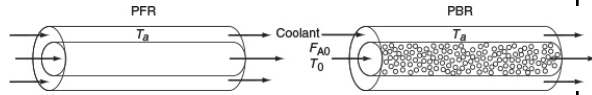


2. **CSTR with heat exchanger**, $UA (T_a - T)$, and large coolant flow rate



$$X_{EB} = \frac{\left(\frac{UA}{F_{AO}} (T - T_a) \right) + \sum \Theta_i C_{p_i} (T - T_0)}{-\Delta H_{Rx}^0} \quad (\text{T11-1.C})$$

3.

PFR/PBR with heat exchange

In general, most of the PFR and PBR energy balances can be written as

3A. PFR in terms of conversion

$$\frac{dT}{dV} = \frac{(\text{Heat "generated"}) - (\text{Heat "removed"})}{\Sigma F_i C_{P_i}} = \frac{Q_g - Q_r}{\Sigma F_i C_{P_i}}$$

3A. PBR in terms of conversion

$$\frac{dT}{dV} = \frac{\overbrace{r_A \Delta H_{R_x}(T)}^{Q_g} - \overbrace{U a (T - T_a)}^{Q_r}}{F_{A0} (\Sigma \Theta_i C_{P_i} + \Delta C_P X)} = \frac{Q_g - Q_r}{F_{A0} (\Sigma \Theta_i C_{P_i} + \Delta C_P X)} \quad (\text{T11-1.D})$$

3B. PBR in terms of conversion

$$\frac{dT}{dW} = \frac{r_A \Delta H_{R_x}(T) - \frac{U a}{\rho_b} (T - T_a)}{F_{A0} (\Sigma \Theta_i C_{P_i} + \Delta C_P X)} \quad (\text{T11-1.E})$$

3C. PBR in terms of molar flow rates

$$\frac{dT}{dW} = \frac{r_A \Delta H_{R_x}(T) - \frac{U a}{\rho_b} (T - T_a)}{\Sigma F_i C_{P_i}} \quad (\text{T11-1.F})$$

3D. PFR in terms of molar flow rates

$$\frac{dT}{dV} = \frac{r_A \Delta H_{R_x}(T) - U a (T - T_a)}{\Sigma F_i C_{P_i}} = \frac{Q_g - Q_r}{\Sigma F_i C_{P_i}} \quad (\text{T11-1.G})$$

4.

Batch

$$\frac{dT}{dt} = \frac{(r_A V)(\Delta H_{Rx}) - U A (T - T_a)}{\sum N_i C_{P_i}} \quad (\text{T11-1.H})$$

5. **For Semibatch or unsteady CSTR**

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s - \sum_{i=1}^n F_{i0} C_{P_i} (T - T_{i0}) + [-\Delta H_{Rx}(T)](-r_A V)}{\sum_{i=1}^n N_i C_{P_i}} \quad (\text{T11-1.I})$$

6. **For multiple reactions in a PFR (q reactions and m species)**

$$\frac{dT}{dV} = \frac{\sum_{i=1}^q r_{ij} \Delta H_{Rxi,j} - U a (T - T_a)}{\sum_{j=1}^m F_j C_{P_j}} \quad (\text{T11-1.J})$$

7. **Variable heat exchange fluid temperature, T_a**

$$\frac{dT_a}{dV} = \frac{U a (T - T_a)}{\dot{m}_c C_{P_c}} \quad (\text{T11-1.K}) \quad \frac{dT_a}{dV} = \frac{U a (T_a - T)}{\dot{m}_c C_{P_c}} \quad (\text{T11-1.L})$$

$V = 0 \quad T_a = T_{a0} \quad V = V_{\text{final}} \quad T_a = T_{a0}$

The equations in **Table 11-1** are the ones we will use to solve reaction engineering problems with heat effects.

Nomenclature:

U = overall heat transfer coefficient, ($\text{J/m}^2 \cdot \text{s} \cdot \text{K}$);

A = CSTR heat-exchange area, (m^2);

a = PFR heat-exchange area per volume of reactor, (m^2/m^3);

C_{P_i} = mean heat capacity of species i , (J/mol/K);

C_{Pc} = the heat capacity of the coolant, (J/kg/K);

\dot{m}_c = coolant flow rate, (kg/s);

$\Delta H_{Rx}(T)$ = heat of reaction at temperature T , (J/mol A);

$\Delta H_{Rx}^o = \left(\frac{d}{d} H_D^o - \frac{c}{a} H_C^o - \frac{b}{a} H_B^o - H_A^o \right)$ J/mol A = heat of reaction at temperature T_R ;

ΔH_{Rxij} = heat of reaction wrt species j in reaction i , (J/mol j);

\dot{Q} = heat added to the reactor, (J/s); and

$\Delta C_p \left(\frac{d}{a} C_{P_D} + \frac{c}{a} C_{P_C} - \frac{b}{a} C_{P_B} - C_{P_A} \right)$ (J/mol A · K) .

All other symbols are as defined in [Chapters 1–10](#).

For example, recall the rate law for a first-order reaction, Equation (E11-1.5) in [Example 11-1](#)

$$-r_A = k_1 \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] C_{A0} (1 - X) \quad (\text{E11-1.5})$$

which can be combined with the *mole balance* to find the concentration, conversion and temperature profiles (i.e., BR, PBR, PFR), exit concentrations, and conversion and temperature in a CSTR. We will now consider four cases of heat exchange in a PFR and PBR: (1) adiabatic, (2) co-current, (3) countercurrent, and (4) constant exchanger fluid temperature. We focus on adiabatic operation in this chapter and the other three cases in [Chapter 12](#).

Case 1: Adiabatic. If the reaction is carried out adiabatically, then we use Equation (T11-1.B) for the reaction $A \rightarrow B$ in [Example 11-1](#) to obtain

Adiabatic

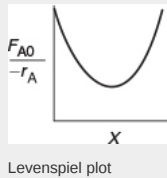
$$T = T_0 + \frac{-\Delta H_{Rx}^o X}{C_{P_A}} \quad (\text{T11-1.B})$$

Consequently, we can now obtain $-r_A$ as a function of X alone by first choosing X , then calculating T from Equation (T11-1.B), then calculating k from Equation (E11-1.3), and then finally calculating $(-r_A)$ from Equation (E11-1.5)

The algorithm

Choose $X \rightarrow$ calculate $T \rightarrow$ calculate $\kappa \rightarrow$ calculate $-r_A \rightarrow$ calculate $\frac{F_{A0}}{-r_A}$

We can use this sequence to prepare a table of $(F_{A0}/-r_A)$ as a function of X . We can then proceed to size PFRs and CSTRs. In the absolute worst case scenario, we could use the techniques in Chapter 2 (e.g., Levenspiel plots or the quadrature formulas in Appendix A). However, instead of using a Levenspiel plot, we will most definitely use software packages such as MATLAB, Wolfram, Python, or Polymath to solve our coupled differential energy and mole balance equations.



Cases 2, 3, and 4: Correspond to Co-Current Heat Exchange, Countercurrent Heat Exchange, and Constant Coolant Temperature T_C , respectively (Chapter 12). If there is cooling along the length of a PFR or PBR, we could then apply Equation (T11-1.D) to this reaction to arrive at two coupled differential equations.

In terms of conversion

$$\frac{dX}{dV} = k_1 \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] C_{A0} (1-X) / F_{A0}$$

Non-adiabatic PFR

In terms of molar flow rate

$$\frac{dF_A}{dV} = r_A = -kC_A = -k \frac{F_A}{v} = -k_1 \frac{F_A}{v} \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right]$$

either of which needs to be coupled with the energy balance

$$\frac{dT}{dV} = \frac{r_A \Delta H_{Rx}(T) - Ua(T - T_a)}{F_{A0} C_{PA}}$$

which are easily solved using an ODE solver such as Polymath. If the temperature of the heat exchanger fluid (T_a) (e.g., coolant) is not constant, we add Equations (T11-1.K) or (T11-1.L) in Table 11-1 to the above equations and solve with Polymath, Wolfram, or MATLAB.

Heat Exchange in a CSTR. Similarly, for the case of the reaction $A \rightarrow B$ in Example 11-1 carried out in a CSTR, we could use Polymath, Python, Wolfram, or MATLAB to solve two nonlinear algebraic equations in X and T . These two equations are the combined mole balance

Non-adiabatic CSTR

$$V = \frac{F_{A0} X}{k_1 \exp\left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T}\right)\right] C_{A0} (1-X)}$$

and the application of Equation (T11-1.C), which is rearranged in the form

$$T = \frac{F_{A0} X (-\Delta H_{Rx}) + U A T_a + F_{A0} C_{PA} T_0}{U A + C_{PA} F_{A0}}$$

From these three cases, (1) adiabatic PFR and CSTR, (2) PFR and PBR with heat effects, and (3) CSTR with heat effects, one can see how to couple the energy balances and mole balances. In principle, one could simply use Table 11-1 to apply to different reactors and reaction systems without further discussion. However, understanding the derivation of these equations will greatly facilitate the proper application to and evaluation of various reactors and reaction systems. Consequently, we now derive the equations given in Table 11-1.

Why bother? Here is why!!

Why bother to derive the equations in Table 11-1? Because I have found that students can *apply* these equations *much* more accurately to solve reaction engineering problems with heat effects if they have gone through the derivation to understand the assumptions and manipulations used in arriving at the equations in Table 11.1. That is, understanding these

derivations, students are more likely to put the correct number in the correct equation symbol.

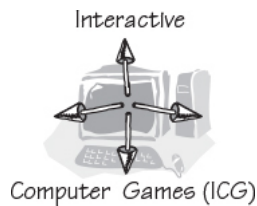
11.3 THE USER-FRIENDLY ENERGY BALANCE EQUATIONS

We will now dissect the molar flow rates and enthalpy terms in Equation (11-9) to arrive at a set of equations we can readily apply to a number of reactor situations.

11.3.1 Dissecting the Steady-State Molar Flow Rates to Obtain the Heat of Reaction

To begin our journey, we start with the energy balance Equation (11-9), and then proceed to finally arrive at the equations given in Table 11-1 by first dissecting two terms:

1. The molar flow rates, F_i and F_{i0}
2. The molar enthalpies, H_i , H_{i0} [$H_i \equiv H_i(T)$, and $H_{i0} \equiv H_i(T_0)$]



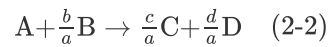
An animated and “somewhat” humorous version of what follows for the derivation of the energy balance can be found in the reaction engineering games “Heat Effects 1” and “Heat Effects 2” on the CRE Web site, <http://www.umich.edu/~elements/6e/icm/index.html>. Here, equations talk to each other as they move around the screen, making substitutions and approximations to arrive at the equations shown in Table 11-1. Visual learners find these two ICGs a very useful resource (<http://www.umich.edu/~elements/6e/icm/heatfx1.html>).

We will now consider flow systems that are operated at steady state. The steady-state energy balance is obtained by setting $(d\hat{E}_{\text{sys}}/dt)$ equal to zero in Equation (11-9) in order to yield

Steady-state energy balance

$$\dot{Q} - \dot{W}_s + \sum_{i=1}^n F_{i0} H_{i0} - \sum_{i=1}^n F_i H_i = 0 \quad (11-10)$$

To carry out the manipulations to write Equation (11-10) in terms of the heat of reaction, we shall use the generic reaction



The inlet and outlet summation terms in Equation (11-10) are expanded, respectively, to

In:

$$\sum H_i F_{i0} = H_{A0} F_{A0} + H_{B0} F_{B0} + H_{C0} F_{C0} + H_{D0} F_{D0} + H_{I0} F_{I0} \quad (11-11)$$

and

Out:

$$\sum H_i F_i = H_A F_A + H_B F_B + H_C F_C + H_D F_D + H_I F_I \quad (11-12)$$

where the capital subscript I represents inert species.

We next express the molar flow rates in terms of conversion. In general, the molar flow rate of species i for the case of no accumulation and a stoichiometric coefficient ν_i is

$$F_i = F_{A0} (\Theta_i + \nu_i X)$$

Specifically, for Reaction (2-2), $A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$, we have

$$\left. \begin{aligned} F_B &= F_{A0} \left[\Theta_B - \frac{b}{a} X \right] \\ F_C &= F_{A0} \left[\Theta_C + \frac{c}{a} X \right] \\ F_D &= F_{A0} \left[\Theta_D + \frac{d}{a} X \right] \\ F_I &= \Theta_I F_{A0} \end{aligned} \right\} \text{ where } \Theta_i = \frac{F_{i0}}{F_{A0}}$$

Steady-state operation

We can substitute these symbols for the molar flow rates into Equations (11-11) and (11-12), then subtract Equation (11-12) from (11-11) to give (11-13)

$$\begin{aligned}
\sum_{i=1}^n F_{i0} H_{i0} - \sum_{i=1}^n F_i H_i = & F_{A0}[(H_{A0} - H_A) + (H_{B0} - H_B)\Theta_B \\
& + (H_{C0} - H_C)\Theta_C + (H_{D0} - H_D)\Theta_D + (H_{I0} - H_I)\Theta_I] \\
& - \underbrace{\left(\frac{d}{a} H_D + \frac{c}{a} H_C - \frac{b}{a} H_B - H_A \right) F_{A0} X}_{\Delta H_{Rx}}
\end{aligned} \quad (11-13)$$

The term in parentheses that is multiplied by $F_{A0}X$ is called the **heat of reaction** at temperature T and is designated $\Delta H_{Rx}(T)$.

$$\Delta H_{Rx}(T) = \frac{d}{a} H_D(T) + \frac{c}{a} H_C(T) - \frac{b}{a} H_B(T) - H_A(T) \quad (11-14)$$

Heat of reaction at temperature T

All enthalpies (e.g., H_A , H_B) are evaluated at a temperature T in the reactor and, consequently, $[\Delta H_{Rx}(T)]$ is the heat of reaction at *that* specific temperature T . *The heat of reaction is always given per mole of the species that is the basis of calculation, that is, species A (Joules per mole of A reacted).*

Substituting Equation (11-14) into (11-13) and reverting to summation notation for the species, Equation (11-13) becomes

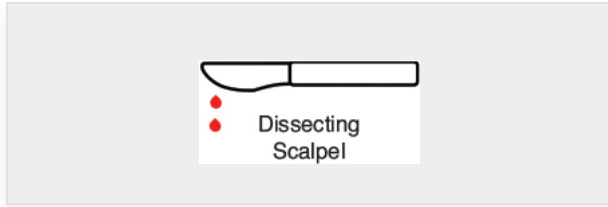
$$\sum_{i=1}^n F_{i0} H_{i0} - \sum_{i=1}^n F_i H_i = F_{A0} \sum_{i=1}^n \Theta_i (H_{i0} - H_i) - \Delta H_{Rx}(T) F_{A0} X \quad (11-15)$$

Combining Equations (11-10) and (11-15), we can now write the *steady-state*, that is, ($d\hat{E}_{sys}/dt = 0$), energy balance in a more usable form:

One can use this form of the steady-state energy balance if the enthalpies are available.

$$\dot{Q} - \dot{W}_s + F_{A0} \sum_{i=1}^n \Theta_i (H_{i0} - H_i) - \Delta H_{Rx}(T) F_{A0} X = 0 \quad (11-16)$$

If a *phase change* takes place during the course of a reaction, this is the form of the energy balance (i.e., Equation (11-16)) that *must* be used.



11.3.2 Dissecting the Enthalpies

We are neglecting any enthalpy changes resulting from mixing so that the partial molal enthalpies are equal to the molal enthalpies of the pure components. The molal enthalpy of species i at a particular temperature and pressure, H_i , is usually expressed in terms of an **enthalpy of formation** of species i at some reference temperature T_R , $H_i^\circ(T_R)$, plus the change in enthalpy, ΔH_{Qi} , that results when the temperature is raised from the reference temperature, T_R , to some temperature T

$$H_i = H_i^\circ(T_R) + \Delta H_{Qi} \quad (11-17)$$

The reference temperature at which is $H_i^\circ(T_R)$ given is usually 25°C. For any substance i that is being heated from T_1 to T_2 in the *absence* of phase change

$$\Delta H_{Qi} = \int_{T_1}^{T_2} C_{P_i} dT \quad (11-18)$$

No phase change

Typical units of the heat capacity, C_{P_i} , are

$$(C_{P_i}) = \frac{\text{J}}{(\text{mol of } i) (\text{K})} \text{ or } \frac{\text{Btu}}{(\text{lb mol of } i) (^\circ\text{R})} \text{ or } \frac{\text{cal}}{(\text{mol of } i) (\text{K})}$$

A large number of chemical reactions carried out in industry do not involve phase change. Consequently, we shall further refine our energy balance to apply to *single-phase* chemical reactions. Under these conditions, the enthalpy of species i at temperature T is related to the enthalpy of formation at the reference temperature T_R by

$$H_i(T) = H_i^\circ(T_R) + \int_{T_R}^T C_{P_i} dT \quad (11-19)$$

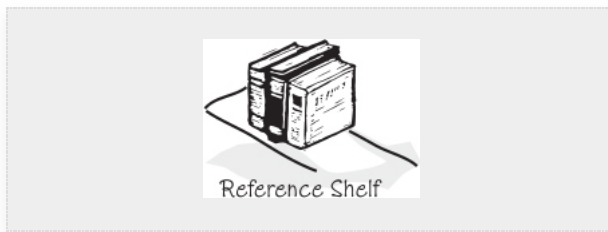
If phase changes do take place in going from the temperature for which the enthalpy of formation is given and the reaction

temperature T , Equation (11-17) must be used instead of Equation (11-19).

The heat capacity at temperature T is frequently expressed as a quadratic function of temperature; that is

$$C_{P_i} = \alpha_i + \beta_i T + \gamma_i T^2 \quad (11-20)$$

However, while this text will consider only **constant heat capacities**, the PRS R11.1 on the CRE Web site has examples with variable heat capacities (<http://www.umich.edu/~elements/6e/11chap/prof.html>).



To calculate the change in enthalpy ($H_i - H_{i0}$) when the reacting fluid is heated without phase change from its entrance temperature, T_{i0} , to a temperature T , we integrate Equation (11-19) for *constant* C_{P_i} to write

$$\begin{aligned} H_i - H_{i0} &= \left[H_i^\circ(T_R) + \int_{T_R}^T C_{P_i} dT \right] - \left[H_i^\circ(T_R) + \int_{T_R}^{T_{i0}} C_{P_i} dT \right] \\ &= \int_{T_R}^T C_{P_i} dT = C_{P_i} [T - T_{i0}] \end{aligned} \quad (11-21)$$

Substituting for H_i and H_{i0} into Equation (11-16) yields

$$\dot{Q} - \dot{W}_s + F_{A0} \sum_{i=1}^n \Theta_i C_{P_i} (T - T_{i0}) - \Delta H_{R_x}(T) F_{A0} X = 0 \quad (11-22)$$

Result of dissecting the enthalpies

11.3.3 Relating $\Delta H_{R_x}(T)$, $\Delta H_{R_x}^\circ(T_R)$, and ΔC_P

Recall that the heat of reaction at temperature T was given in terms of the enthalpy of each reacting species at temperature T in Equation (11-14); that is

$$\Delta H_{R_x}(T) = \frac{d}{a} H_D(T) + \frac{c}{a} H_C(T) - \frac{b}{a} H_B(T) - H_A(T) \quad (11-14)$$

where the enthalpy of each species is given by

$$H_i(T) = H_i^\circ(T_R) + \int_{T_R}^T C_{P_i} dT = H_i^\circ(T_R) + C_{P_i}(T - T_R) \quad (11-19)$$

If we now substitute for the enthalpy of each species, we have

$$\Delta H_{R_x}(T) = \left[\frac{d}{a} H_D^\circ(T_R) + \frac{c}{a} H_C^\circ(T_R) - \frac{b}{a} H_B^\circ(T_R) - H_A^\circ(T_R) \right] + \left[\frac{d}{a} C_{P_D} + \frac{c}{a} C_{P_C} - \frac{b}{a} C_{P_B} - C_{P_A} \right] (T - T_R) \quad (11-23)$$

For the generic reaction $A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$

The first term in brackets on the right-hand side of Equation (11-23) is the heat of reaction at the reference temperature T_R

$$\Delta H_{R_x}^\circ(T_R) = \frac{d}{a} H_D^\circ(T_R) + \frac{c}{a} H_C^\circ(T_R) - \frac{b}{a} H_B^\circ(T_R) - H_A^\circ(T_R) \quad (11-24)$$

The enthalpies of formation of many compounds, $H_i^\circ(T_R)$, are usually tabulated at 25°C and can readily be found in the *Handbook of Chemistry and Physics* and similar handbooks.¹ That is, we can look up the heats of formation at T_R , then calculate the heat of reaction at this reference temperature. The heat of combustion (also available in these handbooks) can be used to determine the enthalpy of formation, $H_i^\circ(T_R)$, and this method of calculation is also described in these handbooks. From these values of the standard heat of formation, $H_i^\circ(T_R)$, we can calculate the heat of reaction at the reference temperature T_R using Equation (11-24).

¹ CRC Handbook of Chemistry and Physics, 95th ed. Boca Raton, FL: CRC Press, 2014.

The second term in brackets on the right-hand side of Equation (11-23) is the *overall change in the heat capacity per mole of A reacted*, ΔC_P ,

ΔC_P

$$\Delta C_P = \frac{d}{a} C_{P_D} + \frac{c}{a} C_{P_C} - \frac{b}{a} C_{P_B} - C_{P_A} \quad (11-25)$$

Combining Equations (11-25), (11-24), and (11-23) gives us

$$\Delta H_{\text{Rx}}(T) = \Delta H_{\text{Rx}}^{\circ}(T_{\text{R}}) + \Delta C_{\text{P}}(T - T_{\text{R}}) \quad (11-26)$$

Heat of reaction at temperature T $\Delta H_{\text{Rx}}(T)$

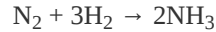
Equation (11-26) gives the heat of reaction at any temperature T in terms of the heat of reaction at a reference temperature (usually 298 K) and the ΔC_{P} term. Techniques for determining the heat of reaction at pressures above atmospheric can be found in Chen.² We note that for the reaction of hydrogen and nitrogen at 400°C, it was shown that the heat of reaction increased by only 6% as the pressure was raised from 1 to 200 atm! Consequently, we will neglect the effects of pressure on the heat of reaction.

² N. H. Chen, *Process Reactor Design*, Needham Heights, MA: Allyn and Bacon, 1983, p. 26.

Example 11-2 Heat of Reaction

Calculate the heat of reaction for the synthesis of ammonia from hydrogen and nitrogen at 150°C in terms of (kcal/mol) of N₂ reacted *and also* in terms of (kJ/mol) of H₂ reacted.

Solution



To calculate the heat of reaction at the reference temperature T_R , we will use the heats of formation of the reacting species obtained from *Perry's Chemical Engineers' Handbook* or the *Handbook of Chemistry and Physics*.³

³ D. W. Green and R. H. Perry, eds., *Perry's Chemical Engineers' Handbook*, 8th ed. New York: McGraw-Hill, 2008.

The enthalpies of formation at 25°C are

$$H_{\text{NH}_3}^\circ(T_R) = -11020 \frac{\text{cal}}{\text{mol NH}_3}, H_{\text{H}_2} = 0, \text{ and } H_{\text{N}_2} = 0$$

Note: The heats of formation of all elements (e.g., H₂, N₂) are by definition **zero** at 25°C.

We now can calculate $\Delta H_{\text{Rx}}^\circ(T_R)$, using Equation (11-24) and inserting the heats of formation of the products (e.g., NH₃) multiplied by their appropriate stoichiometric coefficients (2 for NH₃) minus the heats of formation of the reactants (e.g., N₂, H₂) multiplied by their stoichiometric coefficient (e.g., 3 for H₂, 1 of N₂)

$$\Delta H_{\text{Rx}}^\circ(T_R) = 2H_{\text{NH}_3}^\circ(T_R) - 3H_{\text{H}_2}^\circ(T_R) - H_{\text{N}_2}^\circ(T_R) \quad (\text{E11-2.1})$$

$$\begin{aligned} \Delta H_{\text{Rx}}^\circ(T_R) &= 2H_{\text{NH}_3}^\circ(T_R) - 3(0) - 0 = 2H_{\text{NH}_3}^\circ \\ &= 2(-11020) \frac{\text{cal}}{\text{mol N}_2} \\ &= -22040 \text{ cal/mol N}_2 \text{ reacted} \end{aligned}$$

$$\Delta H_{\text{Rx}}^\circ(298 \text{ K}) = -22.04 \text{ kcal/mol N}_2 \text{ reacted}$$

or in terms of kJ/mol (recall: 1 kcal = 4.184 kJ)

$\Delta H_{\text{Rx}}^\circ(298 \text{ K}) = -92.22 \text{ kJ/mol N}_2 \text{ reacted}$

Exothermic reaction

The minus sign indicates that the reaction is *exothermic*.

If the heat capacities are constant or if the mean heat capacities over the range 25°C–150°C are readily available, the determination of ΔH_{Rx} at 150°C is quite simple. (E11-2.2)

$$\begin{aligned}
 C_{P_{H_2}} &= 6.992 \text{ cal/mol } H_2 \cdot K \\
 C_{P_{N_2}} &= 6.984 \text{ cal/mol } N_2 \cdot K \\
 C_{P_{NH_3}} &= 8.92 \text{ cal/mol } NH_3 \cdot K \\
 \Delta C_P &= 2C_{P_{NH_3}} - 3C_{P_{H_2}} - C_{P_{N_2}} \quad (\text{E11-2.2}) \\
 &= 2(8.92) - 3(6.992) - 6.984 \\
 &= -10.12 \text{ cal/mol } N_2 \text{ reacted} \cdot K
 \end{aligned}$$

$$\begin{aligned}
 \Delta H_{\text{Rx}}(T) &= \Delta H_{\text{Rx}}^\circ(T_R) + \Delta C_P(T - T_R) \\
 \Delta H_{\text{Rx}}(423 \text{ K}) &= -22040 + (-10.12)(423 - 298) \quad (11-26) \\
 &= -23310 \text{ cal/mol } N_2 = -23.31 \text{ cal/mol } N_2
 \end{aligned}$$

in terms of kJ/mol

$$\Delta H_{\text{Rx}}^\circ(298 \text{ K}) = -23.3 \text{ kcal/mol } N_2 \times 4.184 \text{ kJ/kcal}$$

$$\boxed{\Delta H_{\text{Rx}}(423 \text{ K}) = -97.5 \text{ kJ/mol } N_2} \quad \text{Answer}$$

The heat of reaction based on the moles of H_2 reacted is

$$\begin{aligned}
 \Delta H_{\text{Rx}}(423 \text{ K}) &= \frac{1 \text{ mol } N_2}{3 \text{ mol } H_2} \left(-97.53 \frac{\text{kJ}}{\text{mol } N_2} \right) \\
 \Delta H_{\text{Rx}}(423 \text{ K}) &= -32.51 \frac{\text{kJ}}{\text{mol } H_2} \text{ at } 423 \text{ K} \quad \text{Answer}
 \end{aligned}$$

Analysis: This example showed (1) how to calculate the heat of reaction with respect to a given species, given the heats of formation of the reactants and the products, and (2) how to find the heat of reaction with respect to one species, given the heat of reaction with respect to another species in the reaction. Finally, (3) we also saw how the heat of reaction changed as we changed the temperature.

Now that we see that we can calculate the heat of reaction at any temperature, let's substitute Equation (11-22) in terms of $\Delta H_R(T_R)$ and ΔC_P , that is, Equation (11-26). The steady-state energy balance is now

$$\dot{Q} - \dot{W}_s - F_{A0} \sum_{i=1}^n \Theta_i C_{Pi} (T - T_{i0}) - [\Delta H_{Rx}^\circ(T_R) + \Delta C_P (T - T_R)] F_{A0} X = 0 \quad (11-27)$$

Energy balance in terms of mean or constant heat capacities

From here on, for the sake of brevity we will let

$$\Sigma = \sum_{i=1}^n$$

unless otherwise specified.

In most systems, the work term, \dot{W}_s , can be neglected (note the exception in the California Professional Engineers' Registration Exam Problem P12-6B at the end of Chapter 12). Neglecting \dot{W}_s , the energy balance becomes

$$\dot{Q} - F_{A0} \Sigma \Theta_i C_{Pi} (T - T_{i0}) - [\Delta H_{Rx}^\circ(T_R) + \Delta C_P (T - T_R)] F_{A0} X = 0 \quad (11-28)$$

We set $T_{i0} = T_0$

In almost all of the systems we will study, the reactants will be entering the system at the same temperature; therefore, we will set $T_{i0} = T_0$.

We can use Equation (11-28) to relate temperature and conversion and then proceed to evaluate the algorithm described in Example 11-1. However, unless the reaction is carried out adiabatically, Equation (11-28) is still difficult to evaluate because in non-adiabatic reactors, the heat added to or removed from the system can vary along the length of the reactor or \dot{Q} can vary with time. This problem does not occur in reactors operated adiabatically, a situation often found in industry, therefore, the adiabatic tubular reactor will be analyzed first.

11.4 ADIABATIC OPERATION $\therefore \dot{Q} = 0$

Reactions in industry are frequently carried out adiabatically with heating or cooling provided either upstream or downstream. Consequently, analyzing and sizing adiabatic reactors is an important task.

11.4.1 Adiabatic Energy Balance

In the previous section, we derived Equation (11-28), which relates conversion to temperature and the *heat added to the reactor*, \dot{Q} . Let's stop a minute (actually it will probably be more like a couple of days) and consider a system with the special set of conditions of no work, $\dot{W}_s = 0$, adiabatic operation $\dot{Q} = 0$, letting $T_{i0} = T_0$ and then rearranging Equation 11-28 into the form to express the conversion X as a function of temperature, that is,

For adiabatic operation, Example 11.1 can now be solved!

$$X = \frac{\sum \Theta_i C_{P_i} (T - T_0)}{-[\Delta H_{R_x}^\circ(T_R) + \Delta C_P (T - T_R)]} \quad (11-29)$$

In many instances, the $\Delta C_P (T - T_R)$ term in the denominator of Equation (11-29) is negligible with respect to the $\Delta H_{R_x}^\circ$ term, so that a plot of X versus T will usually be linear, as shown in Figure 11-2. To remind us that the conversion in this plot was obtained from the energy balance rather than the mole balance, it is given the subscript EB (i.e., X_{EB}) in Figure 11-2.

Relationship between X and T for *adiabatic* exothermic reactions

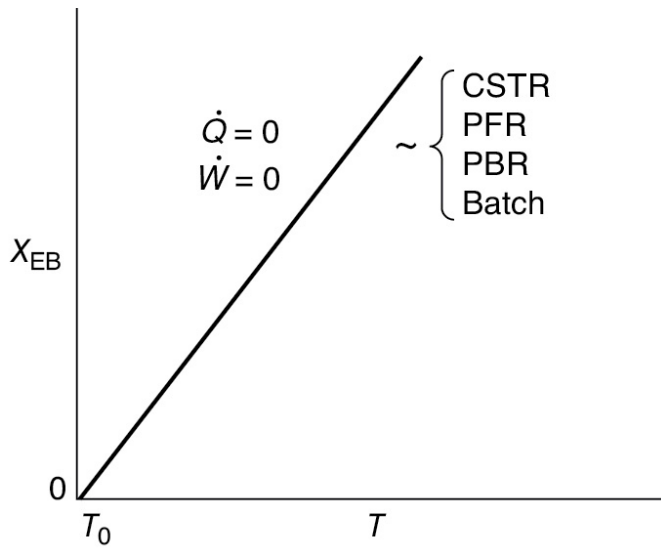


Figure 11-2 Adiabatic temperature–conversion relationship.

Equation (11-29) applies to a CSTR, PFR, or PBR, and also to a BR (as will be shown in Chapter 13). For $\dot{Q} = 0$ and $\dot{W}_s = 0$, Equation (11-29) gives us the explicit relationship between X and T needed to be used in conjunction with the mole balance to solve a large variety of chemical reaction engineering problems as discussed in Section 11.1.

We can rearrange Equation (11-29) to solve for temperature as a function of conversion; that is

$$T = \frac{X[-\Delta H_{R\lambda}(T_R)] + \sum \Theta_i C_{P_i} T_0 + X \Delta C_P T_R}{\sum \Theta_i C_{P_i} + X \Delta C_P} \quad (11-30)$$

Energy balance for adiabatic operation of PFR

11.4.2 Adiabatic Tubular Reactor

Either Equation (11-29) or Equation (11-30) will be coupled with the differential mole balance

$$F_{A0} \frac{dX}{dV} = -r_A(X, T)$$

to obtain the temperature, conversion, and concentration profiles along the length of the reactor. The algorithm for solving PBRs and PFRs operated adiabatically will be illustrated by using a first-order reversible elementary reaction $A \rightleftharpoons B$ as an example. Table 11-2 shows the algorithm using

conversion, X , as the dependent variable while Table 11-3 shows the algorithm for solving the same reaction using molar flow rates instead of conversion.

The solution to reaction engineering problems today is to use software packages with ordinary differential equation (ODE) solvers, such as Polymath, MATLAB, Python, or Wolfram, to solve the coupled mole balance and energy balance differential equations.

We will now apply the algorithm in Table 11-2 and the solution procedure in Table 11-3 to a real reaction.

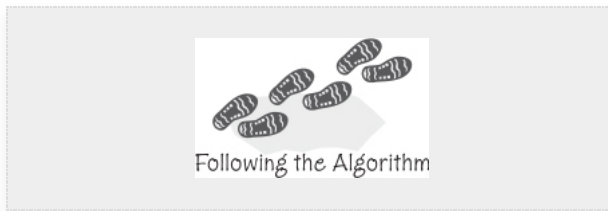


TABLE 11-2 ADIABATIC PFR/PBR ALGORITHM

The elementary reversible gas-phase reaction



is carried out in a PFR in which pressure drop is neglected and species A and inert I enter the reactor.

1. **Mole Balance:**

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} \quad (\text{T11-21})$$

2. **Rate Law:**

$$-r_A = k \left(C_A - \frac{C_B}{K_e} \right) \quad (\text{T11-2.2})$$

$$k = k_1(T_1) \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (\text{T11-2.3})$$

and for the case $\Delta C_P = 0$

$$K_e = K_{e2}(T_2) \exp \left[\frac{\Delta H_{R2}^0}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right) \right] \quad (\text{T11-2.4})$$

3. **Stoichiometry:** Gas, $\varepsilon = 0$, $P = P_0 \therefore P \equiv 1$

$$C_A = C_{A0} \left(1 - X \right)^{\frac{T_0}{T}} \quad (\text{T11-2.5})$$

$$C_B = C_{A0} X \frac{T_0}{T} \quad (\text{T11.26})$$

4. **Combine:**

$$-r_A = k C_{A0} \left[\left(1 - X \right) - \frac{X}{K_e} \right] \frac{T_0}{T} \quad (\text{T11-2.7})$$

At equilibrium $-r_A \equiv 0$, and we can solve Equation (T11-2.7) for the equilibrium conversion, X_e

$$X_e = \frac{K_e}{1 + K_e} \quad (\text{T11-2.8})$$

5. **Energy Balance:**

To relate temperature and conversion, we apply the energy balance to an adiabatic PFR. If all species enter at the same temperature, $T_{i0} = T_0$.

Solving Equation (11-30) for the case of $\Delta C_p = 0$ and when only Species A and an inert I enter, we find the temperature as a function of conversion to be

$$T = T_0 + \frac{X[-\Delta H_{Rx}(T_R)]}{C_{pA} + \Theta_I C_{pI}} \quad (\text{T11-2.9})$$

Using either Equation (11-29) or Equation (T11-2.9), we find the conversion predicted as a function of temperature from the energy balance is

$$X_{EB} = \frac{(C_{pA} + \Theta_I C_{pI})(T - T_0)}{-\Delta H_{Rx}(T_R)} \quad (\text{T11-2.10})$$

We have added the subscript to the conversion to denote that it was calculated from the energy balance, rather than from the mole balance. Equations (T11-2.1)–(T11-2.10) can easily be solved using either Simpson’s rule or an ODE solver.

Parameter values for this example (e.g., ΔH_{Rx}° , k_1) are given in Steps 5 and 6 in Table 11-3.

TABLE 11-3 SOLUTION PROCEDURES FOR ELEMENTARY
ADIABATIC GAS-PHASE PFR/PBR REACTOR

Moles as the Dependent Variable

1.

Mole Balances

$$\frac{dF_A}{dW} = r'_A$$

$$\frac{dF_B}{dW} = r'_B$$

2.

Rates

Rate Law: $-r'_A = k \left(C_A - \frac{C_B}{K_C} \right)$

Relative Rates: $r'_B = -r'_A$

$$k = k_1(T_1) \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right]$$

$$K_C = K_{C2}(T_2) \exp \left[\frac{\Delta H^\circ_{Rx}}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right) \right]$$

Recall that for $\delta \approx 0$, $K_C \approx K_e$.

3.

Stoichiometry

$$C_A = C_{T0} \frac{F_A}{F_T} \frac{T_0}{T} p$$

$$C_B = C_{T0} \frac{F_B}{F_T} \frac{T_0}{T} p$$

$$F_T = F_A + F_B + F_I$$

$$\frac{dp}{dW} = -\frac{\alpha}{2p} \frac{T}{T_0} \frac{F_T}{F_{T0}}$$

$$X = \frac{F_{A0} - F_A}{F_{A0}}$$

4.

Energy

$$T = T_0 + \frac{-\Delta H^\circ_{Rx} X}{C_{PA} + \Theta_I C_{PI}}$$

5.

Parameter Evaluation

$T_1 = 298 \text{ K}$	$\Theta_I = 1$	$C_{T0} = 1.0 \text{ mol/dm}^3$
$T_2 = 298 \text{ K}$	$K_{C2} = 75000$	$\Delta H^\circ_{Rx} = -14000 \text{ cal/mol}$
$C_{PA} = 25 \text{ cal/mol/K}$	$k_1 = 3.5 \times 10^{-5} \text{ min}^{-1}$	$E = 10000 \text{ cal/mol}$
$C_{PI} = 50 \text{ cal/mol/K}$	$F_{A0} = 5 \text{ mol/min}$	

6.

Entering Conditions

When $V = 0$, $F_{A0} = 5$, $F_B = 0$, and $T_0 = 480$ K

These values are also used in LEP 11-6 on the Web site.

**Example 11–3 Adiabatic Liquid-Phase
Isomerization of Normal Butane**

Normal butane, C_4H_{10} , is to be isomerized to isobutane in a plug-flow reactor. Iso-butane is a valuable product that is used in the manufacture of gasoline additives. For example, isobutane can be further reacted to form iso-octane. The 2014 selling price of *n*-butane was \$1.5/gal, while the trading price of isobutane was \$1.75/gal.[†]

[†]Once again, you can buy a cheaper generic brand of *n*- C_4H_{10} at the Sunday markets in downtown Riça, Jofostan, where there will be a special appearance and lecture by Jofostan's own Prof. Dr. Sven Köttlov on February 29th, at the CRE booth.

This elementary reversible reaction is to be carried out *adiabatically* in the liquid phase under high pressure using essentially trace amounts of a liquid catalyst that gives a specific reaction rate of 31.1 h^{-1} at 360 K. We want to process 100000 gal/day (163 kmol/h) and achieve 70% conversion of *n*-butane from a mixture 90 mol % *n*-butane and 10 mol % *i*-pentane, which is considered an inert. The feed enters at 330 K.

1. Set up the CRE algorithm to calculate the PFR volume necessary to achieve 70% conversion.
2. Use an ODE software package (e.g., Polymath) to solve the CRE algorithm to plot and analyze X , X_e , T , and $-r_A$ down the length (volume) of a PFR to achieve 70% conversion.
3. Calculate the CSTR volume for 40% conversion.

The economic incentive \$ = 1.75/gal versus 1.50/gal

Additional information:

$$\Delta H_{R_x}^\circ = -6900 \text{ J/mol } n\text{-butane}, \quad \text{Activation energy} = 65.7 \text{ kJ/mol}$$

$$K_C = 3.03 \text{ at } 60^\circ\text{C}, \quad C_{A0} = 9.3 \text{ mol/dm}^3 = 9.3 \text{ kmol/m}^3$$

Butane

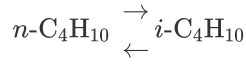
$$C_{P_{n-B}} = 141 \text{ J/mol} \cdot \text{K},$$

$$C_{P_{i-B}} = 141 \text{ J/mol} \cdot \text{K} = 141 \text{ kJ/kmol} \cdot \text{K}$$

i-Pentane

$$C_{P_{i-P}} = 161 \text{ J/mol} \cdot \text{K},$$

Solution



It's risky business to ask for 70% conversion in a reversible reaction.

Problem statement (a) said to set up the CRE algorithm to find the PFR volume necessary to achieve 70% conversion. This problem statement is risky. Why? Because the adiabatic equilibrium conversion may be less than 70%! Fortunately, it's not so for the case discussed here, $0.7 < X_e$. In general, it would be much safer and better to ask for the reactor volume to obtain 95% of the equilibrium conversion, $X_f = 0.95 X_e$.

Part (a) PFR algorithm



1. Mole Balance:

$$F_{A0} \frac{dX}{dV} = -r_A \quad (\text{E11-3.1})$$

2. Rate Law:

$$-r_A = k \left(C_A - \frac{C_B}{K_C} \right) \quad (\text{E11-3.2})$$

The algorithm

with, for the case of $\delta = 0$, $K_C = K_e$,

$$k = k(T_1) e^{\left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right]} \quad (\text{E11-3.3})$$

$$K_C = K_C(T_2) e^{\left[\frac{\Delta H_{Rx}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right) \right]} \quad (\text{E11-3.4})$$

3. Stoichiometry (liquid phase, $v = v_0$):

$$C_A = C_{A0}(1 - X) \quad (\text{E11-3.5})$$

$$C_B = C_{A0}X \quad (\text{E11-3.6})$$



4. Combine:

$$-r_A = kC_{A0} \left[1 - \left(1 + \frac{1}{K_C} \right) X \right] \quad (\text{E11-3.7})$$

5. Energy Balance: Recalling Equation (11-27), we have

$$\dot{Q} - \dot{W}_S - F_{A0} \sum \Theta_i C_{Pj} (T - T_0) - F_{A0} X [\Delta H_{Rx}^\circ(T_R) + \Delta C_P (T - T_R)] = 0 \quad (11-27)$$

From the problem statement

$$\text{Adiabatic:} \quad \dot{Q} = 0$$

$$\text{No work:} \quad \dot{W} = 0$$

$$\Delta C_P = C_{P_B} - C_{P_A} = 141 - 141 = 0$$

Applying the preceding conditions to Equation (11-27) and rearranging gives

$$T = T_0 + \frac{(-\Delta H_{Rx}^\circ)X}{\sum \Theta_i C_{P_i}} \quad (\text{E11-3.8})$$

Nomenclature Note

$$\Delta H_{Rx}(T) \equiv \Delta H_{Rx}$$

$$\Delta H_{Rx}(T_R) \equiv \Delta H_{Rx}^\circ$$

$$\Delta H_{Rx} =$$

$$\Delta H_{Rx}^\circ + \Delta C_P (T - T_R)$$

6. Parameter Evaluation:

Because *n*-butane is 90% of the total molar feed, we calculate F_{A0} to be

$$\begin{aligned}
 F_{A0} &= 0.9F_{T0} = (0.9) \left(163 \frac{\text{kmol}}{\text{h}} \right) = 146.7 \frac{\text{kmol}}{\text{h}} \\
 \Sigma \Theta_i C_{P_i} &= C_{P_A} + \Theta_I C_{P_I} = \left(141 + \left(\frac{0.1}{0.9} \right) 161 \right) \text{J/mol}\cdot\text{K} \\
 &= 159 \text{J/mol}\cdot\text{K}
 \end{aligned} \tag{E11-3.9}$$

$$\begin{aligned}
 T &= 330 + \frac{-(-6900)}{159} X \\
 T &= 330 + 43.4X
 \end{aligned}$$

where T is in degrees Kelvin.

Substituting for the activation energy, T_1 , k_1 and in Equation (E11-3.3), we obtain

$$k = 31.1 \exp \left[\frac{65700}{8.31} \left(\frac{1}{360} - \frac{1}{T} \right) \right] \left(\text{h}^{-1} \right)$$

$$k = 31.1 \exp \left[7906 \left(\frac{T-360}{360T} \right) \right] \left(\text{h}^{-1} \right) \tag{E11-3.10}$$

Substituting for $\Delta H_{\text{Rx}}^\circ$, T_2 and $K_C(T_2)$ in Equation (E11-3.4) yields

$$K_C = 3.03 \exp \left[\frac{-6900}{8.31} \left(\frac{1}{333} - \frac{1}{T} \right) \right]$$

$$K_C = 3.03 \exp \left[-830.3 \left(\frac{T-333}{333T} \right) \right] \tag{E11-3.11}$$

Recalling the rate law gives us

$$-r_A = kC_{A0} \left[1 - \left(1 + \frac{1}{K_C} \right) X \right] \tag{E11-3.7}$$

7. Equilibrium Conversion:

At equilibrium

$$-r_A \equiv 0$$

and therefore we can solve Equation (E11-3.7) for the equilibrium conversion

$$X_e = \frac{K_C}{1+K_C} \tag{E11-3.12}$$

Because we know $K_C(T)$, we can find X_e as a function of temperature.

Note: It doesn't matter what type of reactor we use, for example, BR, PFR, or CSTR, the equilibrium conversion, X_e , will be the same function of temperature.

Part (b) PFR computer solution to plot conversion and temperature profiles We now will use Polymath to solve the preceding set of equations to find the PFR reactor volume and to plot and analyze X , X_e , $-r_A$, and T down the length (volume) of the reactor. The computer solution allows us to easily see how these reaction variables vary down the length of the reactor and also to study the reaction and the reactor by varying the system parameters such as C_{A0} and T_0 (c.f. LEP P11-1A (b)).

Part B is the Polymath solution method we will use to solve most all CRE problems with "heat" effects.

The Polymath program using Equations (E11-3.1), (E11-3.7), (E11-3.9), (E11-3.10), (E11-3.11), and (E11-3.12) is shown in Table E11-3.1.

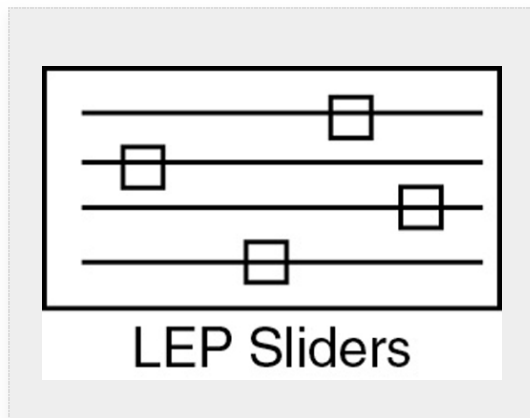


TABLE E11-3.1 POLYMATH PROGRAM ADIABATIC ISOMERIZATION

Differential equations

$$1 \quad d(X)/d(V) = -ra/Fa0$$

Explicit equations

$$1 \quad Ca0 = 9.3$$

$$2 \quad Fa0 = .9*163$$

$$3 \quad T = 330 + 43.3*X$$

$$4 \quad Kc = 3.03 * \exp(-830.3 * ((T-333)/(T*333)))$$

$$5 \quad k = 31.1 * \exp(7906 * (T-360)/(T*360))$$

$$6 \quad Xe = Kc/(1+Kc)$$

$$7 \quad ra = -k*Ca0*(1-(1+1/Kc)*X)$$

$$8 \quad rate = -ra$$

POLYMATH Report

Ordinary Differential Equations

Calculated values of DEQ variables

	Variable	Initial value	Final value
6	rate	39.28165	0.0029845
7	T	330.	360.9227
8	V	0	5.
9	X	0	0.7141504
10	Xe	0.7560658	0.7141573

LEP

Code:

<http://www.umich.edu/~elements/6e/live/chapter11/LEP-11-3.pol>

From Table E11-3.1 and Figure E11-3.1(c) one observes that at the end of the 5 dm³ PFR both the conversion, X , and equilibrium conversion, X_e , reach 71.4%. One also notes in Figures E11-3.1(a) and (b) that the temperature reaches a plateau of 360.9 K where the net reaction rate approaches zero at this point in the reactor as the reactor conversion and equilibrium conversion become virtually the same as shown in Figure E11-3.1(c). Be sure to explore each of the three parts of Figure E11-3.1 using Wolfram.

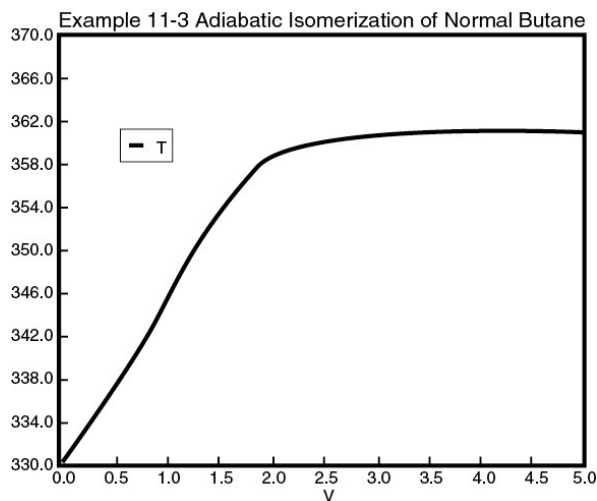
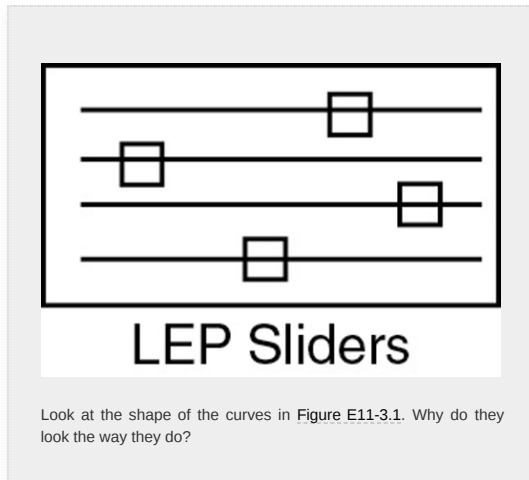


Figure E11-3.1 (a) Adiabatic PFR temperature (K), **(b)** Reaction rate (kmol/m³/h), and **(c)** conversion profiles X and X_e .



Analysis: Parts (a) and (b) for the PFR. The graphical output for the PFR is shown in Figure E11-3.1. We see from Figure E11-3.1(c) that a PFR volume of 1.15 m^3 is required for 40% conversion. The temperature and reaction-rate profiles are also shown. Notice anything strange? One observes that the rate of reaction

$$-r_A = \underbrace{kC_{A0}}_A \underbrace{\left[1 - \left(1 + \frac{1}{K_C} \right) X \right]}_B \quad (\text{E11-3.13})$$

goes through a maximum. Near the entrance to the reactor, T increases as does k , causing term A to increase more rapidly than term B decreases, and thus the rate increases. Near the end of the reactor, term B is decreasing more rapidly than term A is increasing as we approach equilibrium. Consequently, because of these two competing effects, we have a *maximum* in the rate of reaction. Toward the end of the reactor, the temperature reaches a plateau as the reaction approaches equilibrium (i.e., $X \equiv X_e$ at $(V \equiv 3.5 \text{ m}^3)$). As you know, and as do all chemical engineering students at Jofostan University in Riça, at equilibrium ($-r_A \equiv 0$) no further changes in X , X_e , or T take place.

In the fifth edition, a solution by hand calculation was given to supposedly give more insight to the adiabatic algorithm. The students in Jofostan took a vote and the results showed it wasn't that much help, so I decided to eliminate part (c) from fifth edition. However, it can

still be found on the Web site under *Additional Material*.

Part (c) CSTR solution

First, take a guess, is $V_{\text{PFR}} > V_{\text{CSTR}}$ **or is** $V_{\text{PFR}} < V_{\text{CSTR}}$? Let's now calculate the adiabatic CSTR volume necessary to achieve 40% conversion, which is less than the equilibrium conversion of 71.5% shown in [Figure E13-3.1 \(c\)](#). Do you think the CSTR will be larger or smaller than the PFR?

Solution

The CSTR mole balance is

$$V = \frac{F_{A0}X}{-r_A}$$

Using Equation ([E11-3.7](#)) in the mole balance, we obtain

$$V = \frac{F_{A0}X}{kC_{A0}\left[1 - \left(1 + \frac{1}{K_C}\right)X\right]} \quad (\text{E11} - 3.14)$$

From the energy balance, we have Equation ([E11-3.9](#)):

$$T = 330 + 43.4X$$

For 40% conversion

$$T = 330 + 43.4(0.4) = 347.3\text{K}$$

Using Equations ([E11-3.10](#)) and ([E11-3.11](#)) or from [Table E11-3.1](#), at $T = 347.3\text{ K}$, we find k and K_C to be

$$k = 14.02\text{ h}^{-1}$$

$$K_C = 2.73$$

Then

$$\begin{aligned} -r_A &= 58.6\text{ kmol/m}^3 \cdot \text{h} \\ V &= \frac{(146.7\text{ kmol butanc/h})(0.4)}{58.6\text{ kmol/m}^3 \cdot \text{h}} \\ V &= 1.0\text{ m}^3 \end{aligned}$$

We see that the CSTR volume (1 m^3) to achieve 40% conversion in this adiabatic reaction is less than the

PFR volume (1.15 m^3) as shown in Figure E11-3.1(c). Who would have guessed $V_{\text{PFR}} > V_{\text{CSTR}}$?

By recalling the Levenspiel plots from Chapter 2, we can see that the reactor volume for 40% conversion is smaller for a CSTR than for a PFR. Plotting $(F_{A0}/-r_A)$ as a function of X from the data in Table E11-3.1 is shown in Figure E11-3.2.

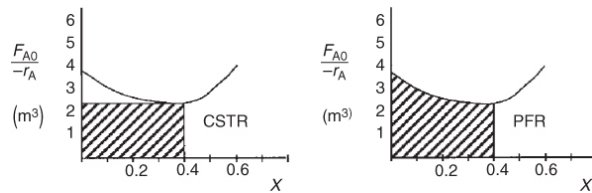


Figure E11-3.2 Levenspiel plots for a CSTR and a PFR.

The PFR area (volume) is greater than the CSTR area (volume).

In this example, the adiabatic CSTR volume is *less* than the PFR volume.

Analysis: In this example we applied the CRE algorithm to a reversible-first-order reaction carried out adiabatically in a PFR and in a CSTR. We note that at the CSTR volume necessary to achieve 40% conversion is smaller than the volume to achieve the same conversion in a PFR. In Figure E11-3.1(c) we also see that at a PFR volume of about 3.5 m^3 , equilibrium is essentially reached, and no further changes in temperature, reaction rate, equilibrium conversion, or conversion take place farther down the reactor.

AspenTech: Example 11-3 has also been formulated in AspenTech and this LEP can be loaded on your computer directly from the CRE Web site. Take a look and let me know what you think!



11.5 ADIABATIC EQUILIBRIUM CONVERSION

The highest conversion that can be achieved in reversible reactions is the equilibrium conversion. For endothermic reactions, the equilibrium conversion increases with increasing temperature up to a maximum of 1.0. For exothermic reactions, the equilibrium conversion decreases with increasing temperature.

For reversible reactions, the equilibrium conversion, X_e , is usually calculated first.

11.5.1 Equilibrium Conversion

Exothermic Reactions. Figure 11-3(a) shows the variation of the concentration equilibrium constant, K_C as a function of temperature for an exothermic reaction (see Appendix C), and Figure 11-3(b) shows the corresponding equilibrium conversion X_e as a function of temperature. In Example 11-3, we saw that for a first-order reaction, the equilibrium conversion could be calculated using Equation (E11-3.12)

$$X_e = \frac{K_c}{1 + K_c} \quad (\text{E11-3.12})$$

First-order reversible reaction

The equilibrium conversion, X_e can be calculated as a function of temperature directly either by using Equation (E11-3.12) or from a plot of Equation (E11-3.12) such as that as shown in Figure 11-3(b).

For exothermic reactions, the equilibrium conversion decreases with increasing temperature.

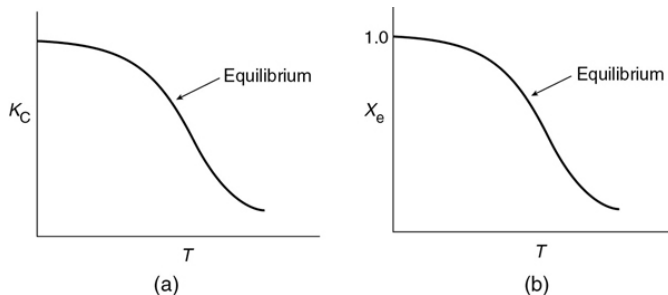


Figure 11-3 Variation of equilibrium constant and conversion with temperature for an exothermic reaction

(<http://www.umich.edu/~elements/6e/11chap/summary-biovan.html>).

We note that the shape of the X_e versus T curve in Figure 11-3(b) will be similar for reactions that are other than first order.

To determine the maximum conversion that can be achieved in an exothermic reaction carried out adiabatically, we find the intersection of the equilibrium conversion as a function of temperature (Figure 11-3(b)) with temperature–conversion relationships from the energy balance (Figure 11-2 and Equation (T11-1.A)), as shown in Figure 11-4.

$$X_{EB} = \frac{\sum \Theta_i C_{Pi} (T - T_0)}{-\Delta H_{Rx}(T)} \quad (\text{T11-1.A})$$

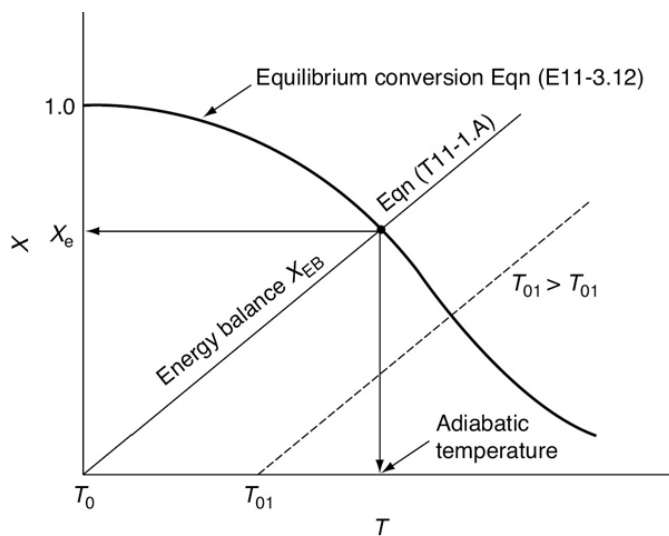


Figure 11-4 Graphical solution of equilibrium and energy balance equations to obtain the adiabatic temperature and the adiabatic equilibrium conversion X_e .

Adiabatic equilibrium conversion for exothermic reactions

This intersection of the energy balance line, X_{EB} , with the thermodynamic equilibrium X_e curve gives the adiabatic-equilibrium conversion X_e and temperature for an entering temperature T_0 as shown in Figure 11-4.

If the entering temperature is increased from T_0 to T_{01} , the energy balance line will be shifted to the right and be parallel to the original line, as shown by the dashed line. Note that as the inlet temperature increases, the adiabatic equilibrium conversion decreases.

**Example 11–4 Calculating the Adiabatic
Equilibrium Temperature and Conversion**

For the elementary liquid-phase reaction



we want to make a plot of equilibrium conversion as a function of temperature. The reacting species in this industrially important reaction to Jofostan's economy have been coded with the letters A and B for reasons of National Security and for the company's proprietary reasons.

1. Combine the rate law and stoichiometry to write $-r_A$ as a function of k , C_{A0} , X , and X_e .
2. Determine the adiabatic equilibrium temperature and conversion when species A and inert I are fed to the reactor at a temperature of 480 K.
3. What is the CSTR volume necessary to achieve 90% of the adiabatic equilibrium conversion for $C_{A0} = 1.0 \text{ mol/dm}^3$ and $v_0 = 5 \text{ dm}^3/\text{min}$?

Additional information:[†]

$$\begin{aligned} H_A^\circ(298 \text{ K}) &= -46,000 \text{ cal/mol} & H_B^\circ(298 \text{ K}) &= -60,000 \text{ cal/mol} \\ C_{P1} &= 50 \text{ cal/mol} \cdot \text{K}, & C_{PA} &= 25 \text{ cal/mol} \cdot \text{K}, & C_{PB} &= 25 \text{ cal/mol} \cdot \text{K}, & \Theta_I &= 1 \\ k &= 0.000035 \exp \left(\frac{E}{R} \left(\frac{1}{298} - \frac{1}{T} \right) \right) \text{ min}^{-1} & \text{ with } & E &= 10000 \frac{\text{cal}}{\text{mol}} \\ K_e &= 75000 & \text{ at } & 298 \text{ K} \end{aligned}$$

[†]Jofostan Journal of Thermodynamic Data, Vol. 23, p. 74 (1999).

Solution

1. **Combine rate law and stoichiometry to write $-r_A$ as a function of X**

1. Mole Balance:

$$\frac{dX}{dV} = -r_A / F_{A0} \quad (\text{E11-4.1})$$

2. Rate Law:

$$-r_A = k \left(C_A - \frac{C_B}{K_e} \right) \quad (\text{E11-4.2})$$

3. Stoichiometry: Liquid ($v = v_0$)

We follow the algorithm given in Table 11-2 **except** we apply it to a liquid-phase reaction in this case so that the concentrations are written as

$$C_A = C_{A0}(1-X) \quad (\text{E11-4.3})$$

$$C_B = C_{A0}X \quad (\text{E11-4.4})$$

$$-r_A = kC_{A0}\left(1 - X - \frac{X}{K_e}\right) \quad (\text{E11-4.5})$$

At equilibrium: $-r_A = 0$; so

$$X_e = \frac{C_{A0}X_e}{C_{A0}(1-X_e)} = \frac{X_e}{(1-X_e)} \quad (\text{E11-4.6})$$

Substituting for K_e in terms of X_e in Equation (E11-4.5) and simplifying

$$\boxed{-r_A = kC_{A0}\left(1 - \frac{X}{X_e}\right)} \quad (\text{E11-4.7})$$

Solving Equation (E11-4.6) for X_e gives

$$\boxed{X_e = \frac{K_e(T)}{1+K_e(T)}} \quad (\text{E11-4.8})$$

(b) Find adiabatic equilibrium temperature and conversion

4. **Equilibrium Constant:** Calculate ΔC_p , then $K_e(T)$ as a function of temperature

$$\Delta C_p = C_{pB} - C_{pA} = 25 - 25 = 0 \text{ cal/mol} \cdot \text{K}$$

For $\Delta C_p = 0$, the equilibrium constant varies with temperature according to the van't Hoff relation

$$K_e(T) = K_e(T_1) \exp\left[\frac{\Delta H_{Rx}}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] \quad (\text{E11-4.9})$$

$$\Delta H_{Rx}^o = H_B^o - H_A^o = -14000 \text{ cal/mol}$$

$$K_e(T) = 75000 \exp\left[\frac{-14000}{1.987}\left(\frac{1}{298} - \frac{1}{T}\right)\right] \quad (\text{E11-4.10})$$

$$K_e = 75000 \exp\left[-23.64\left(\frac{T-298}{T}\right)\right]$$

Substituting Equation (E11-4.10) into (E11-4.8), we can calculate the equilibrium conversion as a function of temperature:

5. **Equilibrium Conversion from Thermodynamics:**

$$\boxed{X_e = \frac{75000 \exp[-23.64(T-298)/T]}{1 + 75000 \exp[-23.64(T-298)/T]}} \quad (\text{E11-4.11})$$

We will use the tutorial in the Chapter 11 LEP “ X_e vs. T ” on the Web site to generate a figure of the equilibrium conversion as a function of temperature. We do this by “fooling” Polymath by using a dummy independent variable “ t ” to generate X_e and X_{EB} . Next we change variables in the plotting program to make T the independent variable and X_e and X_{EB} the dependent variables to obtain Figure E11-4.1. See tutorial

(http://www.umich.edu/~elements/6e/software/Polymath_fooling_tutorial.pdf).

The calculations are shown in Table E11-4.1.

TABLE E11-4.1 EQUILIBRIUM CONVERSION AS A FUNCTION OF TEMPERATURE

$T(K)$	K_e	X_e	$k \text{ (min}^{-1}\text{)}$
--------	-------	-------	-------------------------------

298	75,000.00	1.00	0.000035
350	2236.08	1.00	0.000430
400	180.57	0.99	0.002596
450	25.51	0.96	0.010507
500	5.33	0.84	0.032152
550	1.48	0.60	0.080279
620	0.35	0.26	0.225566

Note in this case the equilibrium constant K_e decreases by a factor of 10^5 and the reaction rate constant k increases by a factor of 10^4 .

6. Energy Balance:

For a reaction carried out adiabatically, the energy balance, Equation (T11-1.A), reduces to

$$X_{EB} = \frac{\sum \Theta_i C_{Pi} (T - T_0)}{-\Delta H_{Rx}} = \frac{(C_{PA} + \Theta_i C_{Pi}) (T - T_0)}{-\Delta H_{Rx}^o}$$

(E11-4.12)

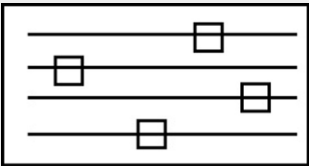
$$X_{EB} = \frac{75(T - 480)}{14000} = 5.36 \times 10^{-3} (T - 480)$$

(E11-4.13)

Conversion calculated from energy balance

Data from Table E11-4.1 and the following data are plotted in Figure E11-4.1.

$T(K)$	480	525	575	620
X_{EB}	0	0.24	0.51	0.75



LEP Sliders

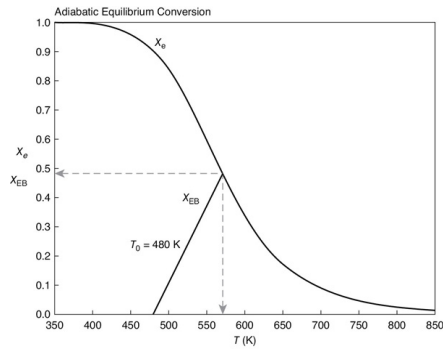


Figure E11-4.1 Finding the adiabatic equilibrium temperature (T_e) and conversion (X_e). Note: Curve uses approximate interpolated points.

Adiabatic equilibrium conversion and temperature

The intersection of $X_{EB}(T)$ and $X_e(T)$ gives $X_e = 0.49$ and $T_e = 572$ K.

(C) Calculate the CSTR volume to achieve 90% of the adiabatic equilibrium conversion corresponding to an entering temperature of 480 K

$$V = \frac{F_{A0}X}{-r_A} = \frac{C_{A0}v_0X}{kC_{A0}\left(1 - \frac{X}{X_e}\right)} = \frac{v_0X}{k\left(1 - \frac{X}{X_e}\right)} \quad (\text{E11-4.14})$$

$$k = \left(3.5 \times 10^{-5} \exp\left[\frac{10000}{1.987}\left(\frac{1}{298} - \frac{1}{T}\right)\right]\right) = 3.5 \times 10^{-5} \exp\left[16.89\left(\frac{T-298}{T}\right)\right] \quad (\text{E11-4.15})$$

From Figure E11-4.1 we see that for a feed temperature of 480 K, the adiabatic equilibrium temperature is 572 K and the corresponding adiabatic equilibrium conversion is only $X_e = 0.49$. For $X = 0.9 X_e$, the exit conversion is

$$X = 0.9 X_e = 0.9(0.49) = 0.44$$

From the adiabatic energy balance, the temperature corresponding to $X = 0.44$ is

$$T = T_0 + \left(\frac{-\Delta H_{Rx}}{C_{pA} + C_{pI}}\right)X = 480 \text{ K} + \frac{14000 \text{ cal/mol}}{75 \text{ cal/molK}}(0.44) = 562 \text{ K} \quad (\text{E11-4.16})$$

$$T = 562 \text{ K}$$

Now calculate V , for $T = 562 \text{ K}$, $X_e = 0.53$, and $k = 0.098 \text{ min}^{-1}$

$$V = \frac{(0.44) \left(5 \frac{\text{dm}^3}{\text{min}} \right)}{0.098 \text{ min}^{-1} \left(1 - \frac{0.44}{0.53} \right)} = 132.2 \text{ dm}^3 \quad (\text{E11-4.17})$$

The molar flow rates will **not** affect the value of the equilibrium conversion!!

Analysis: The purpose of this example is to introduce the concept of the adiabatic equilibrium conversion and temperature. The adiabatic equilibrium conversion, X_e , is one of the first things to determine when carrying out an analysis involving reversible reactions. It is the maximum conversion one can achieve for a given entering temperature, T_0 , and feed composition. If X_e is too low to be economical, try lowering the feed temperature and/or adding inerts. From Equation (E11-4.6), we observe that changing the flow rate has no effect on the equilibrium conversion. For exothermic reactions, the adiabatic conversion decreases with increasing entering temperature T_0 , and for endothermic reactions the conversion increases with increasing entering T_0 . One can easily generate Figure E11-4.1 using Polymath with Equations (E11-4.5) and (E11-4.7).

If adding inerts or lowering the entering temperature is not feasible, then one should consider reactor staging.

11.6 REACTOR STAGING WITH INTERSTAGE COOLING OR HEATING

11.6.1 Exothermic Reactions

Conversions higher than those shown in Figure E11-4.1 can be achieved for adiabatic operations by connecting reactors in series with interstage cooling.



Figure 11-5 Reactor in series with interstage cooling.

In [Figure 11-5](#), we show the case of an exothermic adiabatic reaction taking place in a PBR reactor train. The exit temperature from Reactor 1 is very high, 800 K, and the equilibrium conversion, X_e , is low as is the reactor conversion X_1 , which approaches X_e . Next, we pass the exit stream from adiabatic reactor 1 through a heat exchanger to lower the temperature back to 500 K where X_e is high but X is still low. To increase the conversion, the stream then enters adiabatic reactor 2 where the conversion increases to X_2 , which is followed by a heat exchanger and the process is repeated.

The conversion–temperature plot for this scheme is shown in [Figure 11-6](#). We see that with three interstage coolers, 88% conversion can be achieved, compared to an equilibrium conversion of 35% for no interstage cooling.

11.6.2 Endothermic Reactions

Typical values for gasoline composition

Another example of the need for interstage heat transfer in a series of reactors can be found when upgrading the octane number of gasoline. The more compact the hydrocarbon molecule for a given number of carbon atoms is, the higher the octane rating (see [Section 10.3.5](#)). Consequently, it is desirable to convert straight-chain hydrocarbons to branched isomers, naphthenes, and aromatics. The reaction sequence is

Interstage cooling used for exothermic reversible reactions

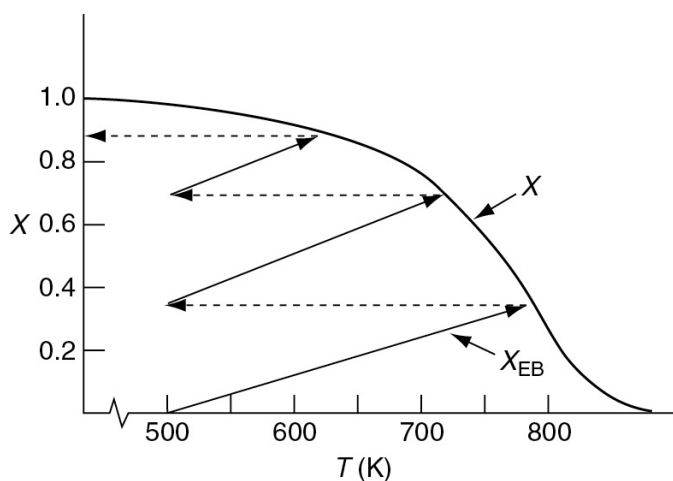


Figure 11-6 Increasing conversion by interstage cooling for an exothermic reaction. *Note:* Lines and

curves are approximate.

Gasoline	
C ₅	10%
C ₆	10%
C ₇	20%
C ₈	25%
C ₉	20%
C ₁₀	10%
C ₁₁ -C ₁₂	5%

The first reaction step (k_1) is slow compared to the second step, and each step is highly endothermic. The allowable temperature range for which this reaction can be carried out is quite narrow: Above 530°C undesirable side reactions occur, and below 430°C the reaction virtually does not take place to any reasonable extent due to the slow reaction kinetics. A typical feed stock might consist of 75% straight chains, 15% naphthas, and 10% aromatics.

One arrangement currently used to carry out these reactions is shown in Figure 11-7. Note that the reactors are not all the same size. Typical sizes are on the order of 10–20 m high and 2–5 m in diameter. A typical feed rate of gasoline is approximately 200 m³/h at 2 atm. Hydrogen is usually separated from the product stream and recycled.

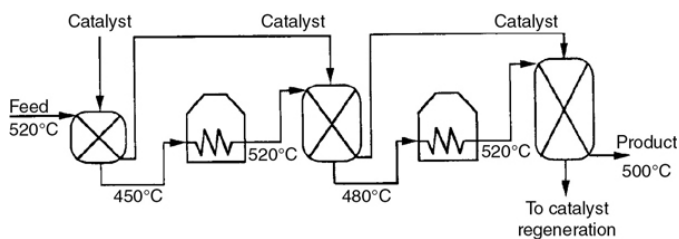


Figure 11-7 Interstage heating for gasoline production in moving-bed reactors.

Summer 2019 \$2.85/gal for octane number (ON) ON = 89

Because the reaction is endothermic, the equilibrium conversion increases with increasing temperature. A typical equilibrium curve and temperature conversion trajectory for the reactor sequence are shown in Figure 11-8.

Interstage heating

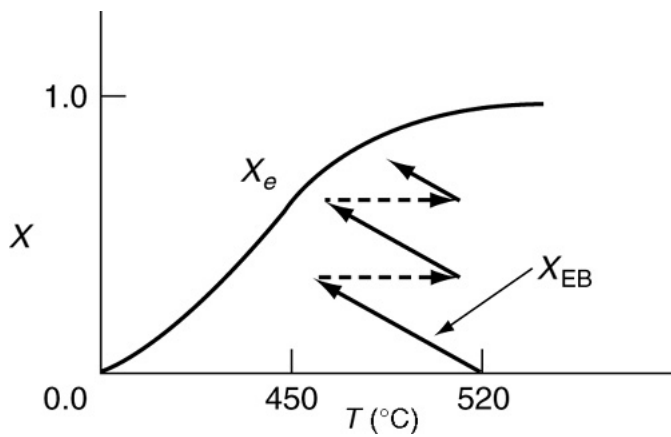


Figure 11-8 Temperature–conversion trajectory for interstage heating of an endothermic reaction analogous to Figure 11-6.

Example 11–5 Interstage Cooling for Highly Exothermic Reactions

What conversion could be achieved in [Example 11-4](#) if two interstage coolers that had the capacity to cool the exit stream to 480 K were available? Next, determine the heat duty of each exchanger for a molar feed rate of A of 40 mol/s. Assume that 95% of the equilibrium conversion is achieved in each reactor. The feed temperature to the first reactor is 480 K.

Solution

1. Calculate Exit Temperature

For the reaction in [Example 11-4](#), that is,



we saw that for an entering temperature of 480 K, the adiabatic equilibrium conversion was 0.49. For 95% of the equilibrium conversion ($X_e = 0.49$), the conversion exiting the first reactor is 0.47.

$$X_e = \frac{K_e(T)}{1+K_e(T)} \quad (\text{E11-4.8})$$

$$X_e = \frac{\sum \Theta_i C_{Pi}(T - T_0)}{-\Delta H_{Rx}} = \frac{(C_{PA} + \Theta_i C_{Pi})(T - T_0)}{-\Delta H_{Rx}} \quad (\text{E11-4.12})$$

The exit temperature is found from a rearrangement of Equation (E11-4.12)

$$T = T_0 + \left(\frac{-\Delta H_{Rx} X}{C_{PA} + \Theta_i C_{Pi}} \right) = 480 + \frac{14,000 X}{25 + 50} = 480 + (186.7)(0.47) \quad (\text{E11-5.1})$$

$T = 568 \text{ K}$ **Answer**

We will now cool the gas stream exiting the reactor at $T_1 = 568 \text{ K}$ back down to $T_2 = T_0 = 480 \text{ K}$ in a heat exchanger ([Figure E11-5.1](#)).

2. Calculate the Heat Load on the Heat Exchanger

The following calculations may be familiar from your course in Heat Transfer. There is no work done on the reaction gas mixture in the exchanger, and the reaction does not take place in the exchanger. Under these conditions ($F_{i|in} = F_{i|out}$), the energy balance given by Equation (11-10)

$$\dot{Q} - \dot{W}_s + \sum F_{i0} H_{i0} - \sum F_i H_i = 0 \quad (11-10)$$

for $\dot{W}_s = 0$ becomes

$$\dot{Q} = \sum F_i H_i - \sum F_{i0} H_{i0} = \sum F_{i0} (H_i - H_{i0}) \quad (\text{E11-5.2})$$

Energy balance on the reaction gas mixture in the heat exchanger

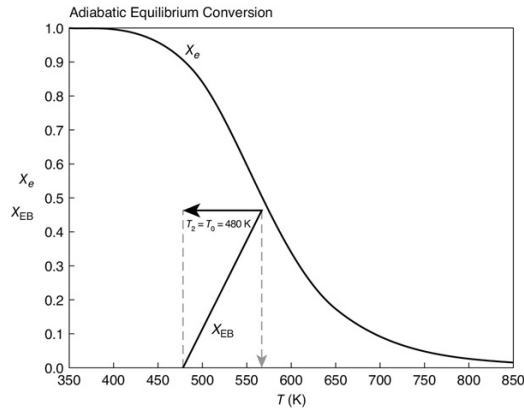


Figure E11-5.1 Reaching 95% of adiabatic equilibrium conversion, that is, $X = 0.47$, and then cooling back down to 480 K.

$$= \sum F_i C_{P_i} (T_2 - T_1) = (F_A C_{P_A} + F_B C_{P_B} + F_I C_{P_I}) (T_2 - T_1) \quad (\text{E11-5.3})$$

$$\text{But } C_{P_A} = C_{P_B}$$

$$\dot{Q} = ((F_A + F_B) C_{P_A} + F_I C_{P_I}) (T_2 - T_1) \quad (\text{E11-5.4})$$

$$\text{Also, for this example, } F_{A0} = F_A = F_B$$

$$\begin{aligned} \dot{Q} &= F_{A0} (C_{P_A} + C_I \Theta_{P_I}) (T_2 - T_1) \\ &= \frac{40 \text{ mol}}{\text{s}} \cdot \frac{75 \text{ cal}}{\text{mol} \cdot \text{K}} (480 - 568) \text{ K} \\ &= -264 \frac{\text{kcal}}{\text{s}} \end{aligned} \quad (\text{E11-5.5})$$

Answer

That is, 264 kcal/s must be removed to cool the reacting mixture from 568 K to 480 K for a feed rate of 40 mol/s.

3. Second Reactor

Now let's return to determine the conversion in the second reactor. Rearranging Equation (E11-4.12) for the second reactor

$$\begin{aligned} T_2 &= T_{20} + \Delta X \left(\frac{-\Delta H_{R_x}^0}{C_{P_A}} \right) \\ &= 480 + 186.7 \Delta X \end{aligned} \quad (\text{E11-5.6})$$

The conditions entering the second reactor are $T_{20} = 480$ K and $X = 0.47$. The energy balance starting from this point is shown in Figure E11-5.2. The corresponding adiabatic equilibrium conversion is 0.72. Ninety-five percent of the equilibrium conversion is 68.1% and the corresponding exit temperature is $T = 480 + (0.68 - 0.47)186.7 = 519$ K.

$$X = 0.9 \quad X_e = 0.9/0.72$$

$$\therefore X = 0.681$$

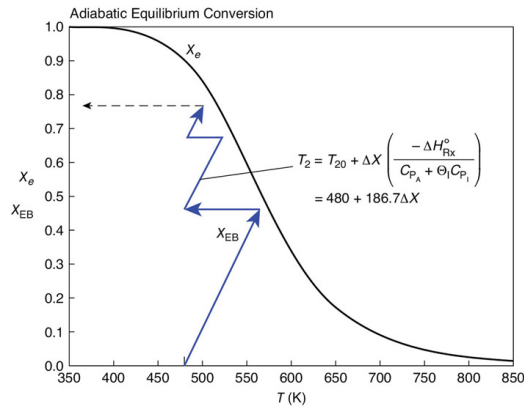


Figure E11-5.2 Three reactors in series with interstage cooling. *Note:* Curve uses approximate interpolated points.

4. Heat Load

The heat-exchange duty to cool the reacting mixture from 519 K back to 480 K can again be calculated from Equation (E11-5.5)

$$\begin{aligned} \dot{Q} &= F_{A0}(C_{PA} + \Theta_i C_{Pi})(480 - 519) = \left(\frac{40 \text{ mol}}{\text{s}} \right) \left(\frac{75 \text{ cal}}{\text{mol} \cdot \text{K}} \right) (-39) \\ &= -117 \frac{\text{kcal}}{\text{s}} \end{aligned}$$

$$= -117 \frac{\text{kcal}}{\text{s}}$$

5. Subsequent Reactors

For the third and final reactor, we begin at $T_0 = 480$ K and $X = 0.68$ and follow the line representing the equation for the energy balance along to the point of intersection with the equilibrium conversion, which is $X_e = 0.82$. Consequently, the final conversion achieved with three reactors and two interstage coolers is $X = (0.95)(0.82) = 0.78$.

Analysis: For highly exothermic, reversible reactions carried out adiabatically, reactor staging with interstage cooling can be used to obtain high conversions. One observes that the exit conversion and temperature from the first reactor are 47% and 568 K respectively, as shown by the energy balance line. The exit stream at this conversion is then cooled back down to 480 K where it enters the second reactor. In the second reactor, the overall conversion and temperature increase to 68% and 519 K. The slope of X versus T from the energy balance is the same as the first reactor.

This example also showed how to calculate the heat load on each exchanger. We also note that the heat load on the third exchanger will be less than the first exchanger because the exit temperature from the second reactor (519 K) is lower than that of the first reactor (568 K). Consequently, less heat needs to be removed by the third exchanger.

A temperature conflict: High T rapid reaction but low X_e versus low T and slow reaction resulting in low X

11.7 OPTIMUM FEED TEMPERATURE

We now consider an adiabatic reactor of fixed size or catalyst weight, and investigate what happens as the feed temperature is varied. The reaction is reversible and exothermic. At one extreme, using a very high feed temperature, the specific reaction rate will be large and the reaction will proceed rapidly, but the equilibrium conversion will be close to zero. Consequently, very little product will be formed. At the other extreme of low feed temperatures, the equilibrium conversion is high. So the question is, “Why not cool the feed to the lowest possible entering temperature, T_0 ?” The answer is that we know at low temperatures the rate constant k is small and it’s possible the reaction would not proceed to any reasonable extent, resulting in virtually no or little conversion. So we have these two extremes, low conversion at high temperatures due to equilibrium limitations and low conversion at low temperatures because of a small rate of reaction. Example 11-6 explores how to find the optimum temperature.

Bonding with Unit Operations and Heat Transfer

Example 11-6 Finding the Optimum Entering Temperature for Adiabatic Operation

We are going to continue the reaction we have been discussing in [Examples 11-4](#) and [11-5](#).



To illustrate the concept of an optimum inlet temperature, we are going to plot the conversion profiles for different inlet temperatures for this isomerization, cf. [Figures E11-6.2](#) and [E11-6.3](#). We will use all the same parameter values and conditions we used in [Examples 11-4](#) and [11-5](#) and only vary the entering temperature. We start by applying Equations (T11-2.1)–(T11-2.8) to a *liquid system* so where there is no temperature dependence in the concentration term, that is, $C_A = C_{A0} (1 - X)$. Starting with the mole balance

$$\frac{dX}{dV} = \frac{-r_{A0}}{F_{A0}} \quad (\text{E11-6.1})$$

we combine the mole balance, rate law, and stoichiometry equations to get

$$\frac{dX}{dV} = \frac{kC_0}{F_{A0}} \left(1 - X - \frac{X}{K_e} \right) \quad (\text{E11-6.2})$$

We next consider the energy balance for = 0

$$T = T_0 + \frac{X[-\Delta H_{Rx}^\circ]}{C_{PA} + \Theta C_{PI}} = T_0 + \frac{14,000X}{75} = T_0 + 187X \quad (\text{E11-6.3})$$

$$X_e = \frac{K_e}{1 + K_e} \quad (\text{E11-6.4})$$

We will use the data and equations for X_e , k , and X_{EB} as given in [Example E11-4](#).

Changing the Adiabatic Equilibrium Temperature and Conversion

Again using the values of X_e as a function of T in [Table E11-4.1](#) and the energy balance

$$X_{EB} = \frac{(C_{PA} + \Theta C_{PI})(T - T_0)}{-\Delta H_{Rx}} = 5.36 \times 10^{-3} (T - T_0) \quad (\text{E11-6.5})$$

Figure E11-6.1 shows a plot X_e and X_{EB} on the same plot for different entering temperatures, that is, T_0 .

We see that for an entering temperature of $T_0 = 580$ K, the adiabatic equilibrium conversion X_e is 0.24, and the corresponding adiabatic equilibrium temperature is 625 K. However, for an entering temperature of $T_0 = 380$ K, X_e is 0.75 and the corresponding adiabatic equilibrium temperature is 520 K.

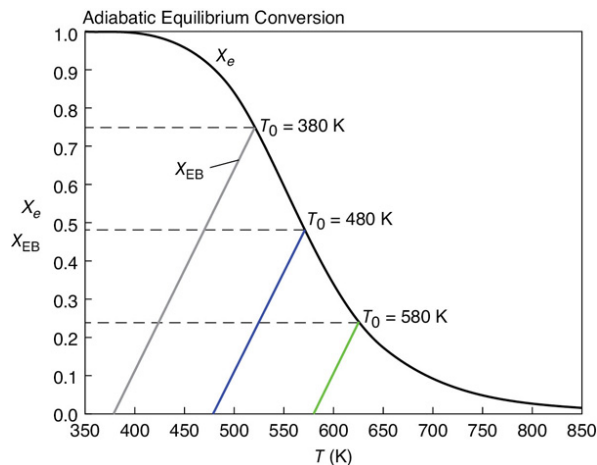


Figure E11-6.1 Adiabatic equilibrium temperature.

Conversion Profiles for X and X_e

To gain insight as to why there is an optimum feed temperature, let's look at the conversion profiles for different entering temperatures, T_0 . First we enter the mole balance, rate law, stoichiometric, and energy balance equations (cf. Equations (E11-6.1)–(E11-6.5)) into Polymath, MATLAB, Python, and Wolfram. The Polymath program and output for $T_0 = 480$ K is shown in [Table E11-6.1](#).

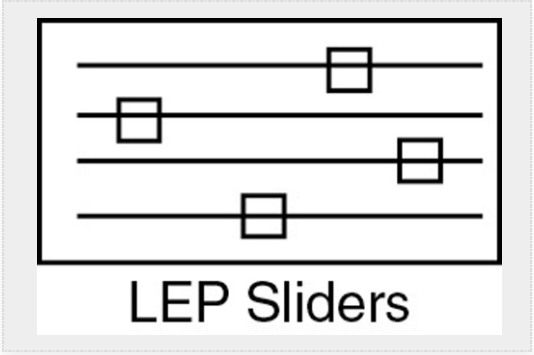


TABLE E11-6.1 POLYMATH PROGRAM AND NUMERICAL OUTPUT

Differential equations	
1	$d(X)/d(V) = -ra/Fao$
Explicit equations	
1	$k1 = 0.000035$
2	$T2 = 298$
3	$dH = -14000$
4	$To = 480$
5	$Cao = 1$
6	$Fao = 5$
7	$R = 1.987$
8	$E = 10000$
9	$Ke2 = 75000$
10	$T = To - dH * X / (75)$

		<div>11 $Ke = Ke2 * \exp((dH/R) * ((1/T2)-(1/T)))$</div> <div>12 $T1 = 298$</div> <div>13 $k = k1 * \exp((E/R) * ((1/T1)-(1/T)))$</div> <div>14 $ra = -k * Cao * ((1-X)-(X/Ke))$</div> <div>15 $Xe = Ke/(1+Ke)$</div>		
		<div>POLYMATH REPORT</div> <div>Ordinary Differential Equations</div> <div>Calculated values of DEQ variables</div>		
		<div>Variable</div>	<div>Initial value</div>	<div>Final value</div>
	1	Cao	1.	1.
	2	dH	-1.4E+04	-1.4E+04
	3	E	10000.	10000.
	4	Fao	5.	5.
	5	k	0.0211 0.021138	0.1092689
	6	k1	3.6e-05	3.6e-05
	7	Ke	9.586656	0.9613053
	8	Ke2	7.6e+04	7.6e+04
	9	R	1.987	1.987

10	ra	-0.021138	-0.0027641
11	T	480.	569.1776
12	T1	298.	298.
13	T2	298.	298.
14	To	480.	480.
15	V	0	100.
16	X	0	0.477737
17	Xe	0.9055415	0.4901355

The conversion profiles for X and X_e are shown in [Figure E11-6.2](#) for $T_0 = 480$ K where we see they approach each other up to the end of the 100 dm^3 reactor.

Because the reactor temperature increases as we move along the reactor, the equilibrium conversion, X_e , also varies and decreases along the length of the reactor, as shown in [Figure E11-6.2](#).

We next plot the corresponding conversion profiles down the length of the reactor for entering temperatures of 380 K, 480 K, and 580 K, as shown in [Figure E11-6.3](#).

For an entering temperature of 580 K, we see that the conversion and temperature increase very rapidly over a short distance (i.e., a small amount of catalyst). This sharp increase is sometimes referred to as the “point” or temperature at which the

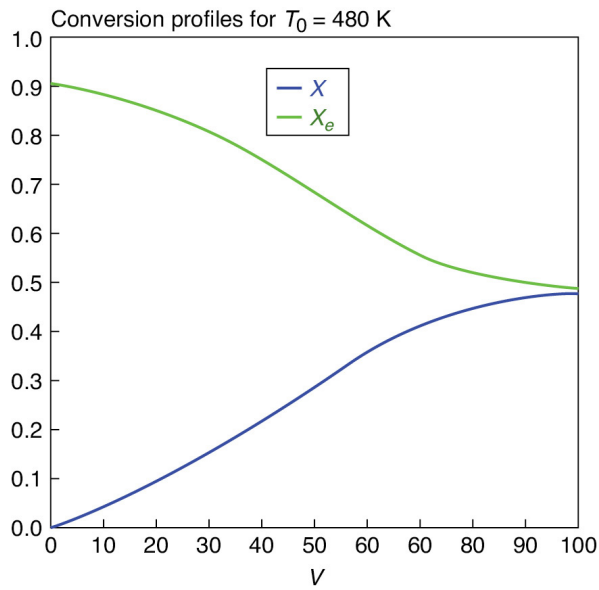
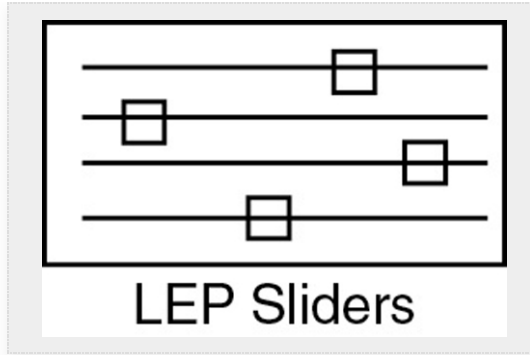


Figure E11-6.2 Conversion profiles.

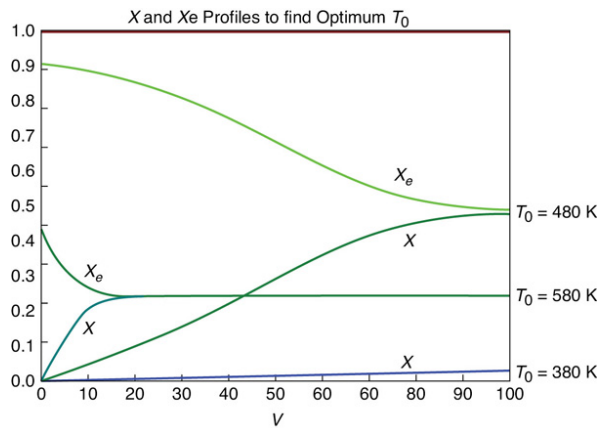


Figure E11-6.3 Equilibrium conversion for different feed temperatures.

reaction “ignites.” We also observe that the conversion, which is relatively small at a value of 0.24, remains

constant from $V = 15 \text{ dm}^3$ to the reactor exit. If the inlet temperature were lowered to 480 K, the corresponding equilibrium conversion would increase to 0.49; however, the reaction rate is slower at this lower temperature so that this conversion is not achieved until close to the end of the reactor. If the entering temperature were lowered further to 380 K, the corresponding equilibrium conversion would be virtually 1.0, but the rate is so slow that a conversion of 0.03 is achieved for the specified reactor volume of 100 dm^3 . At very low feed temperatures, the specific reaction rate will be so small that virtually all of the reactant will pass through the reactor without reacting—that is, the reaction never “ignites” and little conversion is achieved.

It is apparent that with conversions close to zero for both high and low feed temperatures, there must be an optimum feed temperature that maximizes conversion. As the feed temperature is increased from a very low value, the specific reaction rate will increase, as will the conversion. The conversion will continue to increase with increasing feed temperature until the equilibrium conversion is approached in the reaction. Further increases in feed temperature for this exothermic reaction will only decrease the conversion due to the decreasing equilibrium conversion. This optimum inlet temperature is shown in [Figure E11-6.4](#).

If we made similar plots for other entering temperatures, we would obtain the conversion at the exit of the reactor shown in [Table E11-6.2](#).

TABLE E11-6.2 EXIT CONVERSION AS A FUNCTION OF ENTERING TEMPERATURE

T_0	380	420	460	500	540	580	620	660
<hr/>								
X	0.02	0.12	0.43	0.43	0.33	0.24	0.17	0.11

These exit conversions are plotted as a function of the entering temperature in Figure E11-6.4.

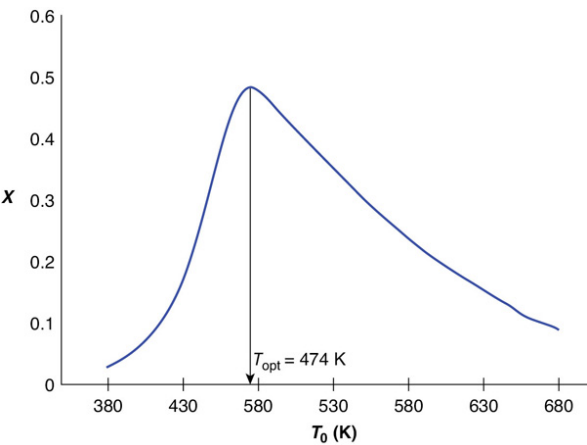


Figure E11-6.4 Conversion at exit of reactor.

Optimum inlet temperature

Analysis: We see that at high temperatures, the rate is rapid and equilibrium is reached near the entrance to the reactor and the conversion will be small. At the other extreme of low temperatures, the reaction never “ignites” and the reactants pass through the reactor virtually unreacted. At entering temperature between these two extremes we find there is an optimum entering feed temperature that maximizes conversion. The optimum feed temperature in this example is 474 K, and the corresponding optimum conversion is 0.48.

11.8 AND NOW... A WORD FROM OUR SPONSOR–SAFETY 11 (AWFOS–S11 ACRONYMS)

The purpose of this tutorial is to get familiarized with commonly used acronyms in various *Incident Investigation* reports. Below is a list of acronyms which will be encountered frequently.

TABLE 11-4 ACRONYMS

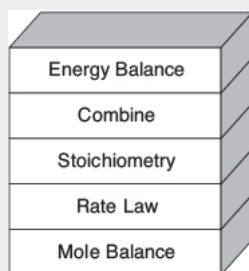
Acronym	Meaning	Link

A I C h E	American Institute of Chemical Engineers	https://www.aiche.org/about
A P I	American Petroleum Institute	https://www.api.org/about
B L E V E	Boiling Liquid Expanding Vapor Explosion	https://inspectapedia.com/plumbing/BLEVE-Explosions.php
C C P S	Center for Chemical Process Safety	https://www.aiche.org/ccps/about
C S B	U.S. Chemical Safety and Hazard Investigation Board	https://www.csb.gov/about-the-csb/
D C S	Distributed Control System	https://www.electricaltechnology.org/2016/08/distributed-control-system-dcs.html
E P A	Environmental Protection Agency	https://www.epa.gov/aboutepa
H A Z O P	Hazard and Operability Study	https://www.oshatrain.org/notes/2bnotes21.html
H S E	Health, Safety and Environment	https://www.workplacetesting.com/definition/16/health-safety-and-environment-hse
L O P A	Layer of Protection Analysis	https://hseengineer.wordpress.com/lopa-layer-of-protection-analysis/

M O C	Management of Change	http://www.lni.wa.gov/safety/grantspartnerships/partnerships/vpp/pdfs/vppmochbestpractices.pdf
M S D S	Material Safety Data Sheet	https://www.osha.gov/Publications/OSHA3514.html
N F P A	National Fire Protection Association	https://www.nfpa.org/About-NFPA
O S H A	Occupational Safety and Health Administration	https://www.osha.gov/about.html
P P E	Personal Protective Equipment	https://www.osha.gov/SLTC/personalprotectiveequipment/
P & I D s	Piping and Instrumentation Diagrams	https://www.lucidchart.com/pages/p-and-id-discovery_top
P S S R	Pre-Startup Safety Review	https://www.chemicalprocessing.com/articles/2018/perform-a-proper-pre-startup-safety-review-5-steps/
P R V s	Pressure Relief Valves	http://www.wermac.org/valves/valves_pressure_relief.html
P H A	Process Hazard Analysis	http://www.wermac.org/valves/valves_pressure_relief.html
P	Process Safety	https://www.osha.gov/SLTC/processsafety

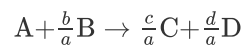
S M	Management	<i>nagement/</i>
R M P	Risk Management Program	https://www.osha.gov/chemicalexecutiveorder/psm_terminology.html
S I L	Safety Integrity Levels	https://www.crossco.com/blog/determining-safety-integrity-levels-sil-your-process-application
S O P s	Standard Operating Procedures	https://www.brampton.ca/EN/Business/BEC/resources/Documents/WhatisaStandardOperatingProcedure(SOP).pdf

Closure. Virtually all reactions that are carried out in industry involve heat effects. This chapter provides the basis to design reactors that operate at steady state and that involve heat effects. To model these reactors, we simply add another step to our algorithm; this step is the energy balance. One of the goals of this chapter is to understand each term of the energy balance and how it was derived. We have found that if the reader understands the various steps in the derivation, they will be in a much better position to apply the equation correctly. In order not to overwhelm the reader while studying reactions with heat effects, we have broken up the different cases and only consider the case of reactors operated adiabatically in this chapter. **Chapter 12** will focus on reactors with heat exchange operated at steady state. **Chapter 13** will focus on reactors not operated at steady state. An industrial adiabatic reaction concerning the manufacture of sulfuric acid that provides a number of *practical details* is included on the CRE Web site in PRS R12.4 (<http://www.umich.edu/~elements/6e/11chap/live.html> and <http://www.umich.edu/~elements/6e/12chap/pdf/sulfuricacid.pdf>).



SUMMARY

For the reaction



1. The heat of reaction at temperature T , per mole of A, is

$$\Delta H_{\text{Rx}}(T) = \frac{c}{a} H_{\text{C}}(T) + \frac{d}{a} H_{\text{D}}(T) - \frac{b}{a} H_{\text{B}}(T) - H_{\text{A}}(T) \quad (\text{S11-1})$$

2. The mean heat capacity difference, ΔC_{P} , per mole of A is

$$\Delta C_{\text{P}} = \frac{c}{a} C_{\text{PC}} + \frac{d}{a} C_{\text{PD}} - \frac{b}{a} C_{\text{PB}} - C_{\text{PA}} \quad (\text{S11-2})$$

where $C_{\text{P}i}$ is the mean heat capacity of species i between temperatures and T_{R} and T .

3. When there are no phase changes, the heat of reaction at temperature T is related to the heat of reaction at the standard reference temperature T_{R} by

$$\Delta H_{\text{Rx}}(T) = H_{\text{Rx}}^{\circ}(T_{\text{R}}) + \Delta C_{\text{P}}(T - T_{\text{R}}) \quad (\text{S11-3})$$

4. The steady-state energy balance on a system volume V is

$$\dot{Q} - F_{\text{A}0} \sum \Theta_i C_{\text{P}i} (T - T_{i0}) - [\Delta H_{\text{Rx}}^{\circ}(T_{\text{R}}) + \Delta C_{\text{P}}(T - T_{\text{R}})] F_{\text{A}0} X = 0 \quad (\text{S11-4})$$

We now couple the first four building blocks *Mole Balance*, *Rate Law*, *Stoichiometry*, and *Combine* with the fifth block, the *Energy Balance*, to solve nonisothermal reaction engineering problems as shown in the Closure box for this chapter.

5. **For adiabatic operation** ($\dot{Q} \equiv 0$) of a PFR, PBR, CSTR, or batch reactor (BR), and neglecting \dot{W}_s , we solve Equation (S11-4) for the adiabatic conversion–temperature relationship, which is

$$X = \frac{\sum \Theta_i C_{\text{P}i} (T - T_{i0})}{-[\Delta H_{\text{Rx}}^{\circ}(T_{\text{R}}) + \Delta C_{\text{P}}(T - T_{\text{R}})]} \quad (\text{S11-5})$$

Solving Equation (S11-5) for the adiabatic temperature–conversion relationship:

$$T = \frac{X [-\Delta H_{\text{Rx}}^{\circ}(T_{\text{R}})] + \sum \Theta_i C_{\text{P}i} T_{i0} + X \Delta C_{\text{P}} T_{\text{R}}}{[\sum \Theta_i C_{\text{P}i} + X \Delta C_{\text{P}}]} \quad (\text{S11-6})$$

Using Equation (S11-4), one can solve nonisothermal adiabatic reactor problems to predict the exit conversion, concentrations, and temperature.

CRE WEB SITE MATERIALS

(<http://www.umich.edu/~elements/6e/11chap/obj.html#/>)

Useful Links

Living
Example
Problems

Extra Help

Additional
Materials

Professional
Reference
Shelf

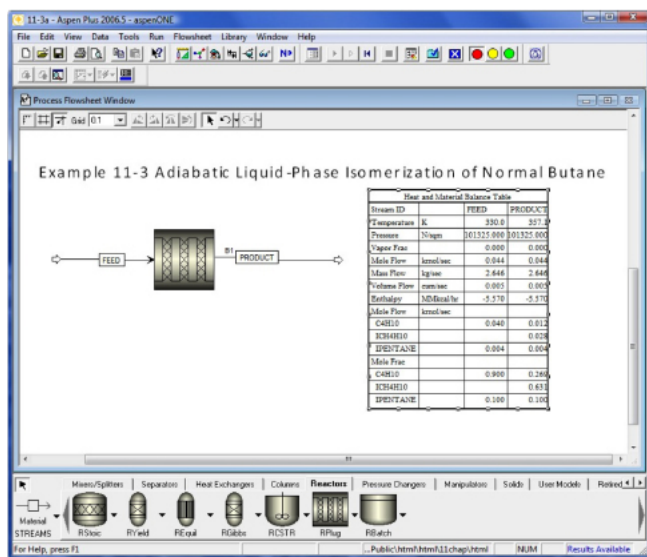
Computer
Simulation
Problem
Statements

Evaluation

Self Tests

Clicker
Questions

Living Example Problem Formulated in AspenTech



A step-by-step AspenTech tutorial is given on the CRE Web site.

(<http://www.umich.edu/~elements/6e/software/aspen.html>)

QUESTIONS, SIMULATIONS, AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$A = \bullet B = \blacksquare C = \blacklozenge D = \blacklozenge\blacklozenge$$



Homework Problems

In each of the questions and problems, rather than just drawing a box around your answer, write a sentence or two describing how you solved the problem, the assumptions you made, the reasonableness of your answer, what you learned, and any other facts that you want to include. See the Preface for additional generic parts (x), (y), (z) to the home problems.

Before solving the problems, state or sketch qualitatively the expected results or trends.

Questions

Q11-1_A i>clicker. Go to the Web site

(http://www.umich.edu/~elements/6e/11chap/iclicker_ch11_q1.html) and view at least five i>clicker questions.

Choose one that could be used as is, or a variation thereof, to be included on the next exam. You also could consider the opposite case: explaining why the question should *not* be on the next exam. In either case, explain your reasoning.

Q11-2_A Prepare a list of safety considerations for designing and operating chemical reactors. What would be the first four items on your list? For example, what safety concerns would you have for operating a reactor adiabatically? (See www.sache.org and www.siri.org/graphics.) The August 1985 issue of *Chemical Engineering Progress* may be useful.

Q11-3_A Suppose the reaction in Table 11-2 were carried out in BR instead of PFR. What steps in Table 11-2 would be different?

Q11-4_A Rework Problem P2-9_D for the case of adiabatic operation.

Q11-5_A What if you were asked to give an everyday example that demonstrates the principles discussed in this chapter? (Would sipping a teaspoon of Tabasco or other hot sauce be one?)

Q11-6_A **Example 11-1: What Additional Information Is Required?** How would this example change if a CSTR were used instead of a PFR?

Q11-7_A **Example 11-2: Heat of Reaction.** (1) What would the heat of reaction be if 50% inerts (e.g., helium) were added to the system? (2) What would be the % error if the ΔC_p term were neglected?

Q11-8_A **Example 11-3: Adiabatic Liquid-Phase Isomerization of Normal Butane.** Can you explain why the CSTR volume is smaller than the PFR volume? *Hint:* Equation (E11-3.13) may be helpful to your explanation.

Q11-9_A Read over the problems at the end of this chapter. Make up an original problem that uses the concepts presented in this chapter. See Problem P5-1_B for guidelines.

Q11-10_A A new energy efficiency saving device, the Turbo Retro Thermo Encabulator has been previewed in the following YouTube video

(<https://www.youtube.com/watch?v=RXJKdh1KZ0w>).

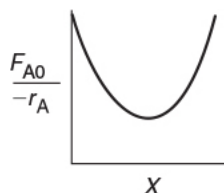
Write a two-sentence evaluation of this device that is currently on sale at a reduced introductory price.

Q11-11_A If you were to carry out a hand calculation using Simpson's integral formula, write a step-by-step procedure to generate a table of X , T , $-r_A(X)$, and $(F_{A0}/-r_b)$. Are there any circumstances in which you would get a plot similar to the following?

Q11-12_A List three things that one should consider in the link to PPE.

Q11-13 Go to the LearnChemE screencasts link for Chapter 11 (<http://www.umich.edu/~elements/6e/11chap/learn-cheme-videos.html>). View one of the screencast 5- to 6-minute video tutorials and list two of the most important points.

Q11-14 AWFOS-S11 View two of the safety acronym links and write an evaluation as to whether or not the link was useful.



Computer Simulations and Experiments

P11-1_A Download the following programs from the CRE Web site where appropriate:

1. Example Table 11.2: Algorithm for Gas-Phase Reaction

Wolfram and Python

1. What happens to X and X_e profiles as you vary T_0 ? Can you explain this trend?
2. Use the base case for all of the variables. Which slider variable— K_{e2} , k_1 , or T_0 —has the greatest effect on the temperature profiles? Which slider variable— E_A , F_{A0} , or —has the greatest effect on X and X_e ?
3. Describe how the reaction rate profile changes as you vary T_0 ?
4. Write three conclusions on what you found in experiments (i)–(iii).

2. Example 11-3: Adiabatic Isomerization of Balance

Wolfram and Python

1. Describe how both X and X_e profiles change for each of the parameter values, T_0 , K_C , and C_{A0} .

- What is the minimum feed temperature that would give that maximum possible conversion at the end of the reactor?
- Vary and $\Delta H_{R,x}^\circ$ describe how the change in the temperature profile changes.
- What parameter value— C_{A0} , T_0 , or y_{A0} —affects the reaction rate profile, $-r_A$, the most, and in which ways does it change?
- Write three conclusions on what you found in experiments (i)–(iv)

Polymath

- What if the butane reaction were carried out in a 0.8-m^3 PFR that can be pressurized to very high pressures? What would be the conversion?
 - What inlet temperature would you recommend?
 - Is there an optimum inlet temperature?
 - Plot the heat that must be removed along the reactor (\dot{Q} vs. V) to maintain isothermal operation.
3. **AspenTech Example 11-3.** Download the AspenTech program from the CRE Web site. (1) Repeat using AspenTech. (2) Vary the inlet flow rate and temperature, and describe what you find. (3) Write three conclusions on what you found by exploring this AspenTech example.

4. Example 11-4: Calculating the Adiabatic Equilibrium Temperature and Conversion

Wolfram and Python

- Go to the extremes of the ranges of the sliders and describe how the adiabatic equilibrium conversion changes with each of the variables, T , $(-\Delta H_{R,x}^\circ)$, K_e , and Θ_1 .
 - What inlet temperatures, T_0 , will give the highest and lowest values of the adiabatic equation temperature?
 - Write a set of three conclusions from your experiments (i) and (ii).
5. **Example 11-5: Interstage Cooling for Highly Exothermic Reactions.** (1) Determine the molar flow rate of cooling water ($C_{Pw} = 18 \text{ cal/mol}\cdot\text{K}$) necessary to remove 220 kcal/s from the first exchanger as shown in Figure P11-1A (e). The cooling water enters at 270 K and leaves at 400 K. (2) Determine the necessary heat-transfer area A (m^2) for an overall heat transfer coefficient, U , of $100 \text{ cal/s}\cdot\text{m}^2\cdot\text{K}$. You must use the log-mean driving force in calculating \dot{Q} .

$$\dot{Q} = UA \frac{[(T_{h2} - T_{c2}) - (T_{h1} - T_{c1})]}{\ln \left(\frac{T_{h2} - T_{c2}}{T_{h1} - T_{c1}} \right)} \quad (\text{E11-5.7})$$

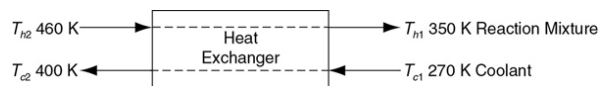


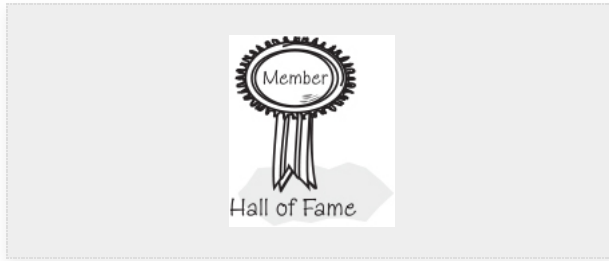
Figure P11-1A (e) Countercurrent heat exchanger.

6. Example 11-6: Optimum Feed Temperature

Wolfram and Python

- Describe what happens to X and X_e as you increase Θ_1 from 0.3 to 4.
- Vary $\Delta H_{R,x}$ and describe what you find.
- Investigate the parameters K_e , k , and Θ_1 by setting each to their base case values and then vary T_0 and describe what you find.
- Set K_{e2} at its maximum value, 150,000, and then vary T_0 . What differences do you observe from the base case?
- Next set Θ_1 at 3, and again vary the other parameters. Write a sentence or two saying how each variable affects the optimum feed temperature.

6. Explain how inert, Θ_I , affects the equilibrium conversion and actual conversion.
7. Write two conclusions about what you found in your experiments (i) through (vi).



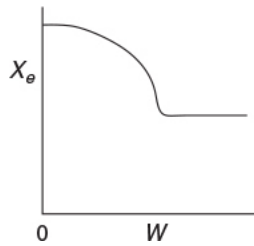
Problems

P11-2_A For elementary reaction



the equilibrium conversion is 0.8 at 127°C and 0.5 at 227°C. What is the heat of reaction?

P11-3_B OEQ (Old Exam Question). The equilibrium conversion is shown below as a function of catalyst weight down a PBR.



Please indicate which of the following statements are true and which are false. Explain each case.

1. The reaction could be first-order endothermic and carried out adiabatically.
2. The reaction is first-order endothermic and the reactor is heated along its length with T_a being constant.
3. The reaction is second-order exothermic and cooled along the length of the reactor with T_a being constant.
4. The reaction is second-order exothermic and carried out adiabatically.

P11-4_A OEQ (Old Exam Question). The elementary, irreversible, organic liquid-phase reaction



is carried out adiabatically in a flow reactor. An equal molar feed in A and B enters at 27°C, and the volumetric

flow rate is $2 \text{ dm}^3/\text{s}$ and $C_{A0} = 0.1 \text{ kmol/m}^3$.

Additional information:

$$H_A^\circ(273\text{K}) = -20 \text{ kcal/mol}, H_B^\circ(273\text{K}) = -15 \text{ kcal/mol},$$

$$H_C^\circ(273\text{K}) = -41 \text{ kcal/mol}$$

$$C_{P_A} = C_{P_B} = 15 \text{ cal/mol} \cdot \text{K}$$

$$C_{P_C} = 30 \text{ cal/mol} \cdot \text{K}$$

$$k = 0.01 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \text{ at } 300 \text{ K} \quad E = 10,000 \text{ cal/mol}$$

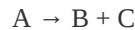
PFR

1. Plot and then analyze the conversion and temperature as a function of PFR volume up to where $X = 0.85$. Describe the trends.
2. What is the maximum inlet temperature one could have so that the boiling point of the liquid (550 K) would not be exceeded even for complete conversion?
3. Plot the heat that must be removed along the reactor (\dot{Q} vs. V) to maintain isothermal operation.
4. Plot and then analyze the conversion and temperature profiles up to a PFR reactor volume of 10 dm^3 for the case when the reaction is reversible with $K_C = 10 \text{ m}^3/\text{kmol}$ at 450 K. Plot the equilibrium conversion profile. How are the trends different than part (a)? (**Ans:** When $V = 10 \text{ dm}^3$ then $X = 0.0051$, $X_{\text{eq}} = 0.517$)

CSTR

5. What is the CSTR volume necessary to achieve 90% conversion?
- BR**
6. The reaction is next carried out in a 25 dm^3 batch reactor charged with $N_{A0} = 10$ moles. Plot the number of moles of A, N_A , the conversion, and the temperature as a function of time.

P11-5A The elementary, irreversible gas-phase reaction



is carried out adiabatically in a PFR packed with a catalyst. Pure A enters the reactor at a volumetric flow rate of $20 \text{ dm}^3/\text{s}$, at a pressure of 10 atm, and a temperature of 450 K.

Additional information:

$$C_{P_A} = 40 \text{ J/mol} \cdot \text{K} \quad C_{P_B} = 25 \text{ J/mol} \cdot \text{K} \quad C_{P_C} = 15 \text{ J/mol} \cdot \text{K}$$

$$H_A^\circ = -70 \text{ kJ/mol} \quad H_B^\circ = -50 \text{ kJ/mol} \quad H_C^\circ = -40 \text{ kJ/mol}$$

All heats of formation are referenced to 273 K.

$$k = 0.133 \exp \left[\frac{E}{R} \left(\frac{1}{450} - \frac{1}{T} \right) \right] \frac{\text{dm}^3}{\text{kg-cat} \cdot \text{s}} \quad \text{with } E = 31.4 \text{ kJ/mol}$$

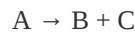
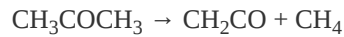
1. Plot and then analyze the conversion and temperature down the plug-flow reactor until an 80% conversion (if possible) is reached. (The maximum catalyst weight that can be packed into the PFR is 50 kg.) Assume that $\Delta P = 0.0$
2. Vary the inlet temperature and describe what you find.

- Plot the heat that must be removed along the reactor (\dot{Q} vs. V) to maintain isothermal operation.
- Now take the pressure drop into account in the PBR with $\rho_b = 1 \text{ kg/dm}^3$. The reactor can be packed with one of two particle sizes. Choose one.

$$\alpha = 0.019/\text{kg-cat for particle diameter } D_1$$

$$\alpha = 0.0075/\text{kg-cat for particle diameter } D_2$$
- Plot and then analyze the temperature, conversion, and pressure along the length of the reactor. Vary the parameters α and P_0 to learn the ranges of values in which they dramatically affect the conversion.
- Apply to this problem one or more of the six ideas discussed in Table P-4 in the Complete preface-introduction on the Web site (<http://www.umich.edu/~elements/6e/toc/Preface-Complete.pdf>).

P11-6B OEQ (Old Exam Question). The irreversible endothermic vapor-phase reaction follows an elementary rate law



and is carried out adiabatically in a 500-dm³ PFR. Species A is fed to the reactor at a rate of 10 mol/min and a pressure of 2 atm. An inert stream is also fed to the reactor at 2 atm, as shown in Figure P11-6B. The entrance temperature of both streams is 1100 K.

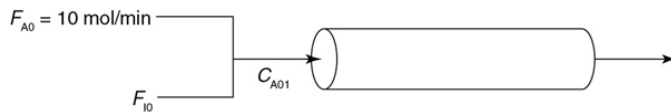


Figure P11-6B Adiabatic PFR with inerts.

Additional information:

$$k = \exp(34.34 - 34222/T) 1/\text{s} C_{PI} 200 \text{ J/mol} \cdot \text{K}$$

(T in degrees Kelvin, K)

$$C_{PA} = 700 \text{ J/mol} \cdot \text{K} \quad C_{PB} = 90 \text{ J/mol} \cdot \text{K}$$

$$C_{PC} = 80 \text{ J/mol} \cdot \text{K} \quad \Delta H_{Rx}^\circ = 80000 \text{ J/mol}$$

- First derive an expression for C_{A01} as a function of C_{A0} and Θ_I .
- Sketch the conversion and temperature profiles for the case when no inerts are present. Using a dashed line, sketch the profiles when a moderate amount of inerts are added. Using a dotted line, sketch the

profiles when a large amount of inerts are added. Qualitative sketches are fine. Describe the similarities and differences between the curves.

3. Sketch or plot and then analyze the exit conversion as a function of Θ_I . Is there a ratio of the entering molar flow rates of inerts (I) to A (i.e., $\Theta_I = F_{I0}/F_{A0}$) at which the conversion is at a maximum? Explain why there “is” or “is not” a maximum.
4. What would change in parts (b) and (c) if reactions were exothermic and reversible with $\Delta H_{Rx}^\circ = -80 \text{ kJ/mol}$ and $K_C = 2 \text{ dm}^3/\text{mol}$ at 1100 K?
5. Sketch or plot F_B for parts (c) and (d), and describe what you find.
6. Plot the heat that must be removed along the reactor (\dot{Q} vs. V) to maintain isothermal operation for pure A fed and an exothermic reaction. Part (f) is “C” level of difficulty, that is, Problem P11-6C(f).

P11-7B OEQ (Old Exam Question). The gas-phase reversible reaction



is carried out under high pressure in a packed-bed reactor with pressure drop. The feed consists of both inerts I and Species A with the ratio of inerts to the species A being 2 to 1. The entering molar flow rate of A is 5 mol/min at a temperature of 300 K and a concentration of 2 mol/dm³. Work this problem in terms of volume. *Hint*:. $V = W/\rho_B$, $r_A = \rho_B r'_A$.

Additional information:

$$F_{A0} = 5.0 \text{ mol/min} \quad K_C = 1000 \text{ at } 300 \text{ K} \quad T_{a0} = 300 \text{ K}$$

$$C_{A0} = 2 \text{ mol/dm}^3 \quad C_{PB} = 160 \text{ cal/mol/K} \quad V = 40 \text{ dm}^3$$

$$C_I = 2C_{A0} \quad \rho_B = 1.2 \text{ kg/dm}^3 \quad \alpha_{PB} = 0.02 \text{ dm}^{-3}$$

$$C_{FI} = 18 \text{ cal/mol/K} \quad T_{00} = 300 \text{ K} \quad \text{Coolant}$$

$$C_{PA} = 160 \text{ cal/mol/K} \quad T_i = 300 \text{ K} \quad \dot{m}_C = 50 \text{ mol/min}$$

$$E = 10000 \text{ cal/mol} \quad k_1 = 0.1 \text{ min}^{-1} \text{ at } 300 \text{ K} \quad C_{PCool} = 20 \text{ cal/mol/K}$$

$$\Delta H_{Rx} = -20000 \text{ cal/mol} \quad Ua = 150 \text{ cal/dm}^3/\text{min/K}$$

1. **Adiabatic Operation.** Plot X , X_e , p , T , and the rate of disappearance as a function of V up to $V = 40 \text{ dm}^3$. Explain why the curves look the way they do.

2. Vary the ratio of inerts to A ($0 \leq \Theta_I \leq 10$) and the entering temperature, and describe what you find.
3. Plot the heat that must be removed along the reactor (\dot{Q} vs. V) to maintain isothermal operation. Part (c) is "C" level of difficulty.

We will continue this problem in [Chapter 12](#).

P11-8_B Algorithm for reaction in a PBR with heat effects

The elementary gas-phase reaction



is carried out in a packed-bed reactor. The entering molar flow rates are $F_{A0} = 5$ mol/s, $F_{B0} = 2F_{A0}$, and $F_I = 2F_{A0}$ with $C_{T0} = 0.3$ mol/dm³. The entering temperature is 330 K.

Additional information:

$$C_{PA} = C_{PB} = C_{PC} = 20 \text{ cal/mol/K}, \quad C_{PI} = 40 \text{ cal/mol/K}, \quad E = 25 \frac{\text{kcal}}{\text{mol}},$$

$$\Delta H_{Rx} = -20 \frac{\text{kcal}}{\text{mol}} @ 298 \text{ K}$$

$$\alpha = 0.0002 \text{ kg}^{-1}, \quad k = 0.004 \frac{\text{dm}^6}{\text{kg} \cdot \text{mol} \cdot \text{s}} @ 310 \text{ K},$$

$$K_C = 1000 @ 298 \text{ K}$$

Note: This problem is continued in Problem P12-1_A with some of the entering conditions (e.g., F_{B0}) modified.

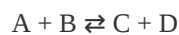
1. Write the mole balance, the rate law, K_C as a function of T , k as a function of T , and C_A , C_B , C_C as a function of X , p , and T .
2. Write the rate law as a function of X , p , and T .
3. Show the equilibrium conversion is

$$X_e = \frac{\frac{3K_C}{4} - \sqrt{\left(\frac{3K_C}{4}\right)^2 - 2K_C\left(\frac{F_C}{4} - 1\right)}}{2\left(\frac{K_C}{4} - 1\right)}$$

and then plot X_e versus T .

4. What are $\Sigma \Theta_i C_{Pi}$, ΔC_P , T_0 , entering temperature T_1 (rate law), and T_2 (equilibrium constant)?
5. Write the energy balance for adiabatic operation.
6. **Case 1 Adiabatic Operation.** Plot and then analyze X_e , X , p , and T versus W when the reaction is carried out adiabatically. Describe why the profiles look the way they do. Identify those terms that will be affected by inerts. Sketch what you think the profiles X_e , X , p , and T will look like before you run the Polymath program to plot the profiles. (**Ans:** At $W = 800$ kg then $X = 0.3583$)
7. Plot the heat that must be removed along the reactor (\dot{Q} vs. V) to maintain isothermal operation. Part (g) is "C" level of difficulty, that is, Problem **P11-8_C(g)**.

P11-9_A The reaction



is carried out adiabatically in a series of staged packed-bed reactors with interstage cooling (see Figure 11-5). The lowest temperature to which the reactant stream may be cooled is 27°C. The feed is equal molar in A and B, and the catalyst weight in each reactor is sufficient to achieve 99.9% of the equilibrium conversion. The feed enters at 27°C and the reaction is carried out adiabatically. If four reactors and three coolers are available, what conversion may be achieved?

Additional information:

$$\Delta H_{\text{Rx}}^{\circ} = 30000 \text{ cal/mol} \quad AC_{\text{PA}} = C_{\text{PB}} = C_{\text{PC}} = C_{\text{PD}} = 25 \text{ cal/mol} \cdot \text{K}$$

$$K_e(50^{\circ}\text{C}) = 500000 F_{\text{A0}} = 10 \text{ mol A/min}$$

First prepare a plot of equilibrium conversion as a function of temperature. (**Partial ans:** $T = 360 \text{ K}$, $X_e = 0.984$; $T = 520 \text{ K}$, $X_e = 0.09$; $T = 540 \text{ K}$, $X_e = 0.057$)

P11-10A Figure P11-10A shows the temperature–conversion trajectory for a train of reactors with interstage heating. Now consider replacing the interstage heating with injection of the feed stream in three equal portions, as shown in Figure P11-10A:

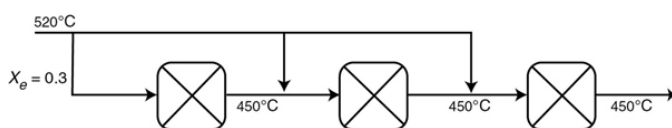


Figure P11-10A

Sketch the temperature–conversion trajectories for (a) an endothermic reaction with entering temperatures as shown, and (b) an exothermic reaction with the temperatures to and from the first reactor reversed, that is, $T_0 = 450^{\circ}\text{C}$.

SUPPLEMENTARY READING

1. An excellent development of the energy balance is presented in

R. ARIS, *Elementary Chemical Reactor Analysis*. Upper Saddle River, NJ: Pearson, 1969, Chaps. 3 and 6.

A number of example problems dealing with nonisothermal reactors may or may not be found in

THORNTON W. BURGESS, *The Adventures of Old Man Coyote*. New York: Dover Publications, Inc., 1916.

JOHN B. BUTT, *Reaction Kinetics and Reactor Design*, Revised and Expanded, 2nd ed. New York: Marcel Dekker, Inc., 1999.

S. M. WALAS, *Chemical Reaction Engineering Handbook of Solved Problems*. Amsterdam: Gordon and Breach, 1995. See the following solved problems: 4.10.1, 4.10.08, 4.10.09, 4.10.13, 4.11.02, 4.11.09, 4.11.03, 4.10.11.

For a thorough discussion on the heat of reaction and equilibrium constant, one might also consult

K. G. DENBIGH, *Principles of Chemical Equilibrium*, 4th ed. Cambridge: Cambridge University Press, 1981.

2. The heats of formation, $H(T)$, Gibbs free energies, $G_e(T_R)$, and the heat capacities of various compounds can be found in

D. W. GREEN, and R. H. PERRY, eds., *Chemical Engineers' Handbook*, 8th ed. New York: McGraw-Hill, 2008.

R. C. REID, M. PRAUSNITZ, and T. K. SHERWOOD, *The Properties of Gases and Liquids*, 3rd ed. New York: McGraw-Hill, 1977.

R. C. WEAST, ed., *CRC Handbook of Chemistry and Physics*, 94th ed. Boca Raton, FL: CRC Press, 2013.

12. Steady-State Nonisothermal Reactor Design: Flow Reactors with Heat Exchange

Research is to see what everybody else sees, and to think what nobody else has thought.

—Albert Szent-Gyorgyi

Overview. This chapter focuses on chemical reactors with heat exchange. The chapter topics are arranged in the following manner:

- Section 12.1 further develops the energy balance for easy application to PFRs and PBRs.
- Section 12.2 describes PFRs and PBRs for four types of heat exchanger operations.
 1. Constant heat-transfer fluid temperature, T_a
 2. Variable fluid temperature T_a with co-current operation
 3. Variable fluid temperature T_a with countercurrent operation
 4. Adiabatic operation
- Section 12.3 gives examples of four types of heat exchanger operations for PFRs and PBRs.
- Section 12.4 applies the energy balance to a CSTR.
- Section 12.5 shows how a CSTR can operate at different steady-state temperatures and conversions, and how to decide which of these conditions are stable and which are unstable.
- Section 12.6 describes one of the most important topics of the entire text, *multiple reactions with heat effects with Living Example Problems*, which is a unique feature of this textbook.
- Section 12.7 discusses radial and axial temperature and concentration gradients.
- Section 12.8 Safety: The causes of batch reactor explosions are discussed and hint of things to come when we do a CSI analysis on the Monsanto and T2 Laboratory explosions in Chapter 13.

The *Chapter 12 Professional Reference Shelf (R12.4)* on the CRE Web site (<http://www.umich.edu/~elements/6e/12chap/pdf/sulfuricacid.pdf>) describes a typical nonisothermal industrial reactor and reaction, SO_2 oxidation, and gives many practical details.

12.1 STEADY-STATE TUBULAR REACTOR WITH HEAT EXCHANGE

In this section, we consider a tubular reactor in which heat is either added or removed through the cylindrical walls of the reactor (Figure 12-1). In modeling plug-flow reactors, we shall assume that “there are no radial gradients” in the reactor and that the heat flux through the wall per unit volume of reactor is as shown in Figure 12-1.¹

¹ Radial gradients are discussed in Section 12.7 and in Chapters 17 and 18.

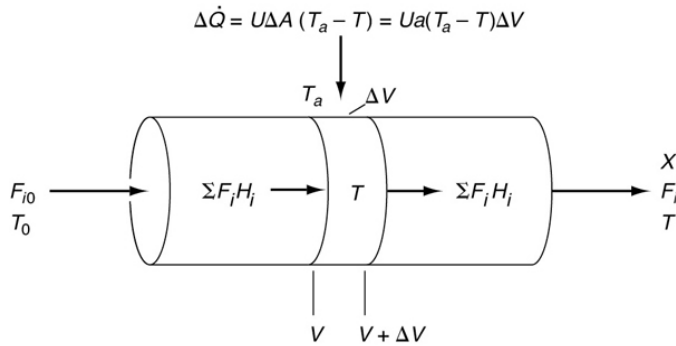


Figure 12-1 Tubular reactor with heat gain or loss.

12.1.1 Deriving the Energy Balance for a PFR

We will carry out an energy balance on the volume ΔV . There is no work done, that is, $\dot{W}_s = 0$, so Equation (11-10) becomes

$$\begin{array}{ccccccc} \text{Heat} & + & \text{Energy} & - & \text{Energy} & = & 0 \\ \text{Added} & & \text{In} & & \text{Out} & & \\ \Delta \dot{Q} & + & \sum F_i H_i|_V & - & \sum F_i H_i|_{V+\Delta V} & = & 0 \quad (12-1) \end{array}$$

The heat flow to the reactor, $\Delta \dot{Q}$, is given in terms of the overall heat-transfer coefficient, U , the heat exchange area, ΔA , and the difference between the ambient temperature, T_a , and the reactor temperature T

$$\Delta \dot{Q} = U \Delta A (T_a - T) = U a \Delta V (T_a - T)$$

where a is the heat exchange area per unit volume of reactor. For a tubular reactor

$$a = \frac{A}{V} = \frac{\pi D L}{\frac{\pi D^2 L}{4}} = \frac{4}{D}$$

where D is the reactor diameter. Substituting for $\Delta \dot{Q}$ in Equation (12-1), dividing by ΔV , and then taking the limit as

$\Delta V \rightarrow 0$, we get

$$Ua(T_a - T) - \frac{d\Sigma(F_i H_i)}{dV} = 0$$

Expanding

$$Ua(T_a - T) - \Sigma \frac{dF_i}{dV} H_i - \Sigma F_i \frac{dH_i}{dV} = 0 \quad (12-2)$$

From a mole balance on species i , we have

$$\frac{dF_i}{dV} = r_i = v_i(-r_A) \quad (12-3)$$

Differentiating the enthalpy Equation (11-19) with respect to V

$$\frac{dH_i}{dV} = C_{P_i} \frac{dT}{dV} \quad (12-4)$$

Substituting Equations (12-3) and (12-4) into Equation (12-2), we obtain

$$Ua(T_a - T) - \underbrace{\Sigma v_i H_i}_{\Delta \hat{H}_{R_x}}(-r_A) - \Sigma F_i C_{P_i} \frac{dT}{dV} = 0$$

Rearranging, we arrive at

$$\frac{dT}{dV} = \frac{\overbrace{r_A \Delta \hat{H}_{R_x}}^{\substack{Q_g \\ \text{Heat} \\ \text{"Generated"}}}} - \overbrace{Ua(T - T_a)}^{\substack{Q_r \\ \text{Heat} \\ \text{"Removed"}}}}}{\Sigma F_i C_{P_i}} \quad (12-5)$$

which is Equation (T11-1.G) in Table 11-1 on pages 547–549.

This form of the energy balance will also be applied to multiple reactions.

$$\frac{dT}{dV} = \frac{Q_g - Q_r}{\Sigma F_i C_{P_i}} \quad (\text{T11-1.G})$$

where

$$Q_g = r_A \Delta \hat{H}_{R_x} \equiv (-r_A)(-\Delta \hat{H}_{R_x}) \quad (12-5a)$$

$$Q_r = Ua(T - T_a) \quad (12-5b)$$

To help remember that Q_r is the **“heat” removed** from the reacting mixture, we note the driving force is from **“ T ” to “ T_a ”**, that is, $Ua(T - T_a)$.

For exothermic reactions, Q_g will be a positive number. We note that when the heat “generated,” Q_g , is greater than the heat “removed,” Q_r (i.e., $Q_g > Q_r$), the temperature will increase down the reactor. When $Q_r > Q_g$, the temperature will decrease down the reactor.

For endothermic reactions ΔH_{Rx} will be a positive number and therefore the heat generated, Q_g in Equation (12-5a), will be a negative number. The heat removed, Q_r in Equation (12-5b), will also be a negative number because heat is added rather than removed $T_a > T$. See Chapter 12 Additional Material on the Web site for a sample calculation on endothermic reactions (<http://www.umich.edu/~elements/6e/12chap/obj.html#/additional-materials/>). This point is also illustrated in Example 12-2 for the case of constant ambient temperature.

We continue development of our algorithm by noting Equation (12-5) is coupled with the mole balances on each species, Equation (12-3). Next, we express r_A as a function of either the concentrations for liquid systems or molar flow rates for gas systems, as described in Chapter 6. We will use the molar flow rate form of the energy balance for membrane reactors and also extend this form to multiple reactions.

We could also write Equation (12-5) in terms of conversion by recalling $F_i = F_{A0}(\Theta_i + v_i X)$ and substituting this expression into the denominator of Equation (12-5).

PFR energy balance

$$\frac{dT}{dV} = \frac{\overbrace{r_A \Delta H_{\text{Rx}}}^{Q_g} - \overbrace{Ua(T-T_a)}^{Q_r}}{F_{A0}(\sum \Theta_i C_{Pi} + \Delta C_p X)} = \frac{Q_g - Q_r}{\sum F_i C_i} \quad (12-6)$$

For a packed-bed reactor $dW = \rho_b dV$ where ρ_b is the bulk density

PFR energy balance

$$\frac{dT}{dW} = \frac{\overbrace{r'_A \Delta H_{Rx}}^{Q'_g} - \overbrace{\frac{U_a(T - T_a)}{\rho_b}}^{Q'_r}}{\sum F_i C_{p_i}} \quad (12-7)$$

Equations (12-6) and (12-7) are also given in Table 11-1 as Equations (T11-1.D) and (T11-1.F). As noted earlier, having gone through the derivation to these equations, it will be easier to apply them accurately to CRE problems with heat effects.

12.1.2 Applying the Algorithm to Flow Reactors with Heat Exchange

We continue to use the algorithm described in the previous chapters and simply add a fifth building block, *the energy balance*.

Gas Phase

If the reaction is in gas phase and pressure drop is included, there are four differential equations that must be solved simultaneously. The differential equation describing the change in temperature with volume (i.e., distance) as we move down the reactor

Energy balance

$$\frac{dT}{dV} = g(X, T, T_a) \quad (A)$$

must be coupled with the mole balance

Mole balance

$$\frac{dT}{dV} = \frac{-r_A}{F_{A0}} = f(X, T, p) \quad (B)$$

and with the pressure-drop equation

Pressure drop

$$\frac{dp}{dV} = -h(p, X, T) \quad (C)$$

and solved simultaneously. If the temperature of the heat-exchange fluid, T_a , varies down the reactor, we must add the energy balance on the heat-exchange fluid. In the next section,

we will derive the following equation for co-current heat transfer

Heat exchanger

$$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}_{C0}C_{PC0}} \quad (\text{D})$$

Numerical integration of the coupled differential equations (A) to (D) is required.

along with the equation for countercurrent heat transfer. A variety of software packages (e.g., Polymath) can be used to solve these four coupled differential equations: **(A)**, **(B)**, **(C)**, and **(D)**.

Liquid Phase

For liquid-phase reactions, the rate is not a function of total pressure, so our mole balance is

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} = f(X, T) \quad (\text{E})$$

Consequently, we need to only solve three equations **(A)**, **(D)**, and **(E)** simultaneously.

12.2 BALANCE ON THE HEAT-TRANSFER FLUID

12.2.1 Co-Current Flow

The heat-transfer fluid will be a coolant for exothermic reactions and a heating medium for endothermic reactions. If the flow rate of the heat-transfer fluid is sufficiently high with respect to the heat released (or absorbed) by the reacting mixture, then the heat-transfer fluid temperature will be virtually constant along the length of the reactor. In the material that follows, we develop the basic equations for a coolant to remove heat from exothermic reactions; however, these same equations apply to endothermic reactions where a heating medium is used to supply heat.

We now carry out an energy balance on *the coolant* in the annulus between R_1 and R_2 , and axially between V and $V + \Delta V$, as shown in [Figure 12-2](#). The mass flow rate of the heat-

exchange fluid (e.g., coolant) is \dot{m}_c . We will consider the case when the reactor is cooled and the outer radius of the coolant channel R_2 is *insulated*. Recall that by convention is the heat **added to** the system.

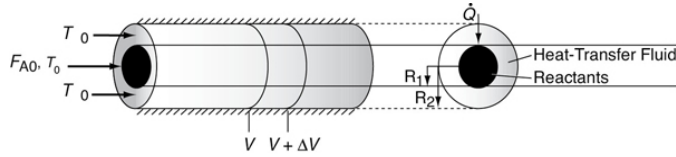
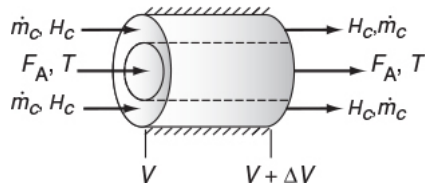


Figure 12-2 Co-current, double-pipe heat exchanger.

For co-current flow, the reactant and the coolant flow in the same direction.



The energy balance on the coolant in the volume between V and $(V + \Delta V)$ is

Coolant energy balance

$$\left[\begin{array}{c} \text{Rate of energy} \\ \text{in at } V \end{array} \right] - \left[\begin{array}{c} \text{Rate of energy} \\ \text{out at } V + \Delta V \end{array} \right] + \left[\begin{array}{c} \text{Rate of heat added} \\ \text{by conduction through} \\ \text{the inner wall} \end{array} \right] = 0$$

$$\dot{m}_c H_c|_V - \dot{m}_c H_c|_{V+\Delta V} + Ua(T - T_a)\Delta V = 0$$

where T_a is the temperature of the heat transfer fluid, that is, coolant, and T is the temperature of the reacting mixture in the inner tube.

Dividing by ΔV and taking limit as $\Delta V \rightarrow 0$

$$-\dot{m}_c \frac{dH_c}{dV} + Ua(T - T_a) = 0 \quad (12-8)$$

Analogous to Equation (12-4), the change in enthalpy of the coolant can be written as

$$\frac{dH_c}{dV} = C_{Pc} \frac{dT_a}{dV} \quad (12-9)$$

The variation of coolant temperature T_a down the length of reactor is

$$\boxed{\frac{dT_a}{dV} = \frac{U_a(T - T_a)}{\dot{m}_c C_{Pc}}} \quad (12-10)$$

The equation is valid whether the heat-transfer fluid is a coolant or a heating medium.

Typical heat-transfer fluid temperature profiles for both exothermic and endothermic reactions when the heat-transfer fluid enters at T_{a0} are shown in Figure 12-3, parts (a) and (b) respectively.

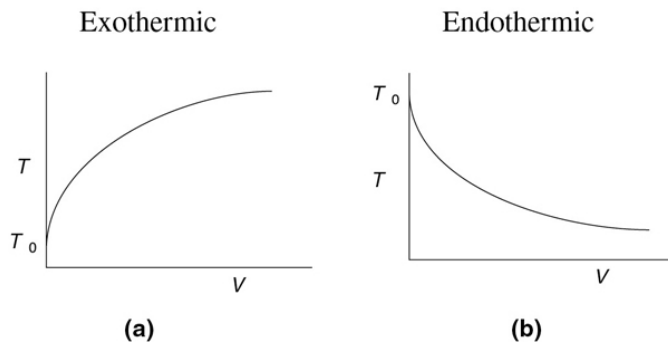


Figure 12-3 Heat-transfer fluid temperature profiles for co-current heat exchanger. (a) Coolant. (b) Heating medium.

12.2.2 Countercurrent Flow

In countercurrent heat exchange, the reacting mixture and the heat-transfer fluid (e.g., coolant) flow in opposite directions. At the reactor entrance, $V = 0$, the reactants enter at temperature T_0 , and the coolant exits at temperature T_{a2} . At the end of the reactor, the reactants and products exit at temperature T , while the coolant enters at T_{a0} .

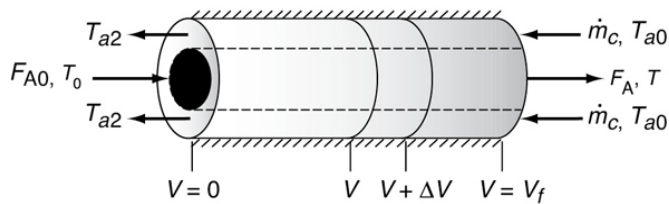


Figure 12-4 Countercurrent, double-pipe heat exchanger.

Again, we write an energy balance on the coolant over a differential reactor volume to arrive at

$$\frac{dT_a}{dV} = \frac{Ua(T_a - T)}{\dot{m}_c C_{Pc}} \tag{12-11}$$

At the entrance, $V = 0$ $X = 0$ and $T_a = T_{a2}$.

At the exit, $V = V_f$ $T_a = T_{a0}$.

We note that the only difference between Equations (12-10) and (12-11) is a minus sign, that is, $(T - T_a)$ versus $(T_a - T)$.

The solution to a countercurrent flow problem to find the exit conversion and temperature requires a *trial-and-error* procedure, as shown in Table 12-1.

Trial-and-error procedure required

TABLE 12-1 PROCEDURE TO SOLVE FOR THE EXIT CONDITIONS FOR PFRs WITH COUNTERCURRENT HEAT EXCHANGE

1. Consider an exothermic reaction where the coolant stream enters at the end of the reactor ($V = V_f$) at a temperature T_{a0} of 300 K. We have to carry out a *trial-and-error* procedure to find the temperature of the coolant T_{a2} exiting the reactor at $V = 0$ (cf. Figure 12-4).

2. Guess an exit coolant temperature T_{a2} at the feed entrance ($X = 0$, $V = 0$) to the reactor to be $T_{a2} = 340$ K, as shown in Figure 12-5(a).

3. Use an ODE solver to calculate X , T , and T_a as a function of V .

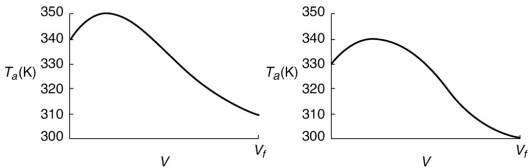


Figure 12-5 Trial-and-error results for countercurrent heat exchanger.

We see from **Figure 12-5(a)** that our guess of 340 K for T_{a2} at the feed entrance ($V = 0$ and $X = 0$) gives an entering temperature of the coolant of 310 K ($V = V_f$), which does not match the actual entering coolant temperature of 300 K. Lets try again!

4. Now guess another coolant temperature at $V = 0$ and $X = 0$ of, say, 330 K. After carrying out the simulation with this guess, we see from **Figure 12-5(b)** that a coolant temperature at $V = 0$ of $T_{a2} = 330$ K will give a coolant entering temperature at V_f of 300 K, which matches the actual T_{a0} . Good guess!

12.3 EXAMPLES OF THE ALGORITHM FOR PFR/PBR DESIGN WITH HEAT EFFECTS

We now have all the tools to solve reaction engineering problems involving heat effects in PFRs and PBRs for the cases of both constant and variable coolant temperatures.

Table 12-2 gives the algorithm for the design of PFRs and PBRs with heat exchange: In **Case A** *Conversion* is the reaction variable and in **Case B** *Molar-Flow-Rates* are the reaction variables. The procedure in Case B must be used to analyze multiple reactions with heat effects.

TABLE 12-2 ALGORITHM FOR PFR/PBR DESIGN FOR GAS-PHASE REACTIONS WITH HEAT EFFECTS

The elementary gas-phase reaction



is to be carried out in a PBR with a co-current heat exchanger.

A. Conversion as the Reaction Variable

1. Mole Balance:

$$\frac{dX}{dW} = \frac{-r'_A}{F_0} \quad (\text{T12-2.1})$$

2. Rate Law:

$$-r'_A = k_1 \left(C_A C_B - \frac{C_c^2}{K_C} \right) \quad (\text{T12-2.2})$$

$$k = k_1 \left(T_1 \right) \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (\text{T12-2.3})$$

$$\text{for } \Delta C_P \cong 0. \quad K_C = K_{C2} (T_2) \exp \left[\frac{\Delta H_{\text{Rx}}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right) \right] \quad (\text{T12-2.4})$$

Again we note that because $\delta \equiv 0$, $K_C \equiv K_e$

3. Stoichiometry (gas phase):

$$C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)} \frac{T_0}{T} p \quad (\text{S4-9})$$

$$\varepsilon = y_{A0} \delta = \frac{1}{3} (2 - 1 - 1) = 0$$

$$C_A = C_{A0} (1 - X) \frac{T_0}{T} p \quad (\text{T12-2.5})$$

$$C_B = C_{A0} (\Theta_B - X) \frac{T_0}{T} p \quad (\text{T12-2.6})$$

$$C_C = 2C_{A0} X \frac{T_0}{T} p \quad (\text{T12-2.7})$$

$$C_I = C_{I0} \frac{T_0}{T} p \quad (\text{T12-2.8})$$

$$\frac{dp}{dW} = -\frac{\alpha}{2p} (1 + \varepsilon X) \frac{T}{T_0} \quad (5-30)$$

$$\delta = (2 - 1 - 1) = 0, \therefore \varepsilon = 0$$

$$\frac{dp}{dW} = -\frac{\alpha}{2p} \frac{T}{T_0} \quad (\text{T12-2.9})$$



- Mole Balance
- Rate Law
- Stoichiometry
- Energy Balance
- Parameters
- Solution
- Analysis

Combine Rate Law and Stoichiometry to find X_e

$$r'_A = k_1 C_{A0}^2 \left[\left(1 - X\right) \left(\Theta_B - X\right) - \frac{4X^2}{K_C} \right] \left(\frac{T_0}{T} p\right)^2 \quad (\text{T12-2.10})$$

at equilibrium and $-r'_A = 0$ and $X = X_e$

Solving for X_e

$$X_e = \frac{(\Theta_B + 1) K_C - \left[((\Theta_B + 1) K_C)^2 - 4 K_C \Theta_B (K_C - 4) \right]^{1/2}}{2(K_C - 4)} \quad (\text{T12-2.11})$$

Because we are solving for the temperature as a function of catalyst weight down the reactor, we can use Equation (T12-2.4) to find the equilibrium constant, K_C , profile and then use Equation (T12-2.11) to find the equilibrium conversion profile, X_e .

4. Energy Balances:

$$\text{Reactor: } \frac{dT}{dW} = \frac{Q'_g - Q'_r}{\Sigma F_i C_{P_i}} \quad (\text{T12-2.12})$$

$$Q'_g = (-r'_A) (-\Delta H_{\text{Rx}}) = (r'_A \Delta H_{\text{Rx}}) \quad (\text{T12-2.13})$$

$$Q'_r = \left(\frac{U_a}{\rho_b} \right) (T - T_a) \quad (\text{T12-2.14})$$

$$\Sigma F_i C_{P_i} = F_{A0} [C_{P_A + \theta_B} C_{P_B} + X \Delta C_p] \quad (\text{T12-2.15})$$

$$\text{Co-Current Coolant: } \frac{dT_a}{dW} = \frac{\left(\frac{U_a}{\rho_b} \right) (T - T_a)}{\dot{m}_c C_{P_{\text{cool}}}} \quad (\text{T12-2.16})$$

B. Molar Flow Rates as the Reaction Variable



1. Mole Balance:

$$\frac{dF_A}{dW} = r'_A \quad (\text{T12-2.17})$$

$$\frac{dF_B}{dW} = r'_B \quad (\text{T12-2.18})$$

$$\frac{dF_C}{dW} = r'_C \quad (\text{T12-2.19})$$

$$F_I = F_{I0} \quad (\text{T12-2.20})$$

2. Rate Law (elementary reaction):

$$-r'_A = k_1 \left(C_A C_B - \frac{C_C^2}{K_C} \right) \quad (\text{T12-2.2})$$

$$k = k_1 (T_1) \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (\text{T12-2.3})$$

$$k_C = k_{C2} (T_2) \exp \left[\frac{\Delta H_{\text{Rx}}}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right) \right] \quad (\text{T12-2.4})$$

3. Stoichiometry (gas phase):

$$r'_B = r'_A \quad (\text{T12-2.21})$$

$$r'_C = -2r'_A \quad (\text{T12-2.22})$$

$$C_A = C_{T0} \frac{T_A}{F_T} \frac{T_0}{T} P \quad (\text{T12-2.23})$$

$$C_B = C_{T0} \frac{T_B}{F_T} \frac{T_0}{T} P \quad (\text{T12-2.24})$$

$$C_C = C_{T0} \frac{T_C}{F_T} \frac{T_0}{T} P \quad (\text{T12-2.25})$$

$$F_T = F_A + F_B + F_C + F_I \quad (\text{T12-2.26})$$

$$\frac{dp}{dw} = \frac{\alpha}{2P} \frac{F_T}{F_{T0}} \frac{T}{T_0} \quad (\text{T12-2.27})$$

4. Energy Balances:

Reactor:

$$\frac{dT}{dW} = \frac{Q'_g - Q'_r}{\sum F_i C_{P_i}} = \frac{(r'_A \Delta H_{Rx}) - \left(\frac{U_a}{\rho_b}\right)(T - T_a)}{F_A C_{P_A} + F_B C_{P_B} + F_C C_{P_C} + F_I C_{P_I}} \quad (\text{T12-2.28})$$

Heat Exchangers: Same as for A. Conversion as the Reaction Variable

Case A: Conversion as the Independent Variable Example Calculation

5. Parameter Evaluation:

Now we enter all the explicit equations with the appropriate parameter values.

$$k_1, E, R, C_{T0}, T_a, T_0, T_1, T_2, K_{C2}, \Theta_B, \Theta_1, \Delta H_{Rx}^\circ, C_{P_A}, C_{P_B}, C_{C_A}, U_a, \rho_b$$

Base Case for Parameter Values

$$\begin{aligned} E &= 25 \text{ kcal/mol} & C_{P_I} &= 40 \text{ cal/mol } K \\ \Delta H_{Rx} &= -20 \text{ kcal/mol} \\ k_1 &= 0.004 \frac{\text{dm}^6}{\text{mol} \cdot \text{kg} \cdot \text{s}} @ 310 K \quad \left(\frac{U_a}{\rho_b}\right) = U_{arho} = 0.5 \frac{\text{cal}}{\text{kg} \cdot \text{s} \cdot K} \\ K_{C2} &= 1000 @ 303 K & \dot{m}_c &= 1000 \text{ g/s} \end{aligned}$$

$$\begin{aligned} \alpha &= 0.0002/\text{kg} & C_{P_{Cool}} &= 18 \text{ cal/g/K} \\ F_{A0} &= 5 \text{ mol/s} & \Theta_B &= 1 \\ C_{P_{Cool}} &= 0.3 \text{ mol/dm}^3 & \Theta_1 &= 1 \\ C_{P_A} &= C_{P_B} = C_{P_C} = 20 \text{ cal/mol/K} \end{aligned}$$

with initial values $T_0 = 330 \text{ K}$, $T_{a0} = 320 \text{ K}$, $p = 1$, and $X = 0$ at $W = 0$ and final values: $W_f = 5000 \text{ kg}$.

6. Solution:

Equations (T12-2.1)–(T12-2) are entered into the Polymath program along with the corresponding parameter values.

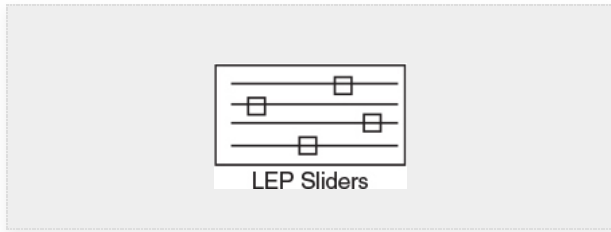
Differential equations

$$1 \quad d(T_a)/d(W) = U_{arho} \cdot (T - T_a) / (m_c \cdot C_{pcool})$$

$$2 \quad d(p)/d(W) = -\alpha/2 \cdot (T/T_0)/p$$

$$3 \frac{d(T)}{d(W)} = (Q_g - Q_r) / (F_{ao} \cdot \sum c_p)$$

$$4 \frac{d(X)}{d(W)} = -r_a / F_{ao}$$



Explicit equations

$$1 \text{ Hr} = -20000$$

$$2 \text{ thetaB} = 1$$

$$3 \text{ Uarho} = 0.5$$

$$4 \text{ alpha} = .0002$$

$$5 \text{ To} = 330$$

$$6 \text{ Qr} = \text{Uarho} \cdot (T - T_a)$$

$$7 \text{ mc} = 1000$$

$$8 \text{ Cpcool} = 18$$

$$9 \text{ Kc} = 1000 \cdot (\exp(\text{Hr} / 1.987 \cdot (1/303 - 1/T)))$$

$$10 \text{ Fao} = 5$$

$$11 \text{ thetaI} = 1$$

$$12 \text{ CpI} = 40$$

$$13 \text{ CpA} = 20$$

$$14 \text{ yao} = 1 / (1 + \text{thetaB} + \text{thetaI})$$

$$15 \text{ CpB} = 20$$

$$16 \text{ Cto} = 0.3$$

$$17 \text{ Ea} = 25000$$

$$18 \text{ Xe} = ((\text{thetaB}+1)*\text{Kc}-(((\text{thetaB}+1)*\text{Kc})^2-4*(\text{Kc}-4)*(\text{Kc}*\text{thetaB}))^{0.5})/(2*(\text{Kc}-4))$$

$$19 \text{ k} = .004*\exp(\text{Ea}/1.987*(1/310-1/\text{T}))$$

$$20 \text{ Cao} = \text{yao}*\text{Cto}$$

$$21 \text{ Cc} = \text{Cao}^2*\text{X}*\text{p}*\text{To}/\text{T}$$

$$22 \text{ sumcp} = (\text{thetaI}*\text{CpI}+\text{CpA}+\text{thetaB}*\text{CpB})$$

$$23 \text{ Ca} = \text{Cao}*(1-\text{X})*\text{p}*\text{To}/\text{T}$$

$$24 \text{ Cb} = \text{Cao}*(\text{thetaB}-\text{X})*\text{p}*\text{To}/\text{T}$$

$$25 \text{ ra} = -\text{k}*(\text{Ca}*\text{Cb}-\text{Cc}^2/\text{Kc})$$

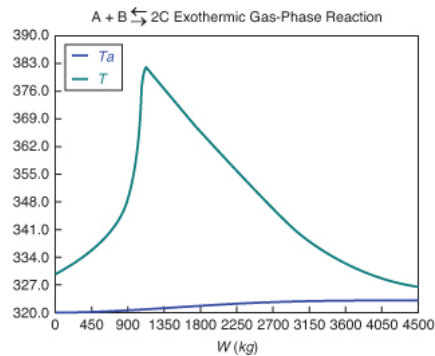
$$26 \text{ Qg} = (-\text{ra})*(-\text{Hr})$$

<http://www.umich.edu/~elements/6e/live/chapter12/T12-3/LEP-T12-2.pol>

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	alpha	0.0002	0.0002
2	Ca	0.1	0.0111092
3	Cao	0.1	0.1
4	Cb	0.1	0.0111092
5	Cc	0	0.0255273
6	CpA	20.	20.
7	CpB	20.	20.
8	Cpcool	18.	18.
9	CpI	40.	40.
10	Cto	0.3	0.3
11	Ea	2.5E+04	2.5E+04
12	Fao	5.	5.
13	Hr	-2.0E+04	-2.0E+04
14	k	0.046809	0.0303238

15	Kc	66.01082	93.4225
16	mc	1000.	1000.
17	p	1.	0.2360408
18	Qg	9.361802	0.0706176
19	Qr	5.	1.615899
20	ra	-0.0004681	-3.531E-06
21	sumcp	80.	80.
22	T	330.	326.2846
23	Ta	320.	323.0528
24	thetaB	1.	1.
25	thetaI	1.	1.
26	To	330.	330.
27	Uarho	0.5	0.5
28	W	0	4500.
29	X	0	0.5346512
30	Xe	0.8024634	0.8285547
31	yao	0.3333333	0.3333333

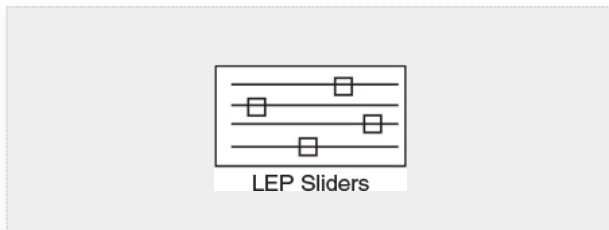


Analysis:

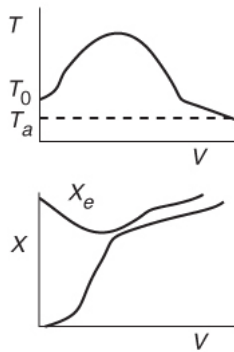
The temperature profiles are shown in [Figure T12-2.1](#). One notes that due to the exothermic heat of reaction, the temperature of the gas in the reactor increases sharply near the entrance then decreases as the reactants are consumed and the fluid is cooled as it moves down the reactor. [Figure T12-2.2](#) shows the conversion X increases and approaches its equilibrium value X_e at approximately $W = 1125$ kg of catalyst where the reaction rate approaches zero. At this point the

conversion cannot increase further unless X_e increases. The increase in X_e occurs because of the cooling of the reactor's contents by the heat exchanger thus shifting the equilibrium to the right. By the end of the reactor, the equilibrium conversion has been increased to 82.9% and the conversion in the reactor to 53.4%. One notes from [Figure T12.2-2](#), that owing to the cooling and consumption of reactants the conversion does not increase significantly above a catalyst weight of 2000 kg, even though X is much below X_e (see Problem P12-1A).

The following figures show “representative” profiles that would result from solving the above equations for different parameter values. The reader is encouraged to download the Living Example Problem for [Table 12-2](#) and use Wolfram to vary a number of parameters, as discussed in Problem P12-1A. Be sure you can explain why these curves look the way they do.

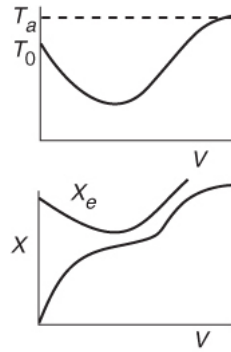


Constant T_a
reversible exothermic
reaction in a PFR with
heat exchange



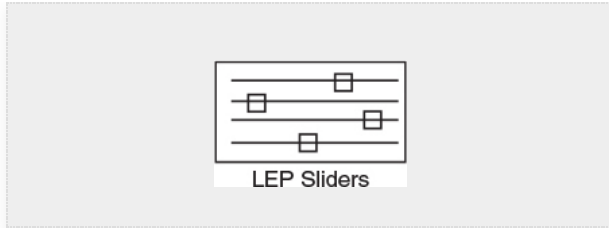
(a)

Constant T_a
endothermic reaction
in a PFR with
heat exchange

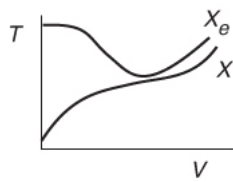
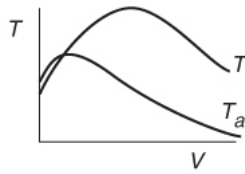


(b)

Be sure you can explain why these curves look the way they do.

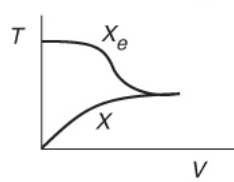
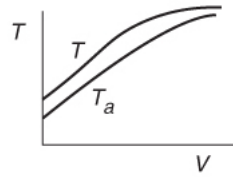


Variable T_a
exothermic
countercurrent
exchange



(c)

Variable T_a
exothermic
co-current exchange

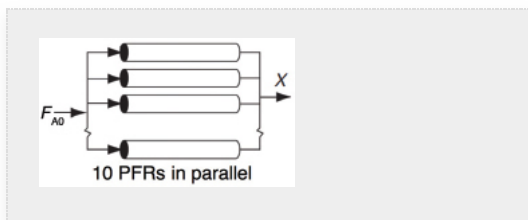


(d)

12.3.1 Applying the Algorithm to an Exothermic Reaction

**Example 12–1 Butane Isomerization Continued—
OOPS!**

When plant engineer Maxwell Anthony looked up the vapor pressure at the exit to the adiabatic reactor in [Example 11-3](#), where the temperature is 360 K, he learned the vapor pressure for isobutene was about 1.5 MPa, which is greater than the rupture pressure of the glass vessel the company had hoped to use. Fortunately, when Max looked in the storage shed, he found there was a bank of 10 tubular reactors, each of which was 5 m^3 . The bank reactors were double-pipe heat exchangers with the reactants flowing in the inner pipe and with $Ua = 5,000 \text{ kJ/m}^3 \cdot \text{h} \cdot \text{K}$. Max also bought some thermodynamic data from one of the companies he found on the Internet that used Colorimeter experiments to find ΔH_{RX} for various reactions. One of the companies had the value of ΔH_{RX} for his reaction on sale this week for the low, low price of \$25,000.00. For this value of ΔH_{RX} the company said it is best to use an initial concentration of A of 1.86 mol/dm^3 . The entering temperature of the reactants is 305 K and the entering coolant temperature is 315 K. The mass flow rate of the coolant, \dot{m}_c , is 500 kg/h and the heat capacity of the coolant, C_{pC} , is 28 kJ/kg·K. The temperature in any one of the reactors cannot rise above 325 K. Carry out the following analyses with the newly purchased values from the Internet:



1. Co-current heat exchange: Plot X , X_e , T , T_a , and $-r_A$ down the length of the reactor.
2. Countercurrent heat exchange: Plot X , X_e , T , T_a , and $-r_A$ down the length of the reactor.
3. Constant ambient temperature, T_a : Plot X , X_e , T , and $-r_A$ down the length of the reactor.
4. Adiabatic operation: Plot X , X_e , T , T_a , and $-r_A$ down the length of the reactor.
5. Compare parts (a) through (d) above and write a paragraph describing what you find.

Additional information:

Recall from [Example 11-3](#) that $F_{T0} = 163 \text{ kmol/h}$ and $F_{A0} = 0.9 F_{T0}$, $C_{PA} = 141 \text{ kJ/kmol} \cdot \text{K}$, $C_{P0} = \sum \Theta_i C_{Pi} = 159 \text{ kJ/kmol} \cdot \text{K}$, and data from the company Maxwell got off the Internet are $\Delta H_{Rx} = -34500 \text{ kJ/kmol}$ with $\Delta C_P = 0$ and $C_{A0} = 1.86 \text{ kmol/m}^3$ and $E/R = 7906 \text{ K}$ with $k = 31.1 \text{ h}^{-1}$ @ 360 K.

Solution

We shall first solve part (a), the co-current heat exchange case and then make small changes in the Polymath program for parts (b) through (d).

The molar flow rate of A to each of the 10 reactors in parallel

$$F_{A0} = (0.9) \left(163 \text{ kmol/h} \right) \times \frac{1}{10} = 14.7 \frac{\text{kmol A}}{\text{h}}$$

The mole balance, rate law, and stoichiometry are the same as in the adiabatic case previously discussed in [Example 11-3](#); that is,

The Algorithm

Mole Balance:

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} \quad (\text{E11-3.1})$$

Rate Law and Stoichiometry:

$$r_A = -k C_{A0} \left[1 - \left(1 + \frac{1}{K_C} \right) X \right] \quad (\text{E11-3.7})$$

with

$$k = 31.1 \exp \left[7906 \left(\frac{T-360}{360T} \right) \text{h}^{-1} \right] \quad (\text{E11-3.10})$$

$$K_C = 3.03 \exp \left[\frac{(\Delta H_{Rx}/R)(T-333)}{333T} \right] \quad (\text{E11-3.11})$$

Same as [Example 11-3](#)

The equilibrium conversion is

$$X_e = \frac{K_c}{1+K_c} \quad (\text{T11-3.12})$$

Note: We could substitute for K_c using Equation (E11-3.12) to write the reaction rate as

$$-r_A = kC_{A0} \left(1 - \frac{X}{X_e}\right) \quad (\text{E12-1.1})$$

Energy Balance:

The energy balance on the reactor is

$$\frac{dT}{dV} = \frac{Q_g - Q_r}{\sum F_i C_{P_i}} \quad (\text{E12-1.2})$$

$$Q_g = r_A \Delta H_{R_x} \quad (\text{E12-1.3})$$

$$Q_g = r_A \Delta H_{R_x}$$

$$Q_r = Ua(T - T_a)$$

$$\frac{dT}{dV} = \frac{Q_g - Q_r}{F_{A0} C_{P0}}$$

$$Q_r = Ua(T - T_a) \quad (\text{E12-1.4})$$

$$\sum F_i C_{P_i} = F_{A0} \underbrace{\sum \Theta_i}_{\tilde{C}_{P0}} C_{P_i} = F_{A0} C_{P0} \quad (\text{E12-1.5})$$

Part (a) Co-Current Heat Exchange

We are now going to solve the coupled, ordinary differential and explicit equations (E11-3.1), (E11-3.7), (E11-3.10), (E11-3.11), (E11-3.12), and (E12-1.2), and the appropriate heat-exchange balance using Polymath. After entering these equations we will enter the parameter values. *By using co-current heat exchange as our Polymath base case*, we only need to change *one line* in the program for each of the other three cases and solve for the profiles of X , X_e , T , T_a , and $-r_A$, and not have to reenter the program.

For co-current flow, the balance on the heat transfer fluid is

$$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}_C C_{P_C}} \quad (\text{E12-1.6})$$

with $T_0 = 305 \text{ K}$ and $T_a = 315 \text{ K}$ at $V = 0$. The Polymath program and solution are shown in Table E12-1.1.

Table E12-1.1 Part (a) CO-CURRENT HEAT EXCHANGE

Differential equations

$$1 \quad d(T_a)/d(V) = U_a \cdot (T - T_a)/m/C_{pc}$$

$$2 \quad d(X)/d(V) = -r_a/Fa_0$$

$$3 \quad d(T)/d(V) = (Q_g - Q_r)/(C_{po} \cdot Fa_0)$$

Explicit equations

$$1 \quad C_{pc} = 28$$

$$2 \quad m = 500$$

$$3 \quad U_a = 5000$$

$$4 \quad \Delta H = -34500$$

$$5 \quad Q_r = U_a \cdot (T - T_a)$$

$$6 \quad Ca_0 = 1.86$$

$$7 \quad Fa_0 = 0.9 \cdot 163 \cdot 1$$

$$8 \quad K_c = 3.03 \cdot \exp((\Delta H/8.314) \cdot ((T-333)/(T \cdot 333)))$$

$$9 \quad k = 31.1 \cdot \exp((7906) \cdot (T-360)/(T \cdot 360))$$

$$10 \quad r_a = -k \cdot Ca_0 \cdot (1 - (1 + 1/K_c) \cdot X)$$

$$11 \quad X_e = K_c/(1 + K_c)$$

$$12 \quad Q_g = r_a \cdot \Delta H$$

$$13 \quad C_{po} = 159$$

$$14 \quad \text{rate} = -r_a$$

Calculated values of DEQ variables

--

	Variable	Initial value	Final value
1	Ca0	1.86	1.86
2	Cpc	28.	28.
3	Cpo	159.	159.
4	deltaH	-3.45E+04	-3.45E+04
5	Fa0	14.67	14.67
6	k	0.5927441	6.80861
7	Kc	9.512006	2.641246
8	m	500.	500.
9	Qg	3.804E+04	4077.238
10	Qr	-5.0E+04	5076.445
11	ra	-1.102504	-0.1181808
12	rate	1.102504	0.1181808
13	T	305.	336.7102
14	Ta	315.	335.6949
15	Ua	5000.	5000.
16	V	0	5.
17	X	0	0.7185996
18	Xe	0.9048707	0.7253687



Figure E12-1.1 shows the profiles for the reactor temperature, T , the coolant temperature, T_a , the conversion, X , the equilibrium conversion, X_e , and the reaction rate, $-r_A$. Note that at the entrance to the reactor the reactor temperature T is below the coolant temperature, but as reacting mixture moves into and through the reactor the mixture heats up and T becomes greater than T_a . When you load the Polymath, Python, or Wolfram Living Example Problem (LEP) code on your computer, one of the things you will want to explore is the value of the ambient

temperature, T_a , or the entering temperature, T_0 , below which the reaction might never take off or “ignite.”

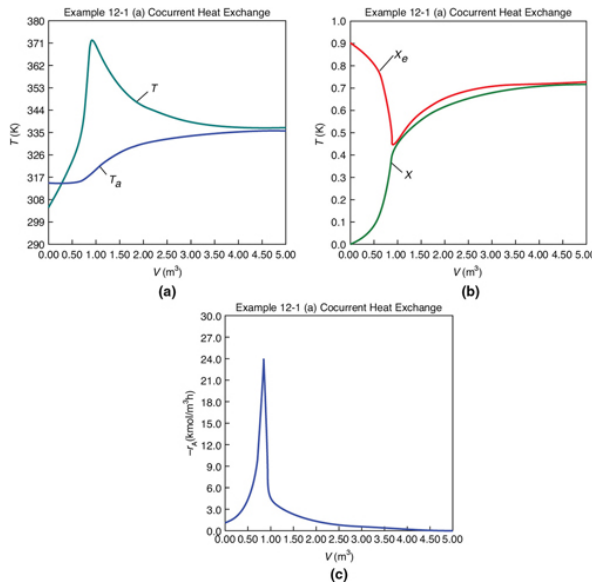


Figure E12-1.1 Profiles down the reactor for co-current heat exchange (a) temperature, (b) conversion, (c) reaction rate.

Analysis: Part (a) Co-Current Exchange: We note that reactor temperature goes through a maximum. Near the reactor entrance, the reactant concentrations are high and therefore the reaction rate is high (cf. Figure E12-1.1(a)) and $Q_g > Q_r$. Consequently, the temperature and conversion increase with increasing reactor volume while X_e decreases because of the increasing temperature. Eventually, X and X_e come close together ($V = 0.95 \text{ m}^3$) and the rate becomes very small as the reaction approaches equilibrium. At this point, the reactant conversion X cannot increase unless X_e increases. We also note that when the ambient heat-exchanger temperature, T_a , and the reactor temperature, T , are essentially equal, there is no longer a temperature driving force to cool the reactor. Consequently, the temperature does not change farther down the reactor, nor does the equilibrium conversion, which is only a function of temperature.

Part (b) Countercurrent Heat Exchange

For countercurrent flow, we only need to make two changes in the program. First, multiply the right-hand

side of Equation (E12-1.6) by minus one to obtain

$$\frac{dT_a}{dV} = \frac{U_a(T-T_a)}{\dot{m}_C C_{PC}} \quad (\text{E12-1.7})$$

Next, we guess T_a at $V = 0$ and see whether it matches T_{a0} at $V = 5 \text{ m}^3$. If it doesn't, we guess again. In this example, we will guess $T_a(V = 0) = 340.3 \text{ K}$ and see whether $T_a = T_{a0} = 315 \text{ K}$ at $V = 5 \text{ m}^3$.

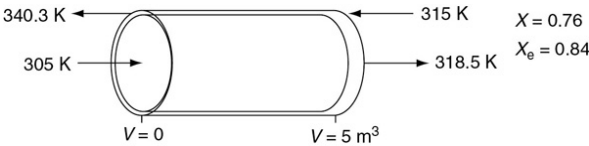


TABLE E12-1.2 PART (b) COUNTERCURRENT HEAT EXCHANGE

Differential equations

1 $d(T_a)/d(V) = -U_a(T-T_a)/m/C_{pc}$

2 $d(X)/d(V) = -r_a/Fa_0$

3 $d(T)/d(V) = (Q_g-Q_r)/C_{po}*Fa_0$

The explicit equations (1)–(14) are the same as in Table E12-1.1 on page 605.

Calculated values of DEQ variables

	Variable	Initial value	Final value
9	Qg	3.804E+04	1.086E+04
10	Qr	-1.765E+05	1.691E+04
11	ra	-1.102504	-0.3146597
12	rate	1.102504	0.3146597
13	T	305.	318.359
14	Ta	340.3	314.9774
15	Ua	5000.	5000.
16	V	0	5.
17	X	0	0.762033
18	Xe	0.9048707	0.8431224

Guess of
 $T_a = 340.3 \text{ K}$
(@ $V = 0$)
← Matches
 $T_{a0} = 315 \text{ K}$

Good guess!



At $V = 0$, we guessed an entering coolant temperature of 340.3 K and found that at $V = V_f$, the calculation showed that it matched the emerging coolant temperature $T_{a0} = 315$ K!! (Was that a lucky guess or what?!) The variable profiles are shown in Figure E12-1.2.

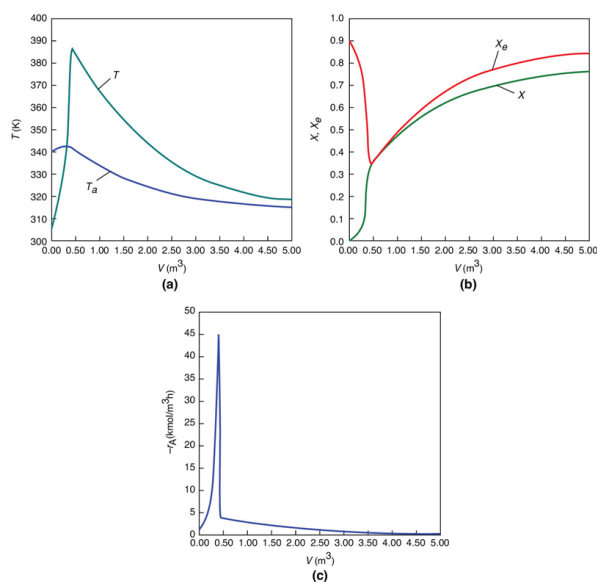


Figure E12-1.2 Profiles down the reactor for countercurrent heat exchange (a) temperature, (b) conversion, (c) reaction rate.

We observe that at $V = 0.5 \text{ m}^3$, $X = 0.36$ and the rate, $-r_A$, drops to a low value as X approaches X_e . Because X can never be greater than X_e the reaction will not proceed further unless X_e is increased. In this case, the reactor is cooled, causing the temperature to decrease and resulting in an increase in the equilibrium conversion beyond a reactor volume of $V = 0.5 \text{ m}^3$.

Analysis: Part (b) Countercurrent Exchange: We note that near the entrance to the reactor, the coolant temperature is above the reactant entrance temperature. However, as we move down the reactor, the reaction generates “heat” and the reactor temperature rises

above the coolant temperature. We note that X_e reaches a minimum (corresponding to the reactor temperature maximum) near the entrance to the reactor. At this point ($V = 0.5 \text{ m}^3$), X cannot increase above X_e . As we move down the reactor, the reactants are cooled and the reactor temperature decreases allowing X and X_e to increase. A higher exit conversion, X , and equilibrium conversion, X_e , are achieved in the countercurrent heat-exchange system than for the co-current system.

Part (c) Constant T_a

For constant T_a , use the Polymath program in part (a), but multiply the right side of Equation (E12-1.6) by zero in the program, that is,

$$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}_C C_{pC}} * 0 \quad (\text{E12-1.8})$$

TABLE E12-1.3 PART (c) CONSTANT T_a

Differential equations		Calculated values of DEQ variables	
1	$d(T_a)/d(V) = Ua(T - T_a)/(\dot{m}_C C_{pC}) * 0$	Variable	Initial value Final value
2	$d(X)/d(V) = -r_a/Fa_0$	9	Qg 3.804E+04 1.052E+04
3	$d(T)/d(V) = (Qg - Qr)/(C_{p0} Fa_0)$	10	Qr -5.0E+04 1.237E+04
The explicit equations (1)–(14) are the same as in Table E12-1.1 on page 605.		11	ra -1.102504 -0.3048421
		12	rate 1.102504 0.3048421
		13	T 305. 317.4737
		14	Ta 315. 315.
		15	Ua 5000. 5000.
		16	V 0 5.
		17	X 0 0.7632038
		18	Xe 0.9048707 0.8478702

The initial and final values are shown in the Polymath report and the variable profiles are shown in Figure E12-1.3.

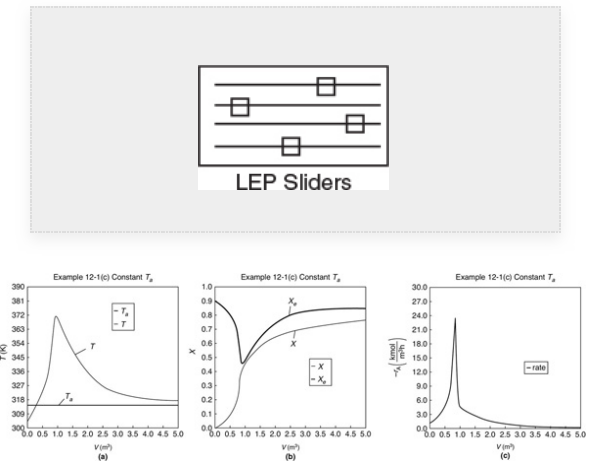


Figure E12-1.3 Profiles down the reactor for constant heat-exchange fluid temperature T_a ; (a) temperature, (b) conversion, (c) reaction rate.

We note that for the parameter values chosen, the profiles for T , X , X_e , and $-r_A$ are similar to those for countercurrent flow. For example, as X and X_e become close to each other at $V = 1.0 \text{ m}^3$, but beyond that point X_e increases because the reactor temperature decreases.

Analysis: Part (c) Constant T_a : When the coolant flow rate is sufficiently large, the coolant temperature, T_a , will be essentially constant. If the reactor volume is sufficiently large, the reactor temperature will eventually reach the coolant temperature, as is the case here. At this exit temperature, which is the lowest achieved in this example (i.e., Part (c)), the equilibrium conversion, X_e , is the largest of the four cases studied in this example.

Part (d) Adiabatic Operation

In Example 11-3, we solved for the temperature as a function of conversion and then used that relationship to calculate k and K_C . An easier way is to solve the general or base case of a heat exchanger for co-current flow and write the corresponding Poly-math program. Next, use Polymath (part (a)), but multiply the parameter Ua by zero, that is,

$$Ua = 5,000 * 0$$

and run the simulation again.

$$\frac{dT}{dV} = \frac{Q_g}{F_{A0} C_{P0}} \text{ Adiabatic}$$

TABLE E12-1.4 PART (d) ADIABATIC OPERATION

Differential equations

$$1 \quad d(T_a)/d(V) = Ua*(T - T_a)/(m*C_{pc})$$

$$2 \quad d(X)/d(V) = -r_a/Fa0$$

3 $d(T)/d(V) = (Q_g - Q_r)/(C_{po} \cdot F_{a0})$

Explicit equations

1 $C_{pc} = 28$

2 $m = 500$

3 $U_a = 5000 \cdot 0$

4 $\Delta H = -34500$

5 $Q_r = U_a \cdot (T - T_a)$

6 $Ca_0 = 1.86$

7 $F_{a0} = 0.9 \cdot 163 \cdot .1$

8 $K_c = 3.03 \cdot \exp((\Delta H/8.314) \cdot ((T-333)/(T \cdot 333)))$

9 $k = 31.1 \cdot \exp((7906) \cdot (T-360)/(T \cdot 360))$

10 $r_a = -k \cdot Ca_0 \cdot (1 - (1 + 1/K_c) \cdot X)$

11 $X_e = K_c/(1 + K_c)$

12 $Q_g = r_a \cdot \Delta H$

13 $C_{po} = 159$

14 $rate = -r_a$

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	Ca0	1.86	1.86
2	Cpc	28.	28.
3	Cpo	159.	159.
4	deltaH	-3.45E+04	-3.45E+04
5	Fa0	14.67	14.67
6	k	0.5927441	124.2488

7	Kc	9.512006	0.5752071
8	m	500.	500.
9	Qg	3.804E+04	-0.4109228
10	Qr	0	0
11	ra	-1.102504	1.191E-05
12	rate	1.102504	-1.191E-05
13	T	305.	384.2335
14	Ta	315.	315.
15	Ua	0	0
16	V	0	5.
17	X	0	0.3651629
18	Xe	0.9048707	0.3651628

The initial and exit conditions are shown in the Polymath report, while the profiles of T , X , X_e , and $-r_A$ are shown in Figure E12-1.4.

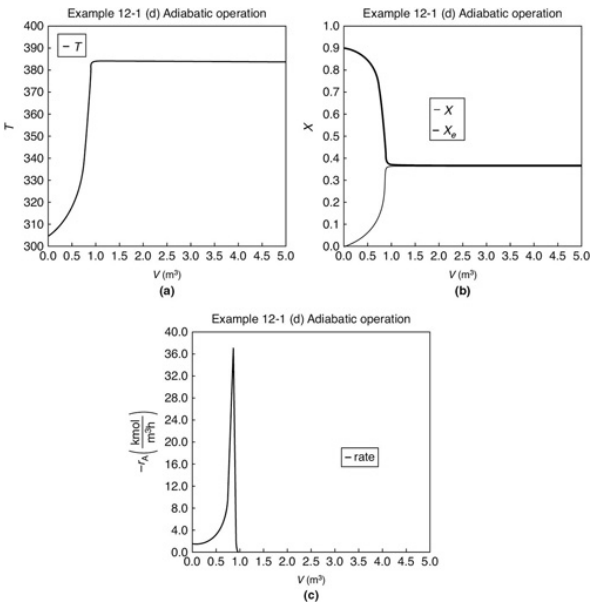
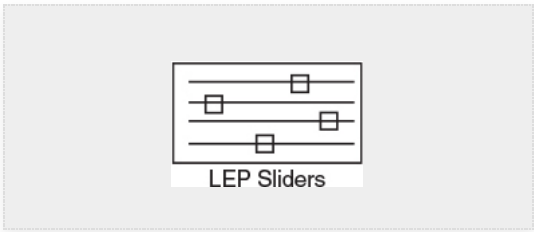


Figure E12-1.4 Profiles down the reactor for *adiabatic reactor*; **(a)** temperature, **(b)** conversion, **(c)** reaction rate.

Analysis: Part (d) Adiabatic Operation: Because there is no cooling, the temperature of this exothermic reaction will continue to increase down the reactor until equilibrium is reached, $X = X_e = 0.365$ at $T = 384$ K, which is the *adiabatic equilibrium temperature*. The profiles for X and X_e are shown in [Figure E12-1.4\(b\)](#) where one observes that the adiabatic equilibrium conversion X_e decreases down the reactor because of the increasing temperature until it becomes equal to the reactor conversion (i.e., $X \equiv X_e$), which occurs at circa 0.9 m^3 . There is no change in temperature, X or X_e , after this point because the reaction rate is virtually zero and thus the remaining reactor volume serves no purpose.

Finally, [Figure E12-1.4\(c\)](#) shows $-r_A$ increases as we move down the reactor as the temperature increases, reaching a maximum and then decreasing until X and X_e approach each other and the rate becomes virtually zero.

Overall Analysis: This is an extremely important example, as we applied our CRE PFR algorithm with heat exchange to a reversible exothermic reaction. We analyzed four types of heat-exchanger operations. We see that the countercurrent exchanger and the constant T_a cases give the highest conversion and adiabatic operation gives the lowest conversion.

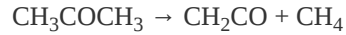
12.3.2 Applying the Algorithm to an Endothermic Reaction

In [Example 12-1](#) we studied the four different types of heat exchanger on an exothermic reaction. In this section we carry out the same study on an *endothermic reaction*.

Example 12-2 Production of Acetic Anhydride

Jeffreys, in a treatment of the design of an acetic anhydride manufacturing facility, states that one of the key steps is the endothermic vapor-phase cracking of acetone to ketene and methane is²

² G. V. Jeffreys, *A Problem in Chemical Engineering Design: The Manufacture of Acetic Anhydride*, 2nd ed. London: Institution of Chemical Engineers.



The article further states that this reaction is first-order with respect to acetone and that the specific reaction rate is given by

$$\ln k = 34.34 - \frac{34222}{T} \quad (\text{E12-2.1})$$

where k is in reciprocal seconds and T is in Kelvin. It is desired to feed 7850 kg of acetone per hour to a tubular reactor. The reactor consists of a bank of 1000 one-inch, schedule-40 tubes. We shall consider four cases of heat-exchanger operation. The inlet temperature and pressure are the same for all cases at 1035 K and 162 kPa (1.6 atm) and the entering heating-fluid temperature available is 1250 K. The heat-exchange fluid has a flow rate, \dot{m}_c , of 0.111 mol/s, with a heat capacity of 34.5 J/mol·K.

A bank of 1000 one-inch, schedule-40 tubes, 1.79 m in length corresponds to 1.0 m³ (0.001 m³/tube = 1.0 dm³/tube) and gives 20% conversion. Ketene is unstable and tends to explode, which is a good reason to keep the conversion low. However, the pipe material and schedule size should be checked to learn whether they are suitable for these temperatures and pressures. In addition, the final design and operating conditions need to be cleared by the safety committee before operation can begin. Also check the Web site, Process Safety Across the Chemical Engineering Curriculum (<http://umich.edu/~safeche/index.html>).

Case 1 The reactor is operated adiabatically.

Case 2 Constant heat-exchange fluid temperature $T_a = 1250$ K

Case 3 Co-current heat exchange with $T_{a0} = 1250$ K

Case 4 Countercurrent heat exchange with $T_{a0} = 1250$ K

Additional information:

CH_3COCH_3 (A): $H_A^\circ(T_R) = -216.67$ kJ/mol, $C_{p_A} = 163$ J/mol · K

CH_2CO (B): $H_B^\circ(T_R) = -61.09$ kJ/mol, $C_{p_B} = 83$ J/mol · K

CH_4 (C): $H_C^\circ(T_R) = -74.81$ kJ/mol, $C_{p_C} = 71$ J/mol · K

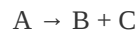
N_2 (I): $C_{p_I} = 28.1$ J/mol · K

$$U = 110 \text{ J/S} \cdot \text{m}^2 \cdot \text{K}$$

The other parameters are given in [Table E12-2.1](#).

Solution

Let A = CH_3COCH_3 , B = CH_2CO , and C = CH_4 .
Rewriting the reaction symbolically gives us



Gas-phase endothermic reaction examples:

1. Adiabatic
2. Heat exchange T_a is constant
3. Co-current heat exchange with variable T_a
4. Countercurrent exchange with variable T_a

Algorithm for a PFR with Heat Effects

1. Mole Balance:

$$\frac{dX}{dV} = \frac{r_A}{F_{A0}} \quad (\text{E12-2.2})$$

2. Rate Law:

$$-r_A = kC_A \quad (\text{E12-2.3})$$

Rearranging ([E12-2.1](#))

$$k = 8.2 \times 10^{14} \exp \left[-\frac{34222}{T} \right] = 3.58 \exp \left[34222 \left[\frac{1}{1035} - \frac{1}{T} \right] \right] \quad (\text{E12-2.4})$$

3. Stoichiometry (gas-phase reaction with no pressure drop):

$$C_A = \frac{C_{A0}(1-X)T_0}{(1+\epsilon X)T} \quad (\text{E12-2.5})$$

$$\epsilon = y_{A0}\delta = 1(1+1-1) = 1$$

4. Combining yields

$$-r_A = \frac{kC_{A0}(1-X)}{1+X} \frac{T_0}{T} \quad (\text{E12-2.5})$$

Before combining Equations (E12-2.2) and (E12-2.6), it is first necessary to use the energy balance to determine T as a function of X .

5. Energy Balance:

1. Reactor balance

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (r_A)[\Delta H_{Rx} + \Delta C_P(T - T_R)]}{F_{A0}(\sum \Theta_i C_{Pi} + X\Delta C_P)} \quad (\text{E12-2.7})$$

2. Heat Exchanger. We will use the heat-exchange fluid balance for co-current flow as our *base case*. We will then show how we can very easily modify our ODE solver program (e.g., Polymath) to solve for the other cases by simply multiplying the appropriate line in the code by either zero or minus one.

For *co-current flow*:

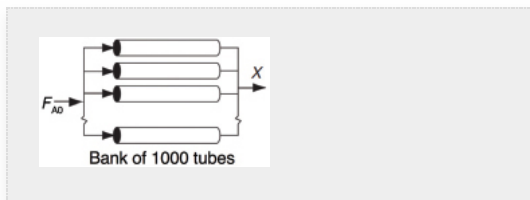
$$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{mC_{Pc}} \quad (\text{E12-2.8})$$

6. Calculation of Mole Balance Parameters on a Per Tube Basis:

$$F_{A0} = \frac{7850 \text{ kg/h}}{58 \text{ kg/kmol}} \times \frac{1}{1000 \text{ Tubes}} = 0.135 \text{ kmol/h} = 0.0376 \text{ mol/s}$$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{162 \text{ b kPa}}{8.31 \frac{\text{kPa}\cdot\text{m}^3}{\text{kmol}\cdot\text{K}} (1035 \text{ K})} = 0.0188 \frac{\text{kmol}}{\text{m}^3} = 18.8 \text{ mol/m}^3$$

$$v_0 = \frac{F_{A0}}{C_{A0}} = \frac{0.0376}{0.0188} = 2.0 \text{ dm}^3/\text{s}, \quad V = \frac{1 \text{ m}^3}{1000 \text{ tubes}} = \frac{0.001 \text{ m}^3}{\text{tube}} = \frac{1.0 \text{ dm}^3}{\text{tube}}$$



7. Calculation of Energy Balance Parameters:

Thermodynamics:

1. $\Delta_{\text{Rx}}^{\circ}(T_R)$: At 298 K, using the standard heats of formation

$$\begin{aligned}\Delta H_{\text{Rx}}^{\circ}(T_R) &= H_B^{\circ}(T_R) + H_C^{\circ}(T_R) - H_A^{\circ}(T_R) \\ &= (-61.09) + (-74.81) - (-216.67) \text{ kJ/mol} \\ &= 80.77 \text{ kJ/mol}\end{aligned}$$

2. ΔC_p : Using the mean heat capacities

$$\Delta C_p = C_{pB} + C_{pC} - C_{pA} = (83 + 71 - 163) \text{ J/mol} \cdot \text{K}$$

$$\Delta C_p = -9 \text{ J/mol} \cdot \text{K}$$

$$\text{Sum } C_{P_i} \Theta_i : \Theta_i C_{P_i} = C_{P_A} + \Theta_I C_{P_I} = 163 + 28.1 \Theta_I, \left(\frac{\text{J}}{\text{mol} \cdot \text{K}} \right)$$

Use Wolfram or Python to vary Θ_I in the LEP.

Heat Exchange:

Energy balance. The heat-transfer area per unit volume of pipe is

$$a = \frac{\pi D L}{(\pi D^2/4)L} = \frac{4}{D} = \frac{4}{0.0266 \text{ m}} = 150 \text{ m}^{-1}$$

$$U = 110 \text{ J/m}^2 \cdot \text{s} \cdot \text{K}$$

Combining the overall heat transfer coefficient with the area yields

$$Ua = 16500 \text{ J/m}^3 \cdot \text{s} \cdot \text{K}$$

TABLE E12-2.1 SUMMARY OF PARAMETER VALUES

Parameter Values		
$\Delta H_{\text{Rx}}^{\circ}(T_R) = 80.77 \text{ kJ/mol}$	$C_{P_I} = 28.1 \frac{\text{J}}{\text{mol} \cdot \text{K}}$	$T_0 = 1035 \text{ K}$
$F_{A0} = 0.0376 \text{ mol/s}$	$\Delta C_p = -9 \text{ J/mol} \cdot \text{K}$	$T_R = 298 \text{ K}$
$C_{pA} = 163 \text{ J/mol} \cdot \text{K}$	$C_{A0} = 18.8 \text{ mol/m}^3$	$\dot{m}_C = 0.111 \text{ mol/s}$
$C_{pC_{\text{Cool}}} \equiv C_{pC} = 34.5 \text{ J/mol} \cdot \text{K}$	$Ua = 16500 \text{ J/m}^3 \cdot \text{s} \cdot \text{K}$	$V_f = 0.001 \text{ m}^3$

We will solve for all four cases of heat-exchanger operation for this endothermic reaction example in the same way we did for the exothermic reaction in Example 12-1. That is, we will write the Polymath

equations for the case of co-current heat exchange and use that as the base case. As noted in the **LEP** for this example one should use *Wolfram* or *Python* to explore the simulation. We will then manipulate the different terms in the heat-transfer fluid balance (Equations 12-10 and 12-11) to solve for the other cases. In the four cases that follow we will take $\Theta_1 = 0$, but on the Wolfram and Python LEPs we allow the reader to vary Θ_1 . We will start with the adiabatic case where we multiply the heat transfer coefficient in the base case by zero.

Case 1 Adiabatic

We are going to start with the adiabatic case first to show the dramatic effects of how the reaction dies out as the temperature drops. In fact, we are now going to extend the length of each tube to make the total reactor volume 5 dm^3 in order to observe this effect of a reaction dying out as well as showing the necessity of adding a heat exchanger. For the adiabatic case, we simply multiply the value of Ua in our Polymath program by zero. No other changes are necessary. For the adiabatic case, the answer will be the same whether we use a bank of 1000 reactors, each a 1-dm^3 reactor, or one of 1 m^3 . To illustrate how an endothermic reaction can virtually die out completely, let's extend the single-pipe volume from 1 to 5 dm^3 .

$$Ua = 16500*0$$

The Polymath program is shown in Table E12-2.2. Figure E12-2.1 shows the graphical output.

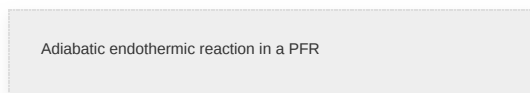


TABLE E12-2.2 POLYMATH PROGRAM AND OUTPUT FOR ADIABATIC OPERATION

Differential equations

$$1 \quad d(X)/d(V) = -r_a/F_{a0}$$

$$2 \quad d(T)/d(V) = (Q_g - Q_r)/(F_{a0}(C_{pa} + X \cdot \Delta C_p))$$

3 $d(T_a)/d(V) = U_a \cdot (T - T_a) / (m \cdot C_{pc})$

Explicit equations

1 $T_o = 1035$

2 $U_a = 16500 \cdot 0$

3 $F_{ao} = .0376$

4 $C_{pa} = 163$

5 $\Delta C_p = -9$

6 $C_{ao} = 18.8$

7 $r_a = -C_{ao} \cdot 3.58 \cdot \exp(34222 \cdot (1/T_o - 1/T)) \cdot (1 - X) \cdot (T_o/T) / (1 + X)$

8 $\Delta H = 80770 + \Delta C_p \cdot (T - 298)$

9 $Q_g = r_a \cdot \Delta H$

10 $Q_r = U_a \cdot (T - T_a)$

11 $m_c = .111$

12 $C_{pc} = 34.5$

13 $rate = -r_a$

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	Cao	1.88	1.88
2	Cpa	163.	163.
3	Cpc	34.5	34.4
4	delCp	-9.	-9.
5	deltaH	7.414E+04	7.414E+04
6	Fao	0.0376	0.0376
7	mc	0.111	0.111
8	Qg	-4.99E+06	-2.79E+04

9	Qr	0	0
10	ra	-67.304	-0.3704982
11	rate	67.304	0.3704982
12	T	1035.	904.8156
13	Ta	1250.	1250.
14	To	1035.	1035.
15	Ua	0	0
16	V	0	0.005
17	X	0	0.2817744

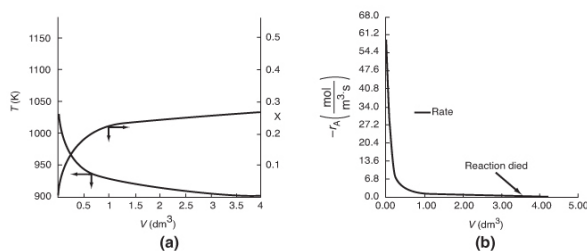
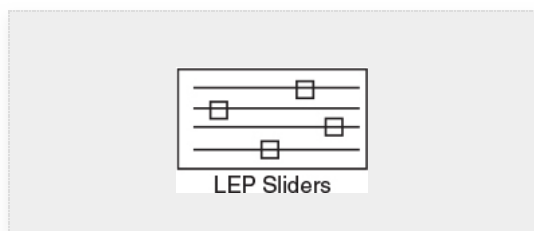
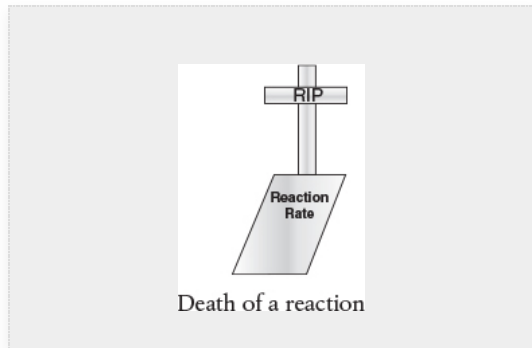


Figure E12-2.1 Adiabatic conversion and temperature **(a)**, and reaction rate **(b)** profiles.

Analysis: Case 1 Adiabatic Operation: As temperature drops, so does k and hence the rate, $-r_A$, drops to an insignificant value. Note that for this adiabatic endothermic reaction, the reaction virtually *dies out* after 3.5 dm^3 , owing to the large drop in temperature, and we observe very little conversion is achieved beyond this point. One way to increase the conversion would be to add a diluent such as nitrogen, which could supply the sensible heat for this endothermic reaction. The Wolfram LEP allows the reader to vary the nitrogen in the feed. However, if too much diluent is added, the concentration, and hence the rate, will be quite low. On the other hand, if too little diluent is added, the temperature will drop and

virtually extinguish the reaction. How much diluent to add is left as an exercise. Figures E12-2.1(a) and (b) give the reactor volume as 5 dm^3 in order to show the reaction “dying out.” However, because the reaction is *nearly* complete near the entrance to the reactor, that is, $-r_A \cong 0$, we are going to study and compare the heat-exchange systems in a 1-dm^3 reactor (0.001 m^3) in each of the next three cases.



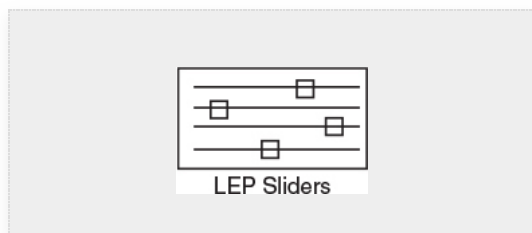
Case 2 Constant heat-exchange fluid temperature, T_a

We make the following changes in our program on line 3 of the base case **(a)**

$$\frac{dT_a}{dV} = \frac{U_a(T - T_a)}{mC_{p_c}} * 0$$

$$Ua = 16500 \text{ J/m}^3/\text{s/K}$$

$$\text{and } V_f = 0.001 \text{ m}^3$$



The Polymath Program is shown in Table E12-2.3 and the profiles for T , X , and $-r_A$ are shown in Figure E12-2.2, parts (a), (b), and (c) respectively.

TABLE E12-2.3 POLYMATH PROGRAM AND OUTPUT FOR CONSTANT T_a

Differential equations

$$1 \quad d(X)/d(V) = -r_a/F_{ao}$$

$$2 \quad d(T)/d(V) = (Q_g - Q_r)/(F_{ao}*(C_{pa} + X*\Delta C_p))$$

$$3 \quad d(T_a)/d(V) = U_a*(T - T_a)/(m_c*C_{pc})*0$$

Explicit equations

$$1 \quad T_o = 1035$$

$$2 \quad U_a = 16500$$

$$3 \quad F_{ao} = .0376$$

$$4 \quad C_{pa} = 163$$

$$5 \quad \Delta C_p = -9$$

$$6 \quad C_{ao} = 18.8$$

$$7 \quad r_a = -C_{ao}*3.58*\exp(34222*(1/T_o - 1/T))*(1-X)*(T_o/T)/(1+X)$$

$$8 \quad \Delta H = 80770 + \Delta C_p*(T - 298)$$

$$9 \quad Q_g = r_a*\Delta H$$

$$10 \quad Q_r = U_a*(T - T_a)$$

$$11 \quad m_c = .111$$

$$12 \quad C_{pc} = 34.5$$

$$13 \quad \text{rate} = -r_a$$

	Variable	Initial value	Final value
1	Cao	1.88	1.88
2	Caa	163.	163.
3	Cpc	34.5	34.5
4	delCp	-9.	-9.
5	deltaH	7.414E+04	7.343E+04
6	Fao	0.0376	0.0376
7	mc	0.111	0.111

8	Qg	-4.99E+06	-1.211E+06
9	Qr	-3.548E+06	-2.242E+06
10	ra	-67.304	-16.48924
11	rate	67.304	16.48924
12	T	1035.	1114.093
13	Ta	1250.	1250.
14	To	1035.	1035.
15	Ua	1.65E+04	1.65E+04
16	V	0	0.001
17	X	0	0.9508067

Endothermic reaction profiles

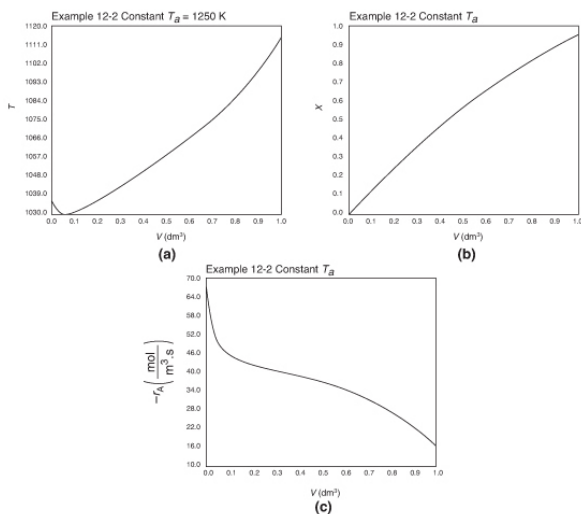


Figure E12-2.2 Profiles for constant heat exchanger fluid temperature, T_a ; **(a)** temperature, **(b)** conversion, **(c)** reaction rate.

Analysis: Case 2 Constant T_a : Just after the reactor entrance, the reaction temperature drops as the sensible heat from the reacting fluid supplies the energy for the endothermic reaction. This temperature decrease in the reactor also causes the rate of reaction to decrease. As we move farther down the reactor, the reaction rate drops further as the reactants are consumed. Beyond V

$= 0.08 \text{ dm}^3$, the heat supplied by the constant T_a heat exchanger becomes greater than that “consumed” by the endothermic reaction and the reactor temperature rises. In the range between $V = 0.2 \text{ dm}^3$ and $V = 0.6 \text{ dm}^3$, the rate decreases slowly owing to the depletion of reactants, which is counteracted, to some extent, by the increase in temperature and hence the rate constant k . Consequently, we are eventually able to achieve an exit conversion of 95%.

Case 3 Co-Current Heat Exchange

The energy balance on a co-current exchanger is

$$\frac{dT_a}{dV} = \frac{Ua(T-T_a)}{\dot{m}C_{P_C}}$$

with $T_{a0} = 1250 \text{ K}$ at $V = 0$.

The Polymath Program is shown in Table E12-2.4 and the variable profiles for T , T_a , X , and $-r_A$ are shown in Figure E12-2.3, parts (a), (b), and (c) respectively. Because the reaction is endothermic, T_a needs to start off at a high temperature at $V = 0$.

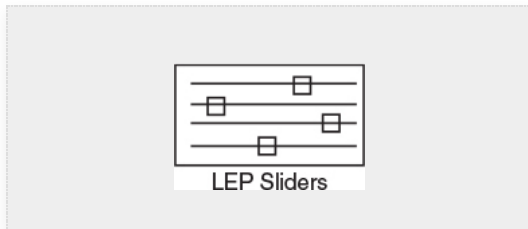


TABLE E12-2.4 POLYMATH PROGRAM AND OUTPUT FOR CO-CURRENT EXCHANGE

Differential equations

1 $d(X)/d(V) = -r_a/F_{a0}$

2 $d(T)/d(V) = (Q_g - Q_r)/(F_{a0}(C_{pa} + X \cdot \Delta C_p))$

3 $d(T_a)/d(V) = Ua(T - T_a)/(mC_{pC})$

Explicit equations

1 $T_0 = 1035$

$$2 \text{ } U_a = 16500$$

$$3 \text{ } F_{ao} = .0376$$

$$4 \text{ } C_{pa} = 163$$

$$5 \text{ } \Delta C_p = -9$$

$$6 \text{ } C_{ao} = 18.8$$

$$7 \text{ } r_a = -C_{ao} \cdot 3.58 \cdot \exp(34222 \cdot (1/T_o - 1/T)) \cdot (1-X) \cdot (T_o/T)/(1+X)$$

$$8 \text{ } \Delta H = 80770 + \Delta C_p \cdot (T - 298)$$

$$9 \text{ } Q_g = r_a \cdot \Delta H$$

$$10 \text{ } Q_r = U_a \cdot (T - T_a)$$

$$11 \text{ } m_c = .111$$

$$12 \text{ } C_{pc} = 34.5$$

$$13 \text{ } \text{rate} = -r_a$$

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	Cao	1.88	1.88
2	Cpa	163.	163.
3	Cpc	34.5	34.5
4	delCp	-9.	-9.
5	deltaH	7.414E+04	7.459E+04
6	Fao	0.0376	0.0376
7	mc	0.111	0.111
8	Qg	-4.99E+06	-3.654E+05
9	Qr	-3.548E+06	-1.881E+05
10	ra	-67.304	-4.899078
11	rate	67.304	4.899078
12	T	1035.	984.8171

13	T _a	1250.	996.215
14	T _o	1035.	1035.
15	U _a	1.65E+04	1.65E+04
16	V	0	0.001
17	X	0	0.456201

Analysis: Case 3 Co-Current Exchange: In co-current heat exchange, we see that the heat-exchanger fluid temperature, T_a , decreases rapidly initially and then continues to decrease along the length of the reactor as it supplies the energy to the heat drawn by the endothermic reaction. Eventually T_a decreases to the point where it approaches T and the rate of heat exchange is small; as a result, the temperature of the reactor, T , continues to decrease, as does the rate, resulting in a small conversion. Because the reactor temperature for co-current exchange is lower than that for *Case 2 constant T_a* , the reaction rate will be lower. As a result, significantly less conversion will be achieved than in the case of constant heat-exchange temperature T_a .

Endothermic reaction profiles

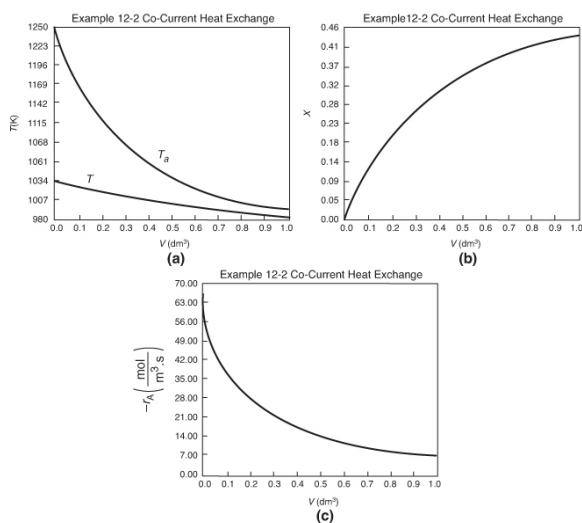
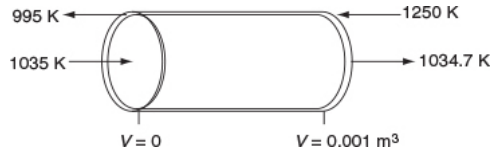


Figure E12-2.3 Profiles down the reactor for an endothermic reaction with co-current heat

exchange; (a) temperature, (b) conversion, and (c) reaction rate.

Case 4 Countercurrent Heat Exchange



For countercurrent exchange, we first multiply the rhs of the co-current heat-exchanger energy balance by -1 , leaving the rest of the Polymath program in Table 12-2.5 the same.

$$\frac{dT_a}{dV} = \frac{U_a(T - T_a)}{\dot{m}_C C_{pC}}$$

Next, **guess** $T_a(V=0) = 995.15$ K to obtain $T_{a0} = 1250$ K at $V = 0.001 \text{ m}^3$. (Don't you believe for a moment 995.15 K was my first guess.) Once this match is obtained as shown in Table E12-2.5, we can report the profiles shown in Figure E12-2.4.

Good guess!

TABLE E12-2.5 POLYMATH PROGRAM AND OUTPUT FOR COUNTERCURRENT EXCHANGE

	Variable	Initial value	Final value
8	Qg	-4.99E+06	-2.357E+06
9	Qr	6.575E+05	-3.556E+06
10	ra	-67.304	-31.79235
11	rate	67.304	31.79235
12	T	1035.	1034.475
13	Ta	995.15	1249.999
14	To	1035.	1035.
15	Ua	1.65E+04	1.65E+04
16	V	0	0.001
17	X	0	0.3512403

{ Guess of $T_{a2} = 995.15$ K
 at $V = 0$
 Matches $T_{a0} = 1250$ K
 At $V_f = 0.001 \text{ m}^3 = 1 \text{ dm}^3$

Differential equations

1. $d(X)/d(V) = -ra/F_{a0}$
2. $d(T)/d(V) = (Qg - Qr)/(F_{a0}(C_{pa} + X \cdot \Delta C_p))$
3. $d(T_a)/d(V) = -U_a(T - T_a)/(m_C C_{pC})$

Explicit equations are the same as Case 3 Co-Current Heat Exchange.

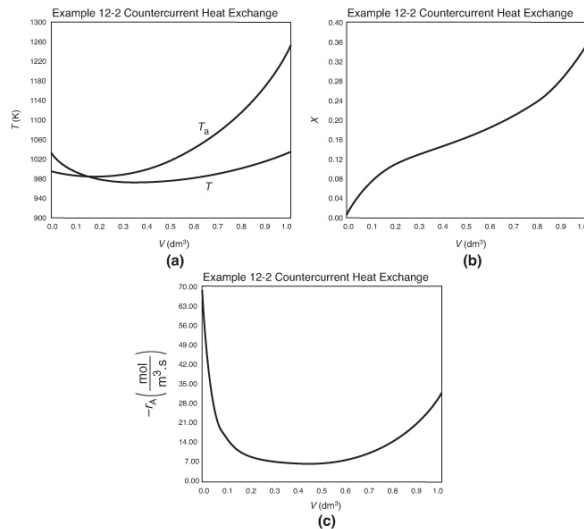
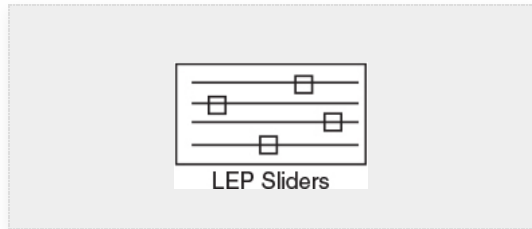


Figure E12-2.4 Profiles down the reactor for countercurrent heat exchange; **(a)** temperature, **(b)** conversion, **(c)** reaction rate.

Endothermic reaction profiles

Analysis: Case 4 Countercurrent Exchange: At the front of the reactor where the reactants enter, that is, $V = 0$, the reaction takes place very rapidly, drawing energy from the sensible heat of the gas and causing the gas temperature to drop because the heat exchanger cannot supply energy at an equal or greater rate to that being drawn by the endothermic reaction. Additional “heat” is lost at the entrance in the case of countercurrent exchange because the temperature of the exchange fluid, T_a , is below the entering reactor temperature, T . One notes there is a minimum in the reaction rate, $-r_A$, profile that is rather flat. In this flat region, the rate is “virtually” constant between $V = 0.2$

dm³ and $V = 0.8 \text{ dm}^3$, because the increase in k caused by the increase in T is balanced by the decrease in rate brought about by the consumption of reactants. Just past the middle of the reactor, the rate begins to increase slowly as the reactants become depleted and the heat exchanger now supplies energy at a rate greater than the reaction draws energy and, as a result, the temperature eventually increases. This lower temperature coupled with the consumption of reactants causes the rate of reaction to be low in the plateau, resulting in a lower conversion than either the co-current or constant T_a heat exchange cases.

Analysis Summary of 4 Cases. The exit temperatures and conversion are shown in the Summary [Table E12-2.6](#).

TABLE E12-2.6 SUMMARY TABLE

Heat Exclusion	X	$T(K)$	$T_a(K)$
Adiabatic	0.28	905	---
Constant T_a	0.95	1114	1250
Co-Current	0.456	985	996
Countercurrent	0.35	1034	995

For this endothermic reaction, the highest conversion is obtained for constant T_a and the lowest conversion is for an adiabatic reaction. These two extremes correspond to the greatest and least amount of heat transfer to the reacting fluid.

AspenTech: [Example 12-2](#) has also been formulated in AspenTech and can be downloaded on your computer directly from the CRE Web site.



12.4 CSTR WITH HEAT EFFECTS

In this section we apply the general energy balance (Equation (11-22)) to a CSTR at steady state. We then present example problems showing how the mole and energy balances are combined to design reactors operating adiabatically and non-adiabatically.

In Chapter 11 the steady-state energy balance was derived as

$$\dot{Q} - \dot{W}_s - F_{A0} \sum \Theta_i C_{p_i} (T - T_{i0}) - [\Delta H_{Rx}^\circ(T_R) + \Delta C_P (T - T_R)] F_{A0} X = 0 \quad (11-28)$$

Recall that \dot{W}_s is the shaft work, that is, the work **done by** a stirrer or mixer in the CSTR **on** the reacting fluid inside the CSTR. Consequently, because the convention that **done by** the system **on** the surroundings is positive, the CSTR stirrer work will be a negative number, for example, $\dot{W}_s = -1,000 \text{ J/S}$. (See Problem P12-6B, a *California Professional Engineers' Exam Problem*.)

Note: In many calculations the CSTR mole balance derived in Chapter 2

$$(F_{A0}X = -r_A V)$$

These are the forms of the steady-state balance we will use.

will be used to replace the term following the brackets in Equation (11-28), that is, $(F_{A0}X)$ will be replaced by $(-r_A V)$ to arrive at Equation (12-12).

Rearranging yields the steady-state energy balance

$$\dot{Q} - \dot{W}_s - F_{A0} \sum \Theta_i C_{p_i} (T - T_{i0}) + (r_A V)(\Delta H_{Rx}) = 0 \quad (12-12)$$

Although the CSTR is well mixed and the temperature is uniform throughout the reaction vessel, these conditions do not mean that the reaction is carried out isothermally. Isothermal operation occurs when the feed temperature is identical to the temperature of the fluid inside the CSTR.

The \dot{Q} Term in the CSTR

12.4.1 Heat Added to the Reactor, \dot{Q}

Figure 12-6 shows the schematics of a CSTR with a heat exchanger. The heat-transfer fluid enters the exchanger at a mass flow rate (e.g., kg/s) at a temperature T_{a1} and leaves at a temperature T_{a2} . The rate of heat transfer *from* the exchanger to the reactor fluid at temperature T is³

³ Information on the overall heat transfer coefficient may be found in J. R. Welty, G. L. Rorrer, and D. G. Foster, *Fundamentals of Momentum Heat and Mass Transfer*, 6th ed. New Jersey: Wiley, 2015, p. 370.

$$\dot{Q} = \frac{UA(T_{a1}-T_{a2})}{\ln[(T-T_{a1})/(T-T_{a2})]} \quad (12-13)$$

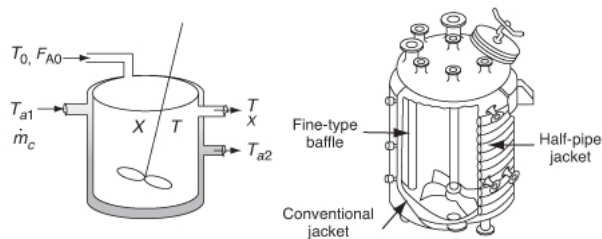


Figure 12-6 CSTR tank reactor with heat exchanger.

The following derivations, based on a coolant (exothermic reaction), apply also to heating mediums (endothermic reaction). As a first approximation, we assume a quasi-steady state operation for the coolant flow and neglect the accumulation term (i.e., $dT_a/dt = 0$). An energy balance on the heat-exchanger fluid entering and leaving the exchanger is

For exothermic reactions ($T > T_{a2} > T_{a1}$)

For endothermic reactions ($T_{a1} > T_{a2} > T$)

Energy balance on heat-exchanger fluid

$$\left[\begin{array}{c} \text{Rate of} \\ \text{energy} \\ \text{in} \\ \text{by flow} \end{array} \right] - \left[\begin{array}{c} \text{Rate of} \\ \text{energy} \\ \text{out} \\ \text{by flow} \end{array} \right] - \left[\begin{array}{c} \text{Rate of} \\ \text{heat transfer} \\ \text{from exchanger} \\ \text{to reactor} \end{array} \right] = 0 \quad (12-14)$$

$$\dot{m}_c C_{P_c} (T_{a1} - T_R) - \dot{m}_c C_{P_c} (T_{a2} - T_R) - \frac{UA(T_{a1}-T_{a2})}{\ln[(T-T_{a1})/(T-T_{a2})]} = 0 \quad (12-15)$$

where C_p is the heat capacity of the heat exchanger fluid and T_R is the reference temperature. Simplifying gives us

$$\dot{Q} = \dot{m}_c C_{P_c} (T_{a1} - T_{a2}) = \frac{UA(T_{a1} - T_{a2})}{\ln[(T - T_{a1})/(T - T_{a2})]} = 0 \quad (12-16)$$

Solving Equation (12-16) for the exit temperature of the heat-exchanger fluid yields

$$T_{a2} = T - (T - T_{a1}) \exp\left(\frac{-UA}{\dot{m}_c C_{P_c}}\right) \quad (12-17)$$

From Equation (12-16)

$$\dot{Q} = \dot{m}_c C_{P_c} (T_{a1} - T_{a2}) \quad (12-18)$$

Substituting for T_{a2} in Equation (12-18), we obtain

$$\dot{Q} = \dot{m}_c C_{P_c} \left\{ (T_{a1} - T) \left[1 - \exp\left(\frac{-UA}{\dot{m}_c C_{P_c}}\right) \right] \right\} \quad (12-19)$$

Heat transfer to a CSTR

For large values of the heat-exchanger fluid flow rate, \dot{m}_c , the exponent will be small and can be expanded in a Taylor series ($e^{-x} = 1 - x + \dots$) where second-order terms are neglected in order to give

$$\dot{Q} = \dot{m}_c C_{P_c} (T_{a1} - T) \left[1 - \left(\frac{UA}{\dot{m}_c C_{P_c}} \right) \right]$$

Then

Valid only for large heat-transfer fluid flow rates!!

$$\dot{Q} = UA (T_a - T) \quad (12-20)$$

where $T_{a1} \cong T_{a2} = T_a$.

With the exception of processes involving highly viscous materials such as in Problem P12-6B, a *California Professional Engineers' Exam Problem*, the work done by the stirrer can usually be neglected. Setting \dot{W}_s equal to zero in Equation (11-27), neglecting ΔC_p , in ΔH_{R_x} substituting for \dot{Q} , and

rearranging, we have the following relationship between conversion and temperature in a CSTR:

$$\frac{UA}{F_{A0}}(T_a - T) - \sum \Theta_i C_{Pi}(T - T_0) - \Delta H_{Rx}^\circ X = 0 \quad (12-21)$$

Solving for X

$$X = \frac{\frac{UA}{F_{A0}}(T - T_a) + \sum \Theta_i C_{Pi}(T - T_0)}{[-\Delta H_{Rx}^\circ(T_R)]} \quad (12-22)$$

Equation (12-22) is coupled with the mole balance equation

$$V = \frac{F_{A0}X}{-r_A(X, T)} \quad (12-23)$$

to design CSTRs.

To help us more easily see the effect of the operating parameters of T , T_0 , and T_a , we collect terms and define three parameters: C_{P0} , κ , and T_c .

We now will further rearrange Equation (12-21) after letting

$$C_{P0} = \sum \Theta_i C_{Pi}$$

then

$$C_{P0} \left(\frac{UA}{F_{A0}C_{P0}} \right) T_a + C_{P0}T_0 - C_{P0} \left(\frac{UA}{F_{A0}C_{P0}} + 1 \right) T - \Delta H_{Rx}^\circ X = 0$$

Let κ and T_c be non-adiabatic parameters defined by

$$\kappa = \frac{UA}{F_{A0}C_{P0}} \quad \text{and} \quad T_c = \frac{\kappa T_a + T_0}{1 + \kappa}$$

Non-adiabatic CSTR heat exchange parameters: κ and T_c

Then

$$-X\Delta H_{Rx}^\circ = C_{P0}(1 + \kappa)(T - T_c) \quad (12-24)$$

The parameters κ and T_c are used to simplify the equations for *non*-adiabatic operation. Solving Equation (12-24) for conversion X

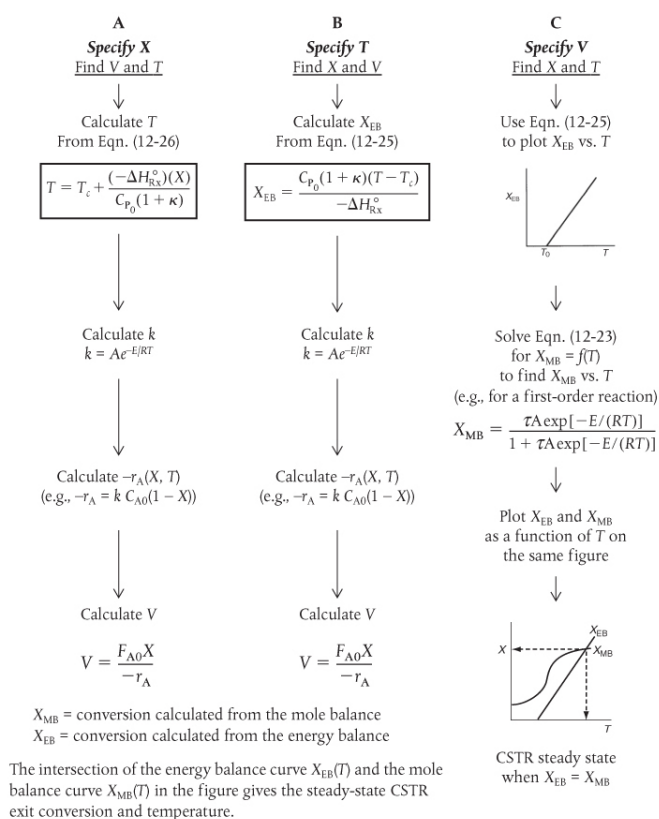
$$X = \frac{C_{P0}(1 + \kappa)(T - T_c)}{-\Delta H_{Rx}^\circ} \quad (12-25)$$

Solving Equation (12-24) for the reactor temperature

$$T = T_c + \frac{(-\Delta H_{Rk}^{\circ})(X)}{C_{P0}(1+k)} \quad (12-26)$$

Table 12-3 shows three ways to specify the design of a CSTR. This procedure for nonisothermal CSTR design will be illustrated by considering a first-order irreversible liquid-phase reaction. To solve CSTR problems of this type, we have three variables X , T , and V and we specify one and then solve for the other two values. The algorithm for working through either cases **A** (X specified), **B** (T specified), or **C** (V specified) is shown in Table 12-3. Its application is illustrated in Example 12-3.

TABLE 12-3 WAYS TO SPECIFY THE SIZING OF A CSTR

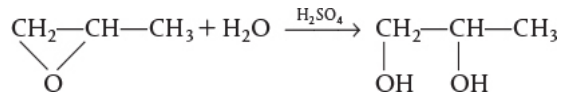


Forms of the energy balance for a CSTR with heat exchange

Production, uses, and economics

Example 12–3 Production of Propylene Glycol in an Adiabatic CSTR

Propylene glycol is produced by the hydrolysis of propylene oxide:



Over 900 million pounds of propylene glycol were produced in 2010 and the selling price was approximately \$0.80 per pound. Propylene glycol makes up about 25% of the major derivatives of propylene oxide. The reaction takes place readily at room temperature when catalyzed by sulfuric acid.

You are the engineer in charge of an adiabatic CSTR producing propylene glycol by this method. Unfortunately, the reactor is beginning to leak, and you must replace it. (You told your boss several times that sulfuric acid was corrosive and that mild steel was a poor material for construction. He wouldn't listen.) There is a nice-looking, bright, shiny overflow CSTR of 300-gal capacity standing idle in Professor Köttlov's storage shed at his mountain vacation home. It is glass-lined, and you would like to use it.

We are going to work this problem in lb_m , s, ft^3 , and lb-moles rather than g, mol, and m^3 in order to give the reader more practice in working in both the English and metric systems. Why?? Many plants still use the English system of units.

You are feeding 2500 lb_m/h (43.04 lb-mol/h) of propylene oxide (P.O.) to the reactor. The feed stream consists of (1) an equivolumetric mixture of propylene oxide (46.62 ft^3/h) and methanol (46.62 ft^3/h), and (2) water containing 0.1 wt % H_2SO_4 . The volumetric flow rate of water is 233.1 ft^3/h , which is 2.5 times the methanol–P.O. volumetric flow rate. The corresponding molar feed rates of methanol and water are 71.87 and 802.8 lb-mol/h , respectively. The water–propylene oxide–methanol mixture undergoes a slight decrease in volume upon mixing (approximately 3%), but you neglect this decrease in your calculations. The

temperature of both feed streams is 58°F prior to mixing, but there is an immediate 17°F temperature rise upon mixing of the two feed streams caused by the heat of mixing. The entering temperature of all feed streams is thus taken to be 75°F (Figure E12-3.1).

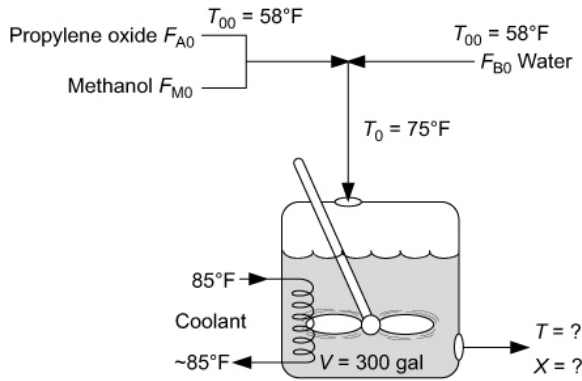


Figure E12-3.1 Propylene glycol manufacture in a CSTR.

The Furusawa Engineering Team in Japan state that under conditions similar to those at which you are operating, the reaction is apparent first-order in propylene oxide concentration and apparent zero-order in excess of water with the specific reaction rate⁴

⁴ T. Furusawa, H. Nishimura, and T. Miyauchi, *J. Chem. Eng. Jpn.*, 2, 95.

$$k = Ae^{-E/RT} = 16.96 \times 10^{12} (e^{-32400/RT}) \text{ h}^{-1}$$

The units of E are Btu/lb-mol and T is in °R.

There is an important constraint on your operation. Propylene oxide is a rather low-boiling-point substance. With the mixture you are using, the company's safety team feels that you cannot exceed an operating temperature of 125°F, or you will lose too much propylene oxide by vaporization through the vent system.

1. Can you use the idle CSTR as a replacement for the leaking one if it will be operated adiabatically?
2. If so, what will be the expected conversion of propylene oxide to glycol?

Solution

(All data used in this problem were obtained from the *CRC Handbook of Chemistry and Physics* unless otherwise noted.) Let the reaction be represented by



where

A is propylene oxide ($C_{P_A} = 35 \text{ Btu/lb-mol} \cdot ^\circ\text{F}$)⁵

⁵ C_{P_A} and C_{P_C} are estimated from the observation that the great majority of low-molecular-weight oxygen-containing organic liquids have a mass heat capacity of $0.6 \text{ cal/g} \cdot ^\circ\text{C} \pm 15\%$.

B is water ($C_{P_B} = 18 \text{ Btu/lb-mol} \cdot ^\circ\text{F}$)

C is propylene glycol ($C_{P_C} = 46 \text{ Btu/lb-mol} \cdot ^\circ\text{F}$)

M is methanol ($C_{P_M} = 19.5 \text{ Btu/lb-mol} \cdot ^\circ\text{F}$)

In this problem, neither the exit conversion nor the temperature of the adiabatic reactor is given. By application of the mole and energy balances, we can solve two equations with two unknowns (X and T), as shown on the right-hand pathway in [Table 12-3](#). Solving these coupled equations, we determine the exit conversion and temperature for the glass-lined reactor to see whether it can be used to replace the present reactor.

1. Mole Balance and Design Equation:

$$F_{A0} - F_A + r_A V = 0$$

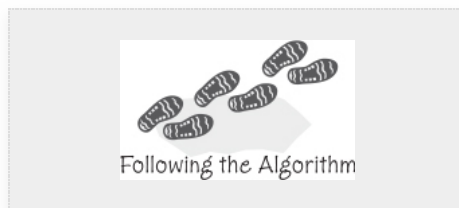
The design equation in terms of X is

$$V = \frac{F_{A0} X}{-r_A} \quad (\text{E12-3.1})$$

2. Rate Law:

$$-r_A = k C_A \quad (\text{E12-3.2})$$

$$k = 16.96 \cdot 10^{12} \exp[-32400/R/T] \text{ h}^{-1}$$



3. Stoichiometry (liquid phase, $v = v_0$):

$$C_A = C_{A0} (1 - X) \quad (\text{E12-3.3})$$

4. Combining yields

$$V = \frac{F_{A0} X}{k C_{A0} (1 - X)} = \frac{v_0 X}{k (1 - X)} \quad (\text{E12-3.4})$$

Solving for X as a function of T and recalling that $\tau = V/v_0$ gives

$$X_{\text{MB}} = \frac{\tau k}{1 + \tau k} = \frac{\tau A_e^{-E/RT}}{1 + \tau A_e^{-E/RT}} \quad (\text{E12-3.5})$$

This equation relates temperature and conversion through the **mole balance**.

Two equations, two unknowns

5. The energy balance for this adiabatic reaction in which there is negligible energy input provided by the stirrer is

$$X_{\text{EB}} = \frac{\sum \Theta_i C_{Pi} (T - T_0)}{-[\Delta H_{Rx}(T_R) + \Delta C_p (T - T_R)]} \quad (\text{E12-3.6})$$

This equation relates X and T through the energy balance. We see that two equations, Equations (E12-3.5) and (E12-3.6), and two unknowns, X and T , must be solved to find the conversion where $X_{\text{EB}} = X_{\text{MB}} = X$.

6. Calculations:

Rather than putting all those numbers in the mole and heat balance equations yourself, you can outsource this task, for a small fee, to Sven Köttlov Consulting Company, located on the third floor of the downtown Market Center Building (called the “MCB”) in Riça, Jofostan. The results of our outsourcing are given below.

1. *Evaluate the mole balance terms* (C_{A0} , Θ_i , τ): The total liquid volumetric flow rate entering the reactor is

$$\begin{aligned} v_0 &= v_{A0} + v_{\text{MD}} + v_{\text{B0}} \\ &= 46.62 + 46.62 + 233.1 = 326.3 \text{ ft}^3/\text{h} \quad (\text{E12-3.7}) \\ V &= 300 \text{ gal} = 40.1 \text{ ft}^3 \end{aligned}$$

$$\tau = \frac{V}{v_0} = \frac{40.1 \text{ ft}^3}{326.3 \text{ ft}^3/\text{h}} = 0.123 \text{ h} \quad (\text{E12-3.8})$$

$$\begin{aligned} C_{A0} &= \frac{F_{A0}}{v_0} = \frac{43.0 \text{ lb-mol/h}}{326.3 \text{ ft}^3/\text{h}} \\ &= 0.132 \text{ lb-mol/ft}^3 \end{aligned} \quad (\text{E12-3.9})$$

I know these are tedious calculations, but someone's gotta know how to do them.



$$\text{For methanol: } \Theta_M = \frac{F_{M0}}{F_{A0}} = \frac{71.87 \text{ lb-mol/h}}{43.0 \text{ lb-mol/h}} = 1.67$$

$$\text{For water: } \Theta_M = \frac{F_{B0}}{F_{A0}} = \frac{802.8 \text{ lb-mol/h}}{43.0 \text{ lb-mol/h}} = 18.65$$

The conversion calculated from the mole balance, X_{MB} , is found from Equation (E12-3.5)

$$X_{MB} = \frac{(16.96 \times 10^{12} \text{ h}^{-1})(0.1229 \text{ h}) \exp(-32400/1.987T)}{1 + (16.96 \times 10^{12} \text{ h}^{-1})(0.1229 \text{ h}) \exp(-32400/1.987T)}$$

Plot X_{MB} as a function of temperature.

$$X_{MB} = \frac{(2.084 \times 10^{12}) \exp(-16306/T)}{1 + (2.084 \times 10^{12}) \exp(-16306/T)}, T \text{ is in } ^\circ R \quad (\text{E12-3.10})$$

2. Evaluating the energy balance terms

(1) Heat of reaction at temperature T

$$\Delta H_{Rx}(T) = \Delta H_{Rx}^\circ(T_R) + \Delta C_P(T - T_R) \quad (11-26)$$

$$\Delta C_P = C_{P_C} - C_{P_C} - C_{P_A} = 46 - 18 - 35 = -7 \text{ Btu/lb-mol/}^\circ F$$

$$\Delta H_{Rx} = -36400 - 7(T - T_R) \quad (\text{E12-3.11})$$

(2) Heat capacity term

$$\begin{aligned} \Sigma \Theta_i C_{P_i} &= C_{P_A} + \Theta_B C_{P_B} + \Theta_M C_{P_M} \\ &= 35 + (18.65)(18) + (1.67)(19.5) \quad (\text{E12-3.12}) \\ &= 403.3 \text{ Btu/lb-mol} \cdot ^\circ F \end{aligned}$$

$$\begin{aligned} T_0 &= T_{00} + \Delta T_{\text{mix}} = 58^\circ F + 17^\circ F = 75^\circ F \\ &= 535^\circ R \end{aligned} \quad (\text{E12-3.13})$$

$$T_R = 68^\circ F = 528^\circ R$$

The conversion calculated from the energy balance, X_{EB} , for an adiabatic reaction is given by Equation (11-29)

$$X_{EB} = \frac{\Sigma \Theta_i C_{P_i} (T - T_{i0})}{\Delta H_{Rx}^\circ(T_R) + \Delta C_P (T - T_R)} \quad (11-29)$$

Substituting all the known quantities into the energy balance gives us

$$X_{EB} = \frac{(403.3 \text{ Btu/lb-mol} \cdot ^\circ F)(T - 535)^\circ F}{-[-36400 - 7(T - 528)] \text{ Btu/lb-mol}}$$

$$X_{EB} = \frac{403.3(T - 535)}{36400 + 7(T - 528)} \quad (\text{E12-3.14})$$

Adiabatic CSTR

7. **Solving:** There are a number of different ways to solve these two simultaneous algebraic equations (E12-3.10) and (E12-3.14). The easiest way is to use the Polymath nonlinear equation solver. However, to give insight into the functional relationship between X and T for the mole and energy balances, we shall obtain a graphical solution. Here, X is plotted as a function of T for both the mole (X_{MB}) and energy (X_{EB}) balances, and the intersection of the two curves gives the solution where both the mole and energy balance solutions are satisfied, that is, $X_{EB} = X_{MB}$. In addition, by plotting these two curves we can learn whether there is more than one intersection (i.e., multiple steady states) for which both the energy balance and mole balance are satisfied. If numerical root-finding techniques were used to solve for X and T , it would be quite possible that you would find only one root when there is actually more than one. If Polymath were used, you could learn whether multiple roots exist by changing your initial guesses in the nonlinear equation solver. We shall discuss multiple steady states further in Section 12-5. We now choose T and then calculate X_{MB} and X_{EB} (Table E12-3.1). The calculations for X_{MB} and X_{EB} are plotted in Figure E12-3.2. The virtually straight line corresponds to the energy balance, Equation (E12-3.14), and the curved line corresponds to the mole balance, Equation (E12-3.10). We observe from this plot that the only intersection

TABLE E12-3.1 CALCULATIONS OF X_{EB} AND X_{MB} AS A FUNCTION OF T

T (°R)	X_{MB} (Eq. (E12-3.10))	X_{EB} (Eq. (E12-3.14))
535	0.108	0.000
550	0.217	0.166
565	0.379	0.330
575	0.500	0.440
585	0.620	0.550
595	0.723	0.656
605	0.800	0.764
615	0.860	0.872
625	0.900	0.980

The reactor cannot be used because it will exceed the specified maximum temperature of 585°R.

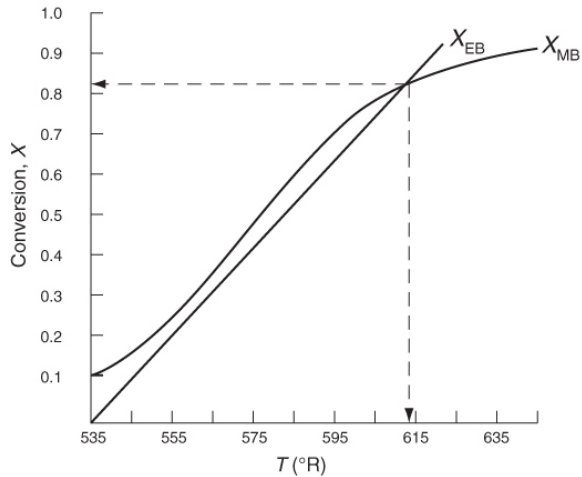
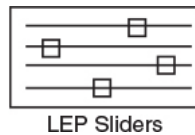


Figure E12-3.2 The conversions X_{EB} and X_{MB} as a function of temperature.



point is at 83% conversion and 613°R. At this point, both the energy balance and mole balance are satisfied. Because the temperature must remain below 125°F (585°R), we cannot use the 300-gal reactor as it is now.

Analysis: After using Equations (E12-3.10) and (E12-3.14) to make a plot of conversion as a function of temperature, we see that there is only one intersection of $X_{EB}(T)$ and $X_{MB}(T)$, and consequently only one steady state. The exit conversion is 83% and the exit temperature (i.e., the reactor temperature) is 613°R (153°F), which is above the acceptable limit of 585°R (125°F) and we thus cannot use the CSTR operating at these conditions. Be sure to go to the LEP 12-3 and use Wolfram to see the X_{MB} and X_{EB} versus T lines change along with their intersection change as you change the parameters in the slider box.

Ouch! Looks like our plant will not be able to be completed and our multimillion-dollar profit has flown the coop. But wait, don't give up, let's ask reaction engineer Maxwell Anthony to fly to our company's plant in the country of Jofostan to look for a cooling coil heat exchanger that we could place in the reactor. See what Max found in [Example 12-4](#).

Example 12-4 CSTR with a Cooling Coil

Fantastic! Max has located a cooling coil in an equipment storage shed in the small, mountainous village of Ölofasis, Jofostan, for use in the hydrolysis of propylene oxide discussed in [Example 12-3](#). The cooling coil has 40 ft² of cooling surface and the cooling-water flow rate inside the coil is sufficiently large that a constant coolant temperature of 85°F can be maintained. A typical overall heat-transfer coefficient for such a coil is 100 Btu/h·ft²·°F. Will the reactor satisfy the previous constraint of 125°F maximum temperature if the cooling coil is used?

Solution

If we assume that the cooling coil takes up negligible reactor volume, the conversion calculated as a function of temperature from the mole balance is the same as that in [Example 12-3](#), Equation (E12-3.10).

1. **Combining the mole balance, stoichiometry, and rate law**, we have, from [Example 12-3](#)

$$X_{EB} = \frac{\tau k}{1 + \tau k} = \frac{(2.084 \times 10^{12}) \exp(-16306/T)}{1 + (2.084 \times 10^{12}) \exp(-16306/T)} \quad (\text{E12-3.10})$$

T is in °R.

2. **Energy balance:** Neglecting the work by the stirrer, we combine Equations (11-27) and (12-20) to write

$$\frac{UA(T_a - T)}{F_{A0}} - X[\Delta H_{Rx}^\circ(T_R) + \Delta C_P(T - T_R)] = \Sigma \Theta_i C_{Pi}(T - T_0) \quad (\text{E12-4.1})$$

Solving the energy balance for X_{EB} yields

$$X_{EB} = \frac{\Sigma \Theta_i C_{Pi}(T - T_0) + [UA(T - T_a)/F_{A0}]}{-[\Delta H_{Rx}^\circ(T_R) + \Delta C_P(T - T_R)]} \quad (\text{E12-4.2})$$

The cooling-coil term in Equation (E12-4.2) is

$$\frac{UA}{F_{A0}} = \left(100 \frac{\text{Btu}}{\text{h} \cdot \text{ft}^2 \cdot ^\circ \text{F}} \right) \frac{(40 \text{ ft}^2)}{(43.04 \text{ lb-mol/h})} = \frac{92.9 \text{ Btu}}{\text{lb-mol} \cdot ^\circ \text{F}} \quad (\text{E12-4.3})$$

Recall that the cooling temperature is

$$T_a = 85^\circ \text{F} = 545^\circ \text{R}$$

The numerical values of all other terms of Equation (E12-4.2) are identical to those given in Equation (E12-3.13), but with the addition of the heat exchange term, X_{EB} becomes

$$X_{EB} = \frac{403.3(T-535)+92.9(T-545)}{36400+7(T-528)} \quad (E12-4.4)$$

We now have two equations, Equations (E12-3.10) and (E12-4.4), and two unknowns, X and T , which we can solve with Polymath. Recall Examples 4-5 and 8-6 to review how to solve nonlinear, simultaneous equations of this type with Polymath. (See **Problem P12-1A(f)** on pages 661–662 to plot X versus T on Figure E12-3.2.) We could generate Figure E12-3.2 by “fooling” Polymath to plot X and T , as explained in the tutorial on the Web site (http://www.umich.edu/~elements/6e/software/Polymath_h_fooling_tutorial.pdf).

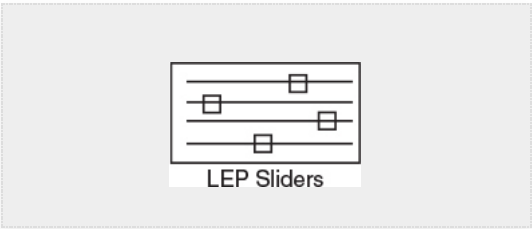


TABLE E12-4.1 POLYMATH: CSTR WITH HEAT EXCHANGE

Nonlinear equations

1 $f(X) = X - (403.3(T-535) + 92.9(T-545)) / (36400 + 7(T-528)) = 0$

2 $f(T) = X - \tau A k / (1 + \tau A k) = 0$

Explicit equations

1 $\tau = 0.1229$

2 $A = 16.96 \times 10^{12}$

3 $E = 32400$

4 $R = 1.987$

5 $k = A \exp(-E/(R \cdot T))$

Variable	Value
1 A	1.696E+13
2 E	3.24E+04
3 k	4.648984
4 R	1.987
5 tau	0.1229

Calculated values of NLE variables			
Variable	Value	f(x)	Initial Guess
1 T	563.7289	-5.411E-10	564.
2 X	0.3636087	2.243E-11	0.367

The Polymath program and solution to these two Equations (E12-3.10) for X_{MB} , and (E12-4.4) for X_{EB} , are given in Table E12-4.1. The exiting temperature and conversion are 103.7°F (563.7°R) and 36.4%, respectively, that is,

$$T = 564^{\circ}R \text{ and } X = 0.36$$

Be sure to go to the LEP 12-3 and use Wolfram or Python to see how X_{MB} and X_{EB} vary as you change the parameters in the slider box.

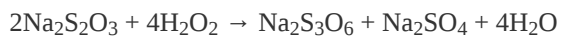
Analysis: We are grateful to the people of the village of Ölofasis in Jofostan for their help in finding this shiny new heat exchanger. By adding heat exchange to the CSTR, the $X_{MB}(T)$ curve is unchanged but the slope of the $X_{EB}(T)$ line in [Figure E12-3.2](#) increases and intersects the X_{MB} curve at $X = 0.36$ and $T = 564^\circ\text{R}$. This conversion is low! We could try to reduce the cooling by increasing T_a or T_0 to raise the reactor temperature closer to 585°R , but not above this temperature. The higher the temperature in this irreversible reaction, the greater the conversion.

We will see in the next section that there may be multiple exit values of conversion and temperature (multiple steady states, MSS) that satisfy the parameter values and entrance conditions.

12.5 MULTIPLE STEADY STATES (MSS)

In this section, we consider the steady-state operation of a CSTR in which a first-order reaction is taking place. An excellent experimental investigation that demonstrates the multiplicity of steady states was carried out by Vejtasa and Schmitz.⁶ They studied the reaction between sodium thiosulfate and hydrogen peroxide

⁶ S. A. Vejtasa and R. A. Schmitz, *AIChE J.*, 16 (3), 415.



in a CSTR operated adiabatically. The multiple steady-state temperatures were examined by varying the flow rate over a range of space times, τ .

To illustrate the concept of MSS, reconsider the $X_{MB}(T)$ curve, Equation (E12-3.10), shown in [Figure E12-3.2](#), which has been redrawn and shown as dashed lines in [Figure E12-3.2A](#). Now consider what would happen if the volumetric flow rate v_0 is increased (τ decreased) just a little. The energy balance line, $X_{EB}(T)$, remains unchanged, but the mole balance line, X_{MB} , moves to the right, as shown by the curved, solid line in [Figure E12-3.2A](#). This shift of $X_{MB}(T)$ to the right results in

the $X_{EB}(T)$ and $X_{MB}(T)$ intersecting three times, $X_{MB} = X_{EB}$, indicating three possible steady-state conditions at which the reactor could operate.

When more than one intersection occurs, there is more than one set of conditions that satisfy both the energy balance and mole balance (i.e., $X_{EB} = X_{MB}$); consequently, there will be multiple steady states at which the reactor may operate. These three steady states are easily determined from a graphical solution, but only one could show up in the Polymath equation solver solution. Thus, when using the Polymath nonlinear equation solver, we need to either choose different initial guesses to find whether there are other solutions that exist for which $X_{MB} = X_{EB}$. **Or** We could also *fool* Polymath to obtain the

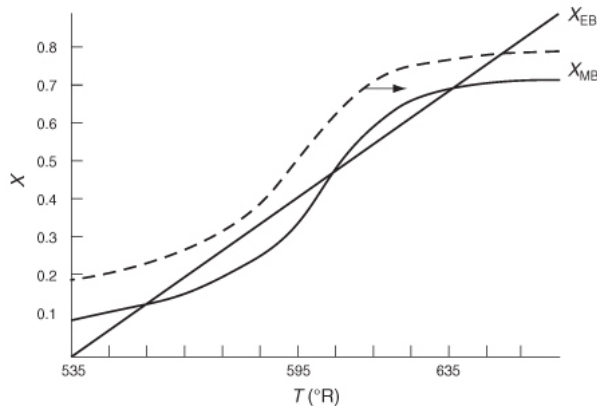


Figure E12-3.2A Plots of $X_{EB}(T)$ and $X_{MB}(T)$ for different spaces times τ .

plot in Figure E12-3.2A by using the ODE solver and setting $\frac{dT}{dt} = 0.1$ and then plot X_{MB} and X_{EB} versus T , as in Example 12-3. Tutorials on “How to Fool Polymath” and generate $G(T)$ and $R(T)$ plots can be found at http://www.umich.edu/~elements/6e/software/Polymath_fooling_tutorial.pdf.

We begin by recalling Equation (12-24), which applies when one neglects shaft work and ΔC_p (i.e., $\Delta C_p = 0$ and therefore $\Delta H_{Rx} = \Delta H_{Rx}^\circ$)

$$-X\Delta H_{Rx}^\circ = C_{P0}(1 + \kappa)(T - T_c) \quad (12-24)$$

where

$$C_{P0} = \sum \Theta_i C_{Pi} \quad (12-26a)$$

$$\kappa = \frac{UA}{C_{P0}F_{A0}} \quad (12-26b)$$

"Fooling" Polymath

and

$$T_c = \frac{T_0 F_{A0} C_{P0} + UA T_a}{UA + C_{P0} F_{A0}} = \frac{\kappa T_a + T_0}{1 + \kappa} \quad (12-27)$$

Using the CSTR mole balance $X = \frac{-r_A V}{F_{A0}}$, Equation (12-24) may be rewritten as

$$(-r_A V / F_{A0}) (-\Delta H_{Rx}^\circ) = C_{P0} (1 + \kappa) (T - T_c) \quad (12-28)$$

The left-hand side is referred to as the *heat-generated term*

$G(T)$ = Heat-generated term

$$G(T) = (-\Delta H_{Rx}^\circ) (-r_A V / F_{A0}) \quad (12-29)$$

The right-hand side of Equation (12-28) is referred to as the *heat-removed term* (by flow and heat exchange) $R(T)$

$R(T)$ = Heat-removed term

$$R(T) = C_{P0} (1 - \kappa) (T - T_c) \quad (12-30)$$

To study the multiplicity of steady states, we shall plot both $R(T)$ and $G(T)$ as a function of temperature on the same graph and analyze the circumstances under which we will obtain multiple intersections of $R(T)$ and $G(T)$.

12.5.1 Heat-Removed Term, $R(T)$

Vary Entering Temperature. From Equation (12-30), we see that $R(T)$ increases linearly with temperature, with slope and intercept T_c . As the entering temperature T_0 is increased, the line retains the same slope but shifts to the right as the intercept T_c increases, as shown in Figure 12-7.

Heat-removed curve $R(T)$

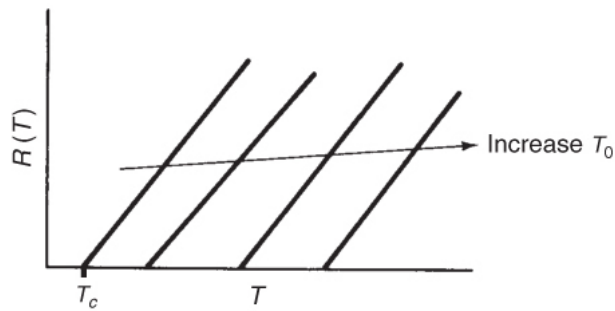


Figure 12-7 Variation of heat-removed line with inlet temperature.

Vary Non-adiabatic Parameter κ . If one increases κ by either decreasing the molar flow rate, F_{A0} , or increasing the heat-exchange area, A , the slope increases and for the case of $T_a < T_0$ the ordinate intercept moves to the left, as shown in Figure 12-8.

$$\kappa = 0 \quad T_c = T_0$$

$$\kappa = \infty \quad T_c = T_a$$

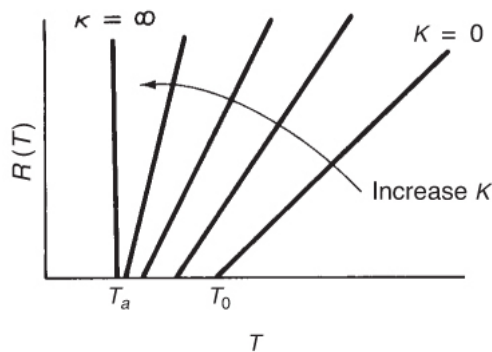


Figure 12-8 Variation of heat-removed line with κ ($\kappa = UA/C_{P0}F_{A0}$).

$$\kappa = \frac{UA}{C_{P0}F_{A0}}$$

$$T_c = \frac{T_0 + \kappa T_a}{1 + \kappa}$$

On the other hand, if $T_a < T_0$, the intercept will move to the right as κ increases.

12.5.2 Heat-Generated Term, $G(T)$

The heat-generated term, Equation (12-29), can be written in terms of conversion. (Recall that $X = -r_A V/F_{A0}$.)

$$G(T) = (-\Delta H_{Rx}^\circ)X \quad (12-31)$$

To obtain a plot of heat generated, $G(T)$, as a function of temperature, we must solve for X as a function of T using the CSTR mole balance, the rate law, and stoichiometry. For example, for a first-order liquid-phase reaction, the CSTR mole balance becomes

$$V = \frac{F_{A0}X}{kC_A} = \frac{v_0 C_{A0}X}{kC_{A0}(1-X)}$$

Solving for X yields

$$X = \frac{\tau k}{1 + \tau k} \quad (5-8)$$

First-order reaction

Substituting for X in Equation (12-31), we obtain

$$G(T) = \frac{-\Delta H_{Rx}^\circ \tau k}{1 + \tau k} \quad (12-32)$$

Finally, substituting for k in terms of the Arrhenius equation, we obtain

$$G(T) = \frac{-\Delta H_{Rx}^\circ \tau A e^{-E/RT}}{1 + \tau A e^{-E/RT}} \quad (12-33)$$

Note that equations analogous to Equation (12-33) for $G(T)$ can be derived for other reaction orders and for reversible reactions simply by solving the CSTR mole balance for X . For example, for the second-order liquid-phase reaction

Second-order reaction

$$X = \frac{(2\tau k C_{A0} + 1) - \sqrt{4\tau k C_{A0} + 1}}{2\tau k C_{A0}}$$

the corresponding heat-generated term is

$$G(T) = \frac{-\Delta H_{\text{Rx}}^{\circ} \left[\left(2\tau C_{A0} A e^{-E/RT} + 1 \right) - \sqrt{4\tau C_{A0} A e^{-E/RT} + 1} \right]}{2\tau C_{A0} A e^{-E/RT}} \quad (12-34)$$

Let's now return to our first-order reaction, Equation (12-33), and examine the behavior of the $G(T)$ curve. At very low temperatures, the second term in the denominator of Equation (12-33) for the first-order reaction can be neglected, so that $G(T)$ varies as

Low T

$$G(T) = -\Delta H_{\text{Rx}}^{\circ} \tau A e^{-E/RT}$$

(Recall that $\Delta H_{\text{Rx}}^{\circ}$ means that the standard heat of reaction is evaluated at T_R .)

At very high temperatures, the second term on the right side in the denominator is large and dominates in Equation (12-33) so that the τk in the numerator and denominator cancel, and $G(T)$ is reduced to

High T

$$G(T) = -\Delta H_{\text{Rx}}^{\circ}$$

$G(T)$ is shown as a function of T for two different activation energies, E , in Figure 12-9. If the flow rate is decreased or the reactor volume increased so as to increase τ , the heat-generated term, $G(T)$, changes, as shown in Figure 12-10.

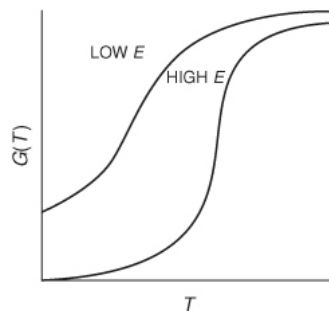


Figure 12-9 Variation of $G(T)$ curve with activation energy.

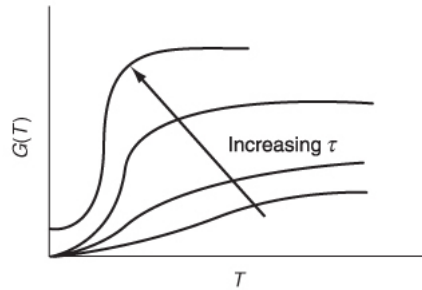


Figure 12-10 Variation of $G(T)$ curve with space time.

Heat-generated curves, $G(T)$

Can you combine [Figures 12-10](#) and [12-8](#) to explain why a Bunsen burner flame goes out when you turn up the gas flow to a very high rate? As an exercise, plot $R(T)$ versus $G(T)$ for different values of T_0 and κ .

12.5.3 Ignition–Extinction Curve

The points of intersection of $R(T)$ and $G(T)$ give us the temperature at which the reactor can operate at steady state. This intersection is the point at which both the energy balance, $R(T)$, and the mole balance, $G(T)$, are satisfied. Suppose that we begin to operate our reactor at some relatively low temperature, T_{01} . If we construct our $G(T)$ and $R(T)$ curves, illustrated by curve $y = G(T)$ and line $a = R(T)$, respectively, in [Figure 12-11](#), we see that there will be only one point of intersection, point 1. From this point of intersection, one can find the steady-state temperature in the reactor, T_{s1} , by following a vertical line down to the T -axis and reading off the temperature, T_{s1} , as shown in [Figure 12-11](#).

Ignition: The point of no return

If one were now to increase the entering temperature to T_{02} , the $G(T)$ curve, y , would remain unchanged, but the $R(T)$ curve would move to the right, as shown by *line b* in [Figure 12-11](#), and will now intersect the $G(T)$ at point 2 and also be tangent at point 3. Consequently, we see from [Figure 12-11](#) that there are two steady-state temperatures, T_{s2} and T_{s3} , that can be realized in the CSTR for an entering temperature T_{02} . If the entering temperature is further increased to T_{03} , the $R(T)$ curve, line *c* ([Figure 12-12](#)), intersects the $G(T)$ curve three

times and there are three steady-state temperatures, T_{s4} , T_{s5} , and T_{s6} . As we continue to increase T_0 , we finally reach *line e*, in which there are only two steady-state temperatures, a point of tangency at T_{s10} and an intersection at T_{s11} . If the entering temperature is slightly increased beyond T_{05} , say to T_{06} , then the point of tangency disappears and there is a jump in reactor temperature, from T_{s10} up to T_{s12} . This jump is called the *ignition point* for the reaction. By further increasing T_0 , we reach *line f*, corresponding to T_{06} , in which we have only one reactor temperature that will satisfy both the mole and energy balances, T_{s12} . For the six entering temperatures, we can form [Table 12-4](#), relating the entering temperature to the possible reactor operating temperatures.

By plotting steady-state reactor temperature T_s as a function of entering temperature T_0 , we obtain the well-known **ignition–extinction curve** shown in

Both the mole and energy balances are satisfied at the points of intersection or tangency.

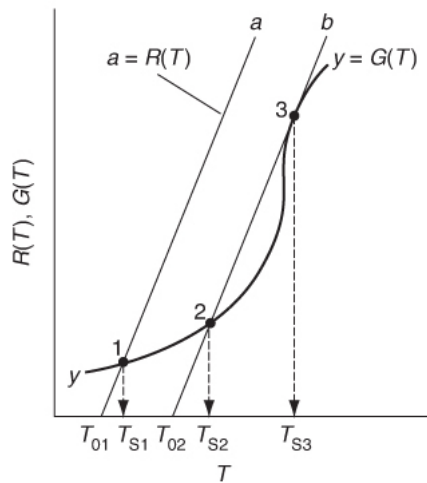


Figure 12-11 Finding multiple steady states with T_0 varied.

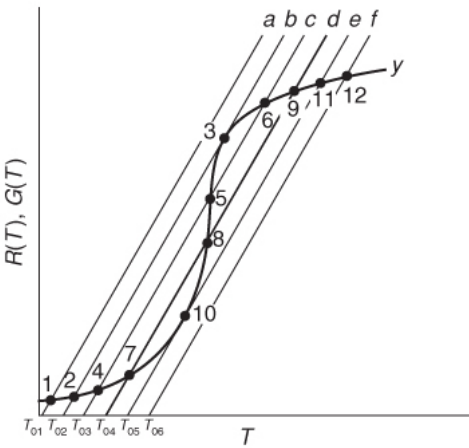


Figure 12-12 Finding multiple steady states with T_0 varied.

TABLE 12-4 MULTIPLE STEADY-STATE TEMPERATURES

Entering Temperature		Reactor Temperatures	
T_{01}		T_{s1}	
T_{02}	T_{s2}	T_{s3}	
T_{03}	T_{s4}	T_{s5}	T_{s6}
T_{04}	T_{s7}	T_{s8}	T_{s9}
T_{05}	T_{s10}	T_{s11}	
T_{06}		T_{s12}	

Figure 12-13. From this figure, we see that as the entering temperature T_0 is increased, the steady-state temperature T_s increases along the bottom line until T_{05} is reached. Any fraction-of-a-degree increase in temperature beyond T_{05} the point of tangency disappears and the steady-state reactor temperature T_s will jump up from T_{s10} to T_{s11} , as shown in **Figure 12-13**. The temperature at which this jump occurs is called the **ignition temperature**. That is, we must exceed a certain feed temperature, T_{05} , to operate at the upper steady state where the temperature and conversion are higher. The ignition point temperature is sometimes also called the *onset temperature for a runaway reaction* or the *point of no return*,

especially when the upper steady state is at a very high temperature.

Runaway reaction?

If a reactor were operating at T_{s12} and we began to cool the entering temperature down from T_{06} , the steady-state reactor temperature, T_{s3} , would eventually be reached, corresponding to an entering temperature, T_{02} . Any slight decrease below T_{02} the point of tangency on *line b* in Figure 12-12 would disappear and the temperature would drop the steady-state reactor temperature to immediately the lower steady-state value T_{s2} . Consequently, T_{02} is called the **extinction temperature**.

The middle points 5 and 8 in Figures 12-12 and 12-13 represent **unstable steady-state temperatures**. Consider the heat-removed *line d* in Figure 12-12, along with the heat-generated curve *y*, which are replotted in Figure 12-14. If we were operating at the middle steady-state temperature T_{s8} , for example, and a

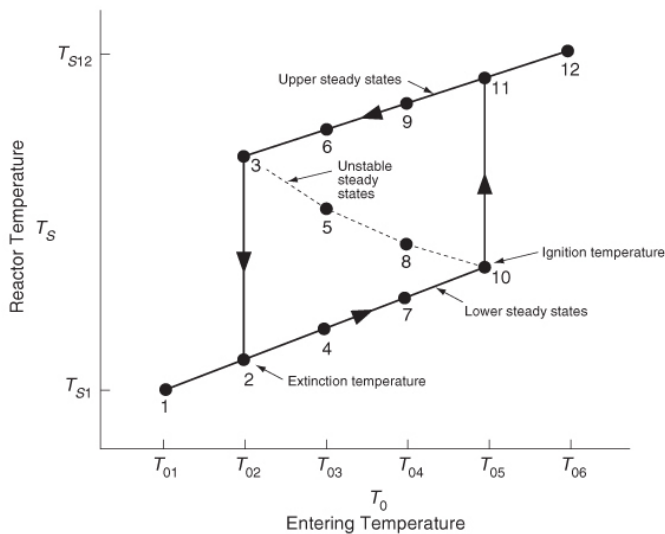


Figure 12-13 Temperature ignition-extinction curve.

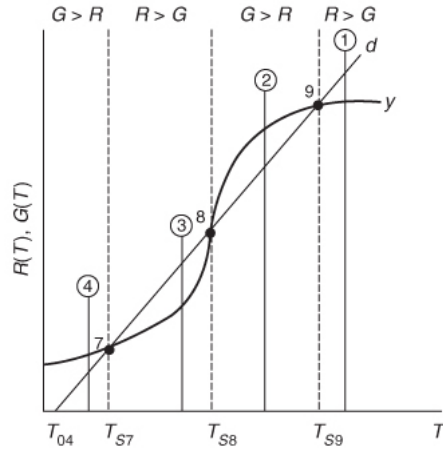
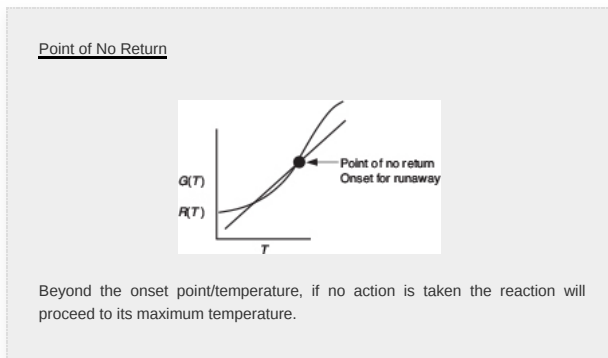


Figure 12-14 Stability of multiple steady-state temperatures.



pulse increase in reactor temperature occurred, we would find ourselves at the temperature shown by vertical line ②, between points 8 and 9. We see that along this vertical line ②, the heat-generated curve, $y \equiv G(T)$, is greater than the heat-removed line $d \equiv R(T)$, that is, $(G > R)$. Consequently, the temperature in the reactor would continue to increase until point 9 is reached at the upper steady state. On the other hand, if we had a pulse decrease in temperature from point 8, we would find ourselves on a vertical line ③ between points 7 and 8. Here, we see that the heat-removed curve d is greater than the heat-generated curve y ($R > G$), so the temperature will continue to decrease until the lower steady state is reached. That is, a small change in temperature either above or below the middle steady-state temperature, T_{S8} , will cause the reactor temperature to move away from this middle steady state. Steady states that behave in this manner are said to be *unstable*.

In contrast to these unstable operating points, there are stable operating points. Consider what would happen if a reactor operating at T_{s9} were subjected to a pulse increase in reactor temperature indicated by line ① in Figure 12-14. We see that the heat-removed line d is greater than the heat-generated curve y ($R > G$), so that the reactor temperature will decrease and return to T_{s9} . On the other hand, if there is a sudden drop in temperature below T_{s9} , as indicated by line ②, we see the heat-generated curve y is greater than the heat-removed line d ($G > R$), and the reactor temperature will increase and return to the upper steady state at T_{s9} . Consequently, T_{s9} is a stable steady state.

Next, let's look at what happens when the lower steady-state temperature at T_{s7} is subjected to pulse increase to the temperature shown as line ③ in Figure 12-14. Here, we again see that the heat removed, R , is greater than the heat generated, G , so that the reactor temperature will drop and return to T_{s7} . If there is a sudden decrease in temperature below T_{s7} to the temperature indicated by line ④, we see that the heat generated is greater than the heat removed ($G > R$), and that the reactor temperature will increase until it returns to T_{s7} . Consequently, T_{s7} is a stable steady state. A similar analysis could be carried out for temperatures T_{s1} , T_{s2} , T_{s4} , T_{s6} , T_{s11} , and T_{s12} , and one would find that reactor temperatures would always return to *locally stable steady-state values* when subjected to both positive and negative fluctuations.

While these points are locally stable, they are not necessarily globally stable. That is, a large perturbation in temperature or concentration may be sufficient to cause the reactor to fall from the upper steady state (corresponding to high conversion and temperature, such as point 9 in Figure 12-14), to the lower steady state (corresponding to low temperature and conversion, point 7).

12.6 NONISOTHERMAL MULTIPLE CHEMICAL REACTIONS

Most reacting systems involve more than one reaction and do not operate isothermally. **This section is one of the most important, if not the most important, sections of the book.** It ties together all the previous chapters to analyze multiple reactions that do not take place isothermally.

12.6.1 Energy Balance for Multiple Reactions in Plug-Flow Reactors

In this section we give the energy balance for multiple reactions. We begin by recalling the energy balance for a single reaction taking place in a PFR, which is given by Equation (12-5)

$$\frac{dT}{dV} = \frac{(-r_A)[- \Delta H_{Rx}(T)] - Ua(T - T_a)}{\sum_{j=1}^m F_j C_{p_j}} \quad (12-5)$$

When we have multiple reactions occurring, we have to account for, and sum up, all the heats of reaction in the reactor for each and every reaction. For q multiple reactions taking place in a PFR where there are m species, it is easily shown that Equation (12-5) can be generalized to (cf. Problem P12-1(j))

Energy balance for multiple reactions

$$\frac{dT}{dV} = \frac{\sum_{i=1}^q (-r_{ij}) [- \Delta H_{R_{xij}}(T)] - Ua(T - T_a)}{\sum_{j=1}^m F_j C_{p_j}} \quad (12-35)$$

i = Reaction number

j = Species

Note that we now have two subscripts on the heat of reaction, the reaction number “ i ” and species “ j ”. The heat of reaction for reaction i must be referenced to the same species in the rate, r_{ij} , by which $\Delta H_{R_{xij}}$ is multiplied, which is

$$\begin{aligned} [-r_{ij}] [- \Delta H_{R_{xij}}] &= \left[\frac{\text{Moles of } j \text{ reaction in reaction } i}{\text{Volume} \cdot \text{time}} \right] \times \left[\frac{\text{Joules “released” in reaction } i}{\text{Moles of } j \text{ reacted in reaction } i} \right] \\ &= \left[\frac{\text{Joules “released” in reaction } i}{\text{Volume} \cdot \text{time}} \right] \end{aligned} \quad (12-36)$$

where again we note the subscript j refers to the species, the subscript i refers to the particular reaction, q is the number of **independent** reactions, and m is the number of species. We are going to let

$$Q_R = \sum_{i=1}^q (-r_{ij}) [- \Delta H_{R_{xij}}(T)]$$

and

$$Q_r = Ua(T - T_a)$$

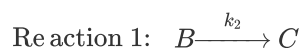
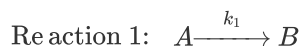
Then Equation (12-35) becomes

$$\frac{dT}{dV} = \frac{Q_g - Q_r}{\sum_{j=1}^m F_j C_{Pj}} \quad (12-37)$$

Equation (12-37) represents a nice compact form of the energy balance for multiple reactions.

12.6.1A Series Reactions in a PFR

Consider the following series reaction sequence carried out in a PFR:



The PFR energy balance becomes

One of the major goals of this text is that the reader will be able to solve multiple reactions with heat effects, and this section shows how!

$$Q_g = (-\Delta H_{R1A})(-r_{1A}) + (-r_{2B})(-\Delta H_{R2B})$$

$$Q_r = Ua(T - T_a)$$

Substituting for Q_g and $-Q_r$ in Equation (12-37) we obtain

$$\frac{dT}{dV} = \frac{Ua(T - T_a) + (-r_{1A})(-\Delta H_{R1A}) + (-r_{2B})(-\Delta H_{R2B})}{F_A C_{PA} + F_B C_{PB} + F_C C_{PC}} \quad (12-38)$$

where ΔH_{R1A} = [J/mol of A reacted in reaction 1] and

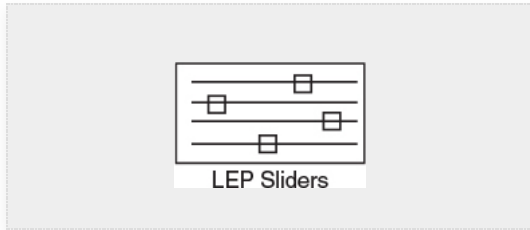
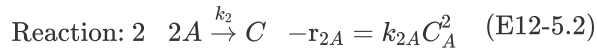
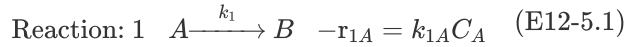
ΔH_{R2B} = [J/mol of B reacted in reaction 2].

12.6.1B Parallel Reactions in a PFR

We will now give three examples of multiple reactions with heat effects: Example 12-5 discusses *parallel reactions*, Example 12-6 discusses *series reactions*, and Example 12-7 discusses *complex reactions*.

Example 12-5 Parallel Reactions in a PFR with Heat Effects

The following gas-phase reactions occur in a PFR:



Pure A is fed at a rate of 100 mol/s, at a temperature of 150°C and at a concentration of 0.1 mol/dm³. Neglect pressure drop and determine the temperature and molar flow rate profiles down the reactor.

Additional information:

$$\Delta_{\text{HRx1A}} = -20000 \text{ J/(mol = of A reacted in reaction 1)}$$

$$\Delta_{\text{HRx2A}} = -60000 \text{ J/(mol = of A reacted in reaction 2)}$$

$$C_{PA} = 90 \text{ J/mol} \cdot ^\circ\text{C} \quad k_{1A} = 10 \exp \left[\frac{E_1}{R} \left(\frac{1}{300} - \frac{1}{T} \right) \right] \text{ s}^{-1}$$

$$C_{PB} = 90 \text{ J/mol} \cdot ^\circ\text{C} \quad E_1/R = 4000 \text{ K}$$

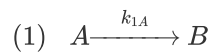
$$C_{PC} = 180 \text{ J/mol} \cdot ^\circ\text{C} \quad k_{2A} = 0.09 \exp \left[\frac{E_2}{R} \left(\frac{1}{300} - \frac{1}{T} \right) \right] \frac{\text{dm}^3}{\text{mol} \cdot \text{s}}$$

$$Ua = 4000 \text{ J/m}^3 \cdot \text{s} \cdot ^\circ\text{C} \quad E_0/R = 9000 \text{ K}$$

$$T_a = 100^\circ\text{C} \quad (\text{Constant})$$

Solution

0. Number Each Reaction: This step was given in the problem statement.



1. Mole Balances:

$$\frac{dF_A}{dV} = r_A \quad (\text{E12-5.3})$$



$$\frac{dF_B}{dV} = r_B \quad (\text{E12-5.4})$$

$$\frac{dF_C}{dV} = r_C \quad (\text{E12-5.5})$$

2. Rates:

Rate laws

$$r_{1A} = -k_{1A}C_A \quad (\text{E12-5.1})$$

$$r_{2A} = -k_{1A}C_A^2 \quad (\text{E12-5.2})$$

Relative rates

$$\text{Reaction 1: } \frac{r_{1A}}{-1} = \frac{r_{1B}}{1}; \quad r_{1B} = -r_{1A} = k_{1A}C_A$$

$$\text{Reaction 2: } \frac{r_{2A}}{-2} = \frac{r_{2B}}{1}; \quad r_{2C} = -\frac{1}{2}r_{2A} = \frac{k_{2A}}{2}C_A^2$$

Net rates

$$r_A = r_{1A} + r_{2A} = k_{1A}C_A - k_{2A}C_A^2 \quad (\text{E12-5.6})$$

$$r_B = r_{1B} = k_{1A}C_A \quad (\text{E12-5.7})$$

$$r_C = r_{2C} = \frac{1}{2}k_{2A}C_A^2 \quad (\text{E12-5.8})$$

3. Stoichiometry (gas-phase but $\Delta P = 0$, i.e., $p = 1$):

$$C_A = C_{T0} \left(\frac{F_A}{F_T} \right) \left(\frac{T_0}{T} \right) \quad (\text{E12-5.9})$$

$$C_B = C_{T0} \left(\frac{F_B}{F_T} \right) \left(\frac{T_0}{T} \right) \quad (\text{E12-5.10})$$

$$C_C = C_{T0} \left(\frac{F_C}{F_T} \right) \left(\frac{T_0}{T} \right) \quad (\text{E12-5.11})$$

$$F_T = F_A + F_B + F_C \quad (\text{E12-5.12})$$

$$k_{1A} = 10 \exp \left[4000 \left(\frac{1}{300} - \frac{1}{T} \right) \right] \text{ s}^{-1} \quad (\text{E12-5.13})$$

(T in K)

$$k_{2A} = 0.09 \exp \left[9000 \left(\frac{1}{300} - \frac{1}{T} \right) \right] \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \quad (\text{E12-5.14})$$

Selectivity:

$$\tilde{S}_{B/C} = \frac{F_B}{F_C} \quad (\text{E12-5.15})$$

Major goal of CRE: Analyze Multiple Reactions with Heat Effects

4. Energy Balance:

The PFR energy balance (cf. Equation (12-35))

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_{1A})(-\Delta H_{R1A}) + (-r_{2A})(-\Delta H_{R2A})}{F_A C_{PA} + F_B C_{PB} + F_C C_{PC}} \quad (\text{E12-5.16})$$

becomes

$$\frac{dT}{dV} = \frac{4000(373 - T) + (-r_{1A})(2000) + (-r_{2A})(60000)}{90F_A + 90F_B + 180F_C} \quad (\text{E12-5.17})$$

5. Evaluation:

The Polymath program and its graphical outputs are shown in Table E12-5.1 and Figures E12-5.1 and E12-5.2.

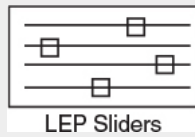


TABLE E12-5.1 POLYMATH PROGRAM

Differential equations

1 $d(F_a)/d(V) = r_{1a} + r_{2a}$

2 $d(F_b)/d(V) = -r_{1a}$

3 $d(F_c)/d(V) = -r_{2a}/2$

4 $d(T)/d(V) = (Q_g - Q_r)/(90 \cdot F_a + 90 \cdot F_b + 180 \cdot F_c)$

Explicit equations

1 $Q_r = 4000 \cdot (T - 373)$

2 $T_o = 423$

3 $k_{1a} = 10 \cdot \exp(4000 \cdot (1/300 - 1/T))$

4 $k_{2a} = 0.09 \cdot \exp(9000 \cdot (1/300 - 1/T))$

5 $C_{to} = 0.1$

$$6 \Delta H_1 = -20000$$

$$7 \Delta H_2 = -60000$$

$$8 F_t = F_a + F_b + F_c$$

$$9 C_a = C_{to} \cdot (F_a/F_t) \cdot (T_o/T)$$

$$10 r_{2a} = -k_{2a} \cdot C_a^2$$

$$11 C_b = C_{to} \cdot (F_b/F_t) \cdot (T_o/T)$$

$$12 C_c = C_{to} \cdot (F_c/F_t) \cdot (T_o/T)$$

$$13 r_{1a} = -k_{1a} \cdot C_a$$

$$14 Q_g = (-r_{1a}) \cdot (-\Delta H_1) + (-r_{2a}) \cdot (-\Delta H_2)$$

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	Ca	0.1	2.069E-09
2	Cb	0	0.0415941
3	Cc	0	0.016986
4	Cto	0.1	0.1
5	Fa	100.	2.738E-06
6	Fb	0	55.04326
7	Fc	0	22.47837
8	Ft	100.	77.52163
9	k1a	482.8247	2.426E+04
10	k2a	553.0557	3.716E+06
11	Qg	1.297E+06	1.003708
12	Qr	2.0E+05	1.396E+06
13	r1a	-48.28247	-5.019E-05
14	r2a	-5.530557	-1.591E-11
15	T	423.	722.0882
16	To	423.	423.
17	V	0	1.

Why does the temperature go through a maximum value?

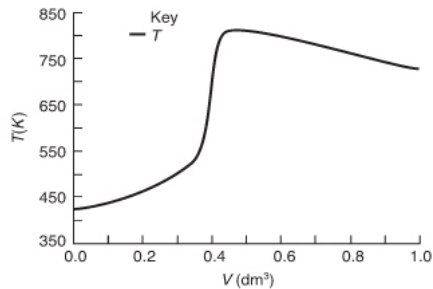


Figure E12-5.1 Temperature profile.

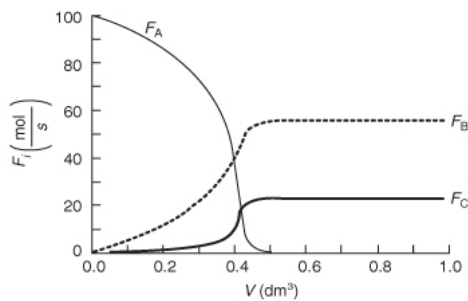


Figure E12-5.2 Profile of molar flow rates F_A , F_B and F_C

Analysis: From Figure E12-5.1 we see that the temperature increases slowly up to a reactor volume of 0.4 dm^3 then suddenly jumps up (*ignites*) to a temperature of 850 K. Correspondingly, from Figure E12-5.2 the reactant molar flow rate decreases sharply at this point. The reactant is virtually consumed by the time it reaches a reactor volume $V = 0.45 \text{ dm}^3$; beyond this point, $Q_r > Q_g$, and the reactor temperature begins to drop. In addition, the selectivity $\tilde{S}_{B/C} = F_B/F_C = 55/22.5 = 2.44$ remains constant after this point. If a high selectivity is required, then the reactor should be shortened to $V = 0.3 \text{ dm}^3$, at which point the selectivity is $\tilde{S}_{B/C} = 21.9/2.5 = 8.9$.

12.6.2 Energy Balance for Multiple Reactions in a CSTR

Recall that for the steady-state mole balance in a CSTR with a single reaction $[-F_{A0}X = r_A V]$, and that

$\Delta H_{\text{Rx}}(T) = \Delta H_{\text{Rx}}^{\circ} + \Delta C_P(T - T_R)$, so that for $T_0 = T_{i0}$
Equation (11-27) may be rewritten as

$$\dot{Q} - \dot{W}_s - F_{A0} \sum_j \Theta_j C_{Pj} (T - T_0) + [\Delta H_{\text{Rx}}(T)] [r_A V] = 0 \quad (11-27A)$$

Again, we must account for the “heat generated” by all the reactions in the reactor. For q multiple reactions and m species, the CSTR energy balance becomes

$$\dot{Q} - \dot{W}_s - F_{A0} \sum_{j=1}^m \Theta_j C_{Pj} (T - T_0) + V \sum_{i=1}^q r_{ij} \Delta H_{\text{Rx}ij}(T) = 0 \quad (12-39)$$

Energy balance for multiple reactions in a CSTR

Substituting Equation (12-20) for \dot{Q} , neglecting the work term, and assuming constant heat capacities and large coolant flow rates \dot{m}_c , Equation (12-39) becomes

$$UA(T_a - T) - F_{A0} \sum_{j=1}^m C_{Pj} \Theta_j (T - T_0) + V \sum_{i=1}^q r_{ij} \Delta H_{\text{Rx}ij}(T) = 0 \quad (12-40)$$

For the two parallel reactions described in Example 12-5, the CSTR energy balance is

$$UA(T_a - T) - F_{A0} \sum_{j=1}^m \Theta_j C_{Pj} (T - T_0) + V r_{1A} \Delta H_{\text{Rx}1A}(T) + V r_{2A} \Delta H_{\text{Rx}2A}(T) = 0 \quad (12-41)$$

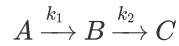
Major goal of CRE

As stated previously, one of the **major goals** of this text is to have the reader solve problems involving multiple reactions with heat effects (cf. Problems P12-23B, P12-24B, P12-25C, and P12-26C). That’s exactly what we are doing in the next two examples!

12.6.3 Series Reactions in a CSTR

Example 12-6 Multiple Reactions in a CSTR

The elementary liquid-phase reactions



take place in a 10-dm³ CSTR. What are the effluent concentrations for a volumetric feed rate of 1000 dm³/min at a concentration of A of 0.3 mol/dm³? The inlet temperature is 283 K.

Additional information:

$$C_{P_A} = C_{P_B} = C_{P_C} = 200 \text{ J/mol} \cdot \text{K}$$

$$k_1 = 3.3 \text{ min}^{-1} \text{ at } 300 \text{ K, with } E_1 = 9900 \text{ cal/mol}$$

$$k_2 = 4.58 \text{ min}^{-1} \text{ at } 500 \text{ K, with } E_2 = 27000 \text{ cal/mol}$$

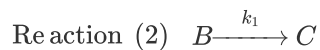
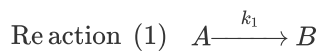
$$\Delta H_{R_{x1A}} = 55000 \text{ J/mol A} \quad UA = 40000 \text{ J/min} \cdot \text{K with } T_a = 57^\circ \text{C}$$

$$\Delta H_{R_{x2B}} = 71500 \text{ J/mol B}$$

Solution

The Algorithm:

0. Number Each Reaction:



1. Mole Balance on Every Species:

Species A: Combined mole balance and rate law for A

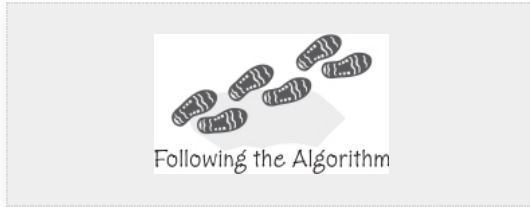
$$V = \frac{F_{A0} - F_A}{-r_A} = \frac{v_0[C_{A0} - C_A]}{-r_{1A}} = \frac{v_0[C_{A0} - C_A]}{k_1 C_A} \quad (\text{E12-6.1})$$

Solving for C_A gives us

$$C_A = \frac{C_{A0}}{1 + \tau k_1} \quad (\text{E12-6.2})$$

Species B: Combined mole balance and rate law for B

$$V = \frac{0 - C_B v_0}{-r_B} = \frac{C_B v_0}{r_B} \quad (\text{E12-6.3})$$



2. Rates:

The reactions follow elementary rate laws

(a) Laws	(b) Relative Rates	(c) Net Rates
$r_{1A} = -k_{1A}C_A \equiv -k_1C_A$	$r_{1B} = -r_{1A}$	$r_A = r_{1A}$
$r_{2B} = -k_{2B}C_B \equiv -k_2C_B$	$r_{2C} = -r_{2B}$	$r_B = r_{1B} + r_{2B}$

3. Combine:

Substituting for r_{1B} and r_{2B} in Equation (E12-6.3) gives

$$V = \frac{C_B v_0}{k_1 C_A - k_2 C_B} \quad (\text{E12-6.4})$$

Solving for C_B yields

$$C_B = \frac{\tau k_1 C_A}{1 + \tau k_2} = \frac{\tau k_1 C_{A0}}{(1 + \tau k_1)(1 + \tau k_2)} \quad (\text{E12-6.5})$$

$$\boxed{-r_{1A} = k_1 C_A = \frac{k_1 C_{A0}}{1 + \tau k_1}} \quad (\text{E12-6.6})$$

$$\boxed{-r_{2B} = k_2 C_B = \frac{k_2 \tau k_1 C_{A0}}{(1 + \tau k_1) + ((1 + \tau k_2))}} \quad (\text{E12-6.7})$$

4. Energy Balances:

Applying Equation (12-41) to this system gives

$$[r_{1A} \Delta H_{R_{x1A}} + r_{2B} \Delta H_{R_{x2B}}]V - UA(T - T_a) - F_{A0} C_{P_A}(T - T_0) = 0 \quad (\text{E12-6.8})$$

Substituting for $F_{A0} = v_0 C_{A0}$, r_{1A} , and r_{2B} and rearranging, we have

$$\overbrace{\left[-\frac{\Delta H_{R_{x1A}} \tau k_1}{1 + \tau k_1} - \frac{\tau k_1 \tau k_2 \Delta H_{R_{x2B}}}{(1 + \tau k_1)(1 + \tau k_2)} \right]}^{G(T)} = \frac{R(T)}{c_{P_A}(1 + \kappa)[T - T_e]} \quad (\text{E12-6.9})$$

$$\boxed{G(T) = \left[-\frac{\Delta H_{R_{x1A}} \tau k_1}{1 + \tau k_1} - \frac{\tau k_1 \tau k_2 \Delta H_{R_{x2B}}}{(1 + \tau k_1)(1 + \tau k_2)} \right]} \quad (\text{E12-6.10})$$

$$R(T) = C_{PA} (1 + \kappa) [T - T_c] \tag{E12-6.11}$$

5. Parameter Evaluation

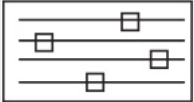
$$\kappa = \frac{UA}{F_{A0}C_{PA}} = \frac{40000\text{J}/\text{min}\cdot\text{K}}{(0.3\text{ mol}/\text{dm}^3)(1000\text{ dm}^3/\text{min})200\text{J}/\text{mol}\cdot\text{K}} = 0.667 \tag{E12-6.12}$$

$$T_c = \frac{T_0 + \kappa T_a}{1 + \kappa} = \frac{283 + (0.666)(330)}{1 + 0.667} = 301.8\text{ K} \tag{E12-6.13}$$

We are going to generate $G(T)$ and $R(T)$ by "fooling" Polymath to first generate T as a function of a dummy variable, t . We then use our plotting options to convert $T(t)$ to $G(T)$ and $R(T)$. The Polymath program to plot $R(T)$ and $G(T)$ vs. T is shown in Table E12-6.1, and the resulting graph is shown in Figure E12-6.1 (http://www.umich.edu/~elements/5e/tutorials/Polymath_h_fooling_tutorial_Example-12-6.pdf).

Fooling Polymath

Incrementing temperature in this manner is an easy way to generate $R(T)$ and $G(T)$ plots.



LEP Sliders

TABLE E12-6.1 POLYMATH: PROGRAM AND OUTPUT

Differential equations		Calculated values of DEQ variables		
1 d(T)/d(t) = 2		Variable	Initial value	Final value
Explicit equations		1 Ca	0.2980966	0.0005469
1 Cp = 200		2 Cao	0.3	0.3
2 Cao = 0.3		3 Cb	0.0019034	0.0014891
3 To = 283		4 Cc	1.341E-14	0.297964
4 tau = .01		5 Cp	200.	200.
5 DH1 = -55000		6 DH1	-5.5E+04	-5.5E+04
6 DH2 = -71500		7 DH2	-7.15E+04	-7.15E+04
7 vo = 1000		8 E1	9900.	9900.
8 E2 = 27000		9 E2	2.7E+04	2.7E+04
9 E1 = 9900		10 F	9948.951	-1.449E+04
10 UA = 40000		11 G	348.9509	1.259E+05
11 Ta = 330		12 k1	0.6385073	5.475E+04
12 k2 = 4.58*exp((E2/1.987)*(1/500-1/T))		13 k2	7.03E-10	2.001E+04
13 k1 = 3.3*exp((E1/1.987)*(1/300-1/T))		14 kappa	0.6666667	0.6666667
14 Ca = Cao/(1+tau*k1)		15 R	-9600.	1.404E+05
15 kappa = UA/(vo*Cao)/Cp		16 T	273.	723.
16 G = -tau*k1/(1+k1*tau)*DH1-k1*tau*k2*tau*DH2/((1+tau*k1)*(1+tau*k2))		17 t	0	225.
17 Tc = (To+kappa*Ta)/(1+kappa)		18 Ta	330.	330.
18 Cb = tau*k1*Ca/(1+k2*tau)		19 tau	0.01	0.01
19 R = Cp*(1+kappa)*(T-Tc)		20 Tc	301.8	301.8
20 Cc = Cao-Ca-Cb		21 To	283.	283.
21 F = G-R		22 UA	4.0E+04	4.0E+04
		23 vo	1000.	1000.

When $F = 0$, then $G(T) = R(T)$ and the steady states can be found.

Wow!

Five (5) multiple steady states!

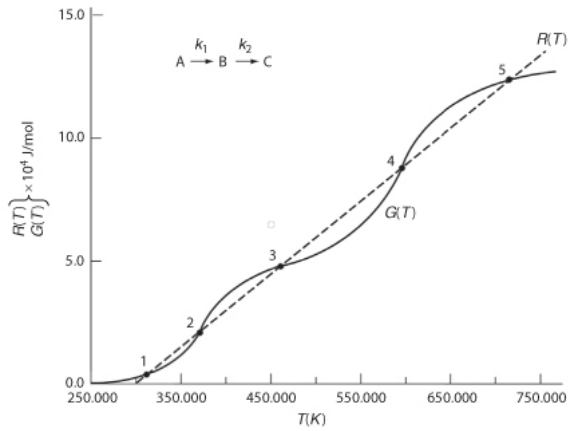


Figure E12-6.1 Heat-removed and heat-generated curves.

TABLE E12-6.2 EFFLUENT CONCENTRATIONS AND TEMPERATURES

S	T(K)	C _A (mol/dm ³)	C _B (mol/dm ³)	C _C (mol/dm ³)
1	310	0.284	0.016	0
2	363	0.189	0.111	0
3	449	0.033	0.267	0.00056
4	558	0.0041	0.167	0.129
5	677	0.00087	0.0053	0.294

Analysis: Wow! We see that five steady states (SS) exist!! The exit concentrations and temperatures listed in Table E12-6.2 were determined from the tabular

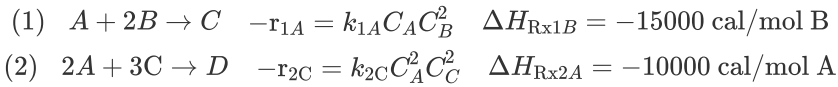
output of the Polymath program. Steady states 1, 3, and 5 are stable steady states, while 2 and 4 are unstable. The selectivity at steady state 3 is $\tilde{S}_{B/C} = \frac{0.0053}{0.294} = 477$, while at steady state 5 the selectivity is $\tilde{S}_{B/C} = \frac{0.0053}{0.294} = 0.018$ and is far too small. Consequently, to operate at a large selectivity we either have to operate at steady state 3 or find a different set of operating conditions. What do you think of the value of tau, that is, $\tau = 0.01$ min? Is it a realistic number? (See Problem P12-1A (h).)

12.6.4 Complex Reactions in a PFR

**Example 12-7 Complex Reactions with Heat Effects
in a PFR**

We will use the reactions that we discussed in Chapter 8 that were coded with dummy names, A, B, C, and D for reasons of national security.

The following complex gas-phase reactions follow elementary rate laws



and take place in a PFR. The feed is stoichiometric for reaction (1) in A and B with $F_{A0} = 5 \text{ mol/min}$. The reactor volume is 10 dm^3 and the total entering concentration is $C_{T0} = 0.2 \text{ mol/dm}^3$. The entering pressure is 100 atm and the entering temperature is 300 K. The coolant flow rate is 50 mol/min and the entering coolant fluid has a heat capacity of $C_{P_{C0}} = 10 \text{ cal/mol} \cdot \text{K}$ and enters at a temperature of 325 K.

Parameters

$$k_{1A} = 40 \left(\frac{\text{dm}^3}{\text{mol}} \right)^2 / \text{min at } 300 \text{ K with } E_1 = 8000 \text{ cal/mol}$$

$$k_{2C} = 2 \left(\frac{\text{dm}^3}{\text{mol}} \right)^4 / \text{min at } 300 \text{ K with } E_2 = 12000 \text{ cal/mol}$$

$$C_{P_A} = 10 \text{ cal/mol/K} \quad Ua = 80 \frac{\text{cal}}{\text{m}^3 \cdot \text{min} \cdot \text{K}}$$

$$C_{P_B} = 12 \text{ cal/mol/K} \quad T_{a0} = 325 \text{ K}$$

$$C_{P_C} = 14 \text{ cal/mol/K} \quad \dot{m}_c = 50 \text{ mol/min}$$

$$C_{P_D} = 16 \text{ cal/mol/K} \quad C_{P_{C0}} = 10 \text{ cal/mol/K}$$

Plot F_A , F_B , F_C , F_D , p , T , and T_a as a function of V for

(a) Co-current heat exchange

(b) Countercurrent heat exchange

(c) Constant T_a

(d) Adiabatic operation

Solution

Gas Phase PFR No Pressure Drop ($p = 1$)

1. Mole Balances:

$$(1) \quad \frac{dF_A}{dV} = r_A \quad (F_{A0} = 5 \text{ mol/min}) \quad (\text{E12-7.1})$$

$$(2) \quad \frac{dF_B}{dV} = r_B \quad (F_{B0} = 10 \text{ mol/min}) \quad (\text{E12-7.2})$$

$$(3) \quad \frac{dF_C}{dV} = r_C \quad V_f = 10 \text{ dm}^3 \quad (\text{E12-7.3})$$

$$(4) \quad \frac{dF_D}{dV} = r_D \quad (\text{E12-7.4})$$

**2. Rates:****2a. Rate Laws**

$$(5) \quad r_{1A} = -k_{1A} C_A C_B^2 \quad (\text{E12-7.5})$$

$$(6) \quad r_{2C} = -k_{2C} C_A^2 C_C^2 \quad (\text{E12-7.6})$$

2b. Relative Rates

$$(7) \quad r_{1B} = 2r_{1A} \quad (\text{E12-7.7})$$

$$(8) \quad r_{1C} = r_{1A} \quad (\text{E12-7.8})$$

$$(9) \quad r_{2A} = \frac{2}{3} r_{2C} = \frac{2}{3} k_{2C} C_A^2 C_C^3 \quad (\text{E12-7.9})$$

$$(10) \quad r_{2D} = -\frac{1}{3} r_{2C} = -\frac{1}{3} k_{2C} C_A^2 C_C^3 \quad (\text{E12-7.10})$$

2c. Net Rates of reaction for species A, B, C, and D are

$$(11) \quad r_A = r_{1A} + r_{2A} = -k_{1A} C_A C_B^2 - \frac{2}{3} k_{2C} C_A^2 C_C^3 \quad (\text{E12-7.11})$$

$$(12) \quad r_B = r_{1B} = -2k_{1A} C_A C_B^2 \quad (\text{E12-7.12})$$

$$(13) \quad r_C = r_{1C} + r_{2C} = k_{1A} C_A C_B^2 - k_{2C} C_A^2 C_C^3 \quad (\text{E12-7.13})$$

$$(14) \quad r_D = r_{2D} = \frac{1}{3} k_{2C} C_A^2 C_C^3 \quad (\text{E12-7.14})$$

3. Selectivity: $\tilde{S}_{C/D} = F_C/F_D$

At $V = 0$, $F_D = 0$ causing $S_{C/D}$ to go to infinity. Therefore, we set $S_{C/D} = 0$ between $V = 0$ and a very

small number, say, $V = 0.0001 \text{ dm}^3$ to prevent the ODE solver from crashing.

$$(15) \quad S_{C/D} = \text{if}\left(V > 0.0001\right) \text{then}\left(\frac{F_C}{F_D}\right) \text{else } (0) \quad (\text{E12-7.15})$$

Major goal of CRE

4. Stoichiometry:

$$(16) \quad C_A = C_{T0} \left(\frac{F_A}{F_T} \right) P \left(\frac{T_0}{T} \right) \quad (\text{E12-7.16})$$

$$(17) \quad C_B = C_{T0} \left(\frac{F_B}{F_T} \right) P \left(\frac{T_0}{T} \right) \quad (\text{E12-7.17})$$

$$(18) \quad C_C = C_{T0} \left(\frac{F_C}{F_T} \right) P \left(\frac{T_0}{T} \right) \quad (\text{E12-7.18})$$

$$(19) \quad C_D = C_{T0} \left(\frac{F_D}{F_T} \right) P \left(\frac{T_0}{T} \right) \quad (\text{E12-7.19})$$

Neglect pressure drop

$$(20) \quad P = 1 \quad (\text{E12-7.20})$$

$$(21) \quad F_T = F_A + F_B + F_C + F_D \quad (\text{E12-7.21})$$

5. Parameters:

$$(22) \quad k_{1A} = 40 \exp \left[\frac{E_1}{R} \left(\frac{1}{300} - \frac{1}{T} \right) \right] \left(\text{dm}^3/\text{mol} \right)^2 / \text{min} \quad (\text{E12-7.22})$$

$$(23) \quad k_{2C} = 2 \exp \left[\frac{E_2}{R} \left(\frac{1}{300} - \frac{1}{T} \right) \right] \left(\text{dm}^3/\text{mol} \right)^4 / \text{min} \quad (\text{E12-7.23})$$

$$(24) \quad C_{A0} = 0.2 \text{ mol/dm}^3$$

$$(25) \quad R = 1.987 \text{ cal/mol/K}$$

$$(26) \quad E_1 = 8,000 \text{ cal/mol}$$

$$(27) \quad E_2 = 12,000 \text{ cal/mol}$$

Other parameters are given in the problem statement, that is, Equations (28) to (34).

$$(28) \quad C_{pA}, (29) \quad C_{pB}, (30) \quad C_{pC}, (31) \quad \dot{m}_c, (32) \quad \Delta H_{R1B}^\circ,$$

$$(33) \quad \Delta H_{R2A}^\circ, (34) \quad C_{pC0}$$

6. Energy Balance:

Recalling Equation (12-37)

$$(35) \quad \frac{dT}{dV} = \frac{Q_g - Q_r}{\sum F_j C_{Pj}} \quad (\text{E12-7.35})$$

The denominator of Equation (E12-7.35) is

$$(36) \quad \sum F_j C_{Pj} = F_A C_{PA} + F_B C_{PB} + F_C C_{PC} + F_D C_{PD} \quad (\text{E12-7.36})$$

The “heat removed” term is

$$(37) \quad Q_r = Ua(T - T_a) \quad (\text{E12-7.37})$$

The “heat generated” is

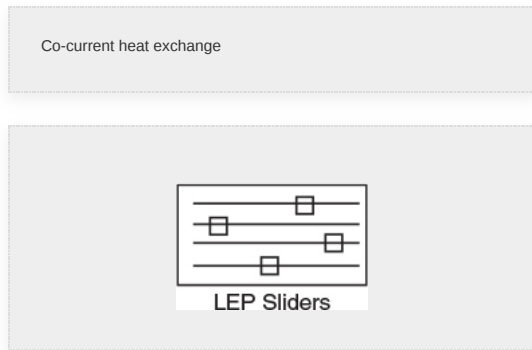
$$(38) \quad Q_r = \sum r_{ij} \Delta H_{Rxi} = r_{1B} \Delta H_{Rx1B} + r_{2B} \Delta H_{Rx2B} \quad (\text{E12-7.38})$$

(a) Co-current heat exchange

The heat exchange balance for co-current exchange is

$$(39) \quad \frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}_C C_{PC0}} \quad (\text{E12-7.39})$$

Part (a) Co-current flow: Plot and analyze the molar flow rates, and the reactor and coolant temperatures as a function of reactor volume. The Polymath code and output for co-current flow are shown in [Table E12-7.1](#).



Solution

TABLE E12-7.1 POLYMATH PROGRAM AND OUTPUT FOR
CO-CURRENT EXCHANGE

Differential equations

- 1 d(Fa)/d(V) = ra
- 2 d(Fb)/d(V) = rb
- 3 d(Fc)/d(V) = rc
- 4 d(Fd)/d(V) = rd
- 5 d(T)/d(V) = (Qg-Qr)/sumFiCpi
- 6 d(Ta)/d(V) = Ua*(T-Ta)/m/Cpco

Explicit equations

- 1 E2 = 12000
- 2 p = 1
- 3 R = 1.987
- 4 Ft = Fa+Fb+Fc+Fd
- 5 To = 300
- 6 k2c = 2*exp((E2/R)*(1/300-1/T))
- 7 E1 = 8000
- 8 Cto = 0.2
- 9 Ca = Cto*(Fa/Ft)*(To/T)^p
- 10 Cc = Cto*(Fc/Ft)*(To/T)^p
- 11 r2c = -k2c*Ca^2*Cc^3
- 12 Cpco = 10
- 13 m = 50
- 14 Cb = Cto*(Fb/Ft)*(To/T)^p
- 15 k1a = 40*exp ((E1/R)*(1/300-1/T))
- 16 r1a = -k1a*Ca*Cb^2
- 17 r1b = 2*r1a
- 18 rb = r1b
- 19 r2a = 2/3*r2c
- 20 DH1b = -15000

Calculated values of DEQ variables

	Variable	Initial value	Maximal value	Final value
1	Ca	0.0666667	0.0666667	0.0077046
2	Cb	0.1333333	0.1333333	0.0156981
3	Cc	0	0.0909427	0.0909427
4	Cpa	10.	10.	10.
5	Cpb	12.	12.	12.
6	Cpc	14.	14.	14.
7	Cpco	10.	10.	10.
8	Cpd	16.	16.	16.
9	Cto	0.2	0.2	0.2
10	DH1b	-1.5E+04	-1.5E+04	-1.5E+04
11	DH2a	-10000.	-10000.	-10000.
12	E1	8000.	8000.	8000.
13	E2	1.2E+04	1.2E+04	1.2E+04
14	Fa	5.	5.	0.3890865
15	Fb	10.	10.	0.7927648
16	Fc	0	4.592674	4.592674
17	Fd	0	0.003648	0.003648
18	Ft	15.	15.	5.778173
19	k1a	40.	2.861E+05	1.248E+04
20	k2c	2.	1.21E+06	1.102E+04
21	m	50.	50.	50.
22	p	1.	1.	1.
23	Qg	1422.222	9.589E+04	714.0015
24	Qr	-2000.	3.863E+04	1450.125
25	R	1.987	1.987	1.987
26	r1a	-0.0474074	-0.0236907	-0.0236907
27	r1b	-0.0948148	-0.0473814	-0.0473814
28	r1c	0.0474074	3.196187	0.0236907

21 DH2a = -10000

22 r1c = -r1a

23 Cpd = 16

24 Cpa = 10

25 Cpb = 12

26 Cpco = 14

27 sumFiCpi = Cpa*Fa+Cpb*Fb+Cpc*Fc+Cpd*Fd

28 rc = r1c+r2c

29 Ua = 80

30 r2d = -1/3*r2c

31 ra = r1a+r2a

32 rd = r2d

33 Qg = r1b*DH1b+r2a*DH2a

34 Qr = Ua*(T-Ta)

	Variable	Initial value	Maximal value	Final value
29	r2a	0	0	-0.000328
30	r2c	0	0	-0.000492
31	r2d	0	0.0021577	0.000164
32	ra	-0.0474074	-0.0240187	-0.0240187
33	rb	-0.0948148	-0.0473814	-0.0473814
34	rc	0.0474074	3.195219	0.0231987
35	rd	0	0.0021577	0.000164
36	sumFiCpi	170.	170.	77.75984
37	T	300.	885.7738	524.395
38	Ta	325.	506.2685	506.2685
39	To	300.	300.	300.
40	Ua	80.	80.	80.
41	V	0	10.	10.

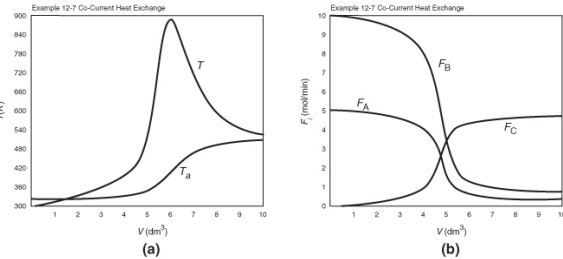
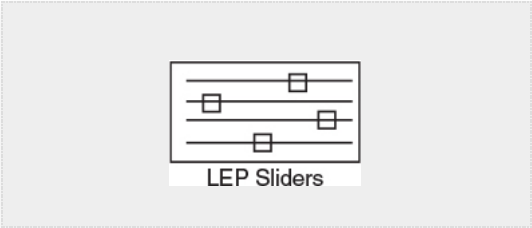


Figure E12-7.1 Profiles for co-current heat exchange; (a) temperature (b) molar flow rates.
Note: The molar flow rate FD is very small and is essentially the same as the bottom axis.

The temperature and molar flow rate profiles are shown in Figure E12-7.1.

Analysis: Part (a): We also note that the reactor temperature, T , increases when $Q_g > Q_r$ and reaches a maximum, $T = 886\text{ K}$, at approximately $V = 6\text{ dm}^3$. After that, $Q_r > Q_g$ the reactor temperature decreases and approaches T_a at the end of the reactor. For co-current heat exchange, the selectivity $\tilde{S}_{C/D} = \frac{4.59}{0.0035} = 1258$ is really quite good.

Part (b) Countercurrent heat exchange: Solution:
We will use the same program as part (a), but will change the sign of the heat-exchange balance and guess T_a at $V = 0$ to be 507 K and see whether the value gives us a T_{a0} of 325 K at $V = V_f$.

$$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{m_c C_{P_{Cool}}}$$

We find our guess of 507 K matches $T_{a0} = 325\text{ K}$. Are we lucky or what?!

The Polymath Program is shown in Table E12-7.2.

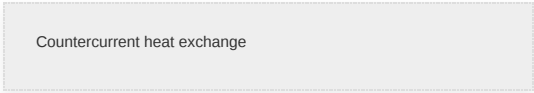


TABLE E12-7.2 POLYMATH PROGRAM AND OUTPUT FOR COUNTERCURRENT EXCHANGE

Differential equations

1 d(Fa)/d(V) = ra

2 d(Fb)/d(V) = rb

3 d(Fc)/d(V) = rc

4 d(Fd)/d(V) = rd

5 d(T)/d(V) = (Qg-Qr)/sumFICpi

6 d(Ta)/d(V) = -Ua*(T-Ta)/m/Cpco

Same **Explicit Equations** as part (a), that is, (1)–(34) pages 648–649.

Calculated values of DEQ variables

	Variable	Initial value	Maximal value	Final value
14	Fa	5.	5.	0.3863414
15	Fb	10.	10.	0.7882685
16	Fc	0	4.594177	4.594177
17	Fd	0	0.0038964	0.0038964
18	Ft	15.	15.	5.772683
37	T	300.	1101.439	327.1645
38	Ta	507.	536.1941	325.4494

↑
Matches

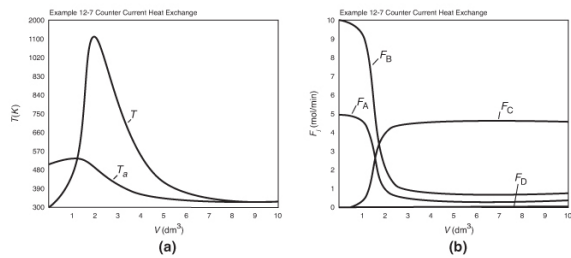


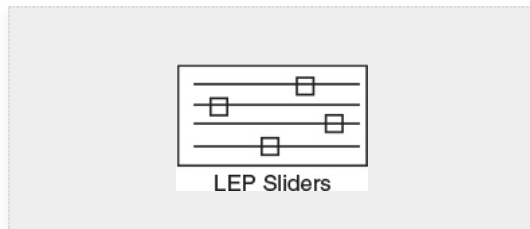
Figure E12-7.2 Profiles for countercurrent heat exchange; (a) temperature (b) molar flow

rates.

Analysis: Part (b): For countercurrent exchange, the coolant temperature reaches a maximum at $V = 1.3 \text{ dm}^3$ while the reactor temperature reaches a maximum at $V = 2.1 \text{ dm}^3$. The reactor with a countercurrent exchanger reaches a maximum reactor temperature of 1100 K, which is greater than that for the co-current exchanger, (i.e., 930 K). Consequently, if there is a concern about additional side reactions occurring at this maximum temperature of 1100 K, one should use a co-current exchanger or if possible use a large coolant flow rate to maintain constant T_a in the exchanger. In [Figure 12-7.2\(a\)](#) we see that the reactor temperature approaches the coolant entrance temperature at the end of the reactor. The selectivity for the countercurrent systems, $\tilde{S}_{C/D} = 1181$, is slightly lower than that for the co-current exchange.

Part (c) Constant T_a : Solution: To solve the case of constant heating-fluid temperature, we simply multiply the right-hand side of the heat-exchanger balance by zero, that is,

$$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}_c C_p} * 0$$



and use Equations (E12-7.1)–(E12-7.39). The Polymath Program is shown in [Table E12-7.3](#) and the temperature and molar flow rate profiles are shown in [Figures E12-7.3\(a\) and E12-7.3\(b\)](#), respectively.



TABLE E12-7.3 POLYMATH PROGRAM AND OUTPUT FOR
CONSTANT T_a

Differential equations

1 $d(F_a)/d(V) = r_a$

2 $d(F_b)/d(V) = r_b$

3 $d(F_c)/d(V) = r_c$

4 $d(F_d)/d(V) = r_d$

5 $d(T)/d(V) = (Q_g - Q_r)/\sum F_i C_{p,i}$

6 $d(T_a)/d(V) = Ua \cdot (T - T_a)/m \cdot C_{p,co} \cdot 0$

Same **Explicit Equations** as parts (a) and (b), pages 648–649.

Calculated values of DEQ variables

Variable	Initial value	Maximal value	Final value
14 Fa	5.	5.	0.5419419
15 Fb	10.	10.	1.093437
16 Fc	0	4.446116	4.446116
17 Fd	0	0.0023884	0.0023884
18 Ft	15.	15.	6.083884
37 T	300.	836.9449	345.643
38 Ta	325.	325.	325.

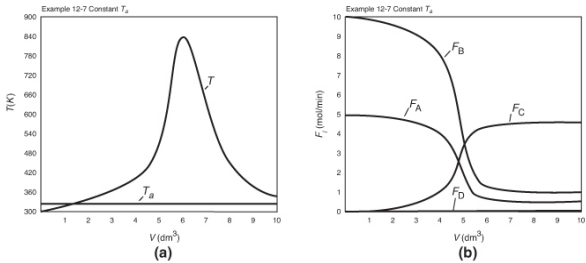
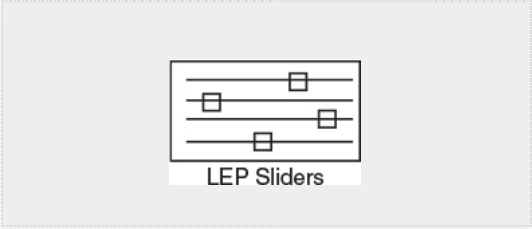


Figure E12-7.3 Profiles for constant T_a : (a) temperature (b) molar flow rates.

Analysis: Part (c): For constant T_a , the maximum reactor temperature, 837 K, is less than either co-current or countercurrent exchange while the selectivity, $\tilde{S}_{C/D} = 1861$ is greater than either co-current or countercurrent exchange. Consequently, one should investigate how to achieve sufficiently high mass flow of the coolant in order to maintain constant T_a .

Part (d) Adiabatic: To solve for the adiabatic case, we simply multiply the overall heat transfer coefficient by zero.

$$Ua = 80 \cdot 0$$

The Polymath Program is shown in Table E12-7.4 while the temperature and molar flow rate profiles are shown in Figures E12-7.4(a) and E12-7.4(b), respectively.



TABLE E12-7.4 POLYMATH PROGRAM AND OUTPUT FOR ADIABATIC OPERATION

Differential equations

1 d(Fa)/d(V) = ra

2 d(Fb)/d(V) = rb

3 d(Fc)/d(V) = rc

4 d(Fd)/d(V) = rd

5 d(T)/d(V) = (Qg-Qr)/sumFiCpi

6 d(Ta)/d(V) = Ua*(T-Ta)/m/Cpco

Explicit equations

29 Ua = 80*0

33 Qg = r1b*DH1b+r2a*DH2a

34 Qr = Ua*(T-Ta)

Explicit equations

Same as parts (a), (b), and (c) except change line 29 on page 649 to the following:

29 Ua = 80*0

Calculated values of DEQ variables

	Variable	Initial value	Final value
14	Fa	5.	0.1857289
15	Fb	10.	0.4123625
16	Fc	0	4.773366
17	Fd	0	0.0068175
18	Fi	15.	5.378275
37	T	300.	1548.299
38	Ta	325.	325.

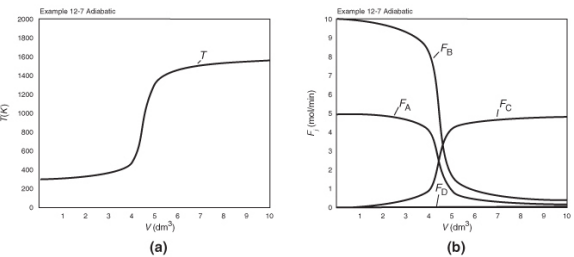
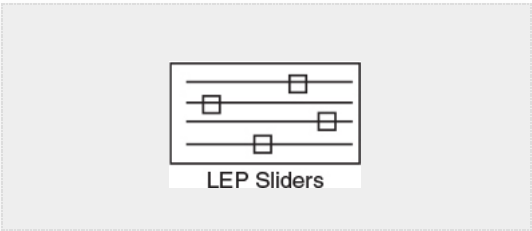


Figure E12-7.4 Profiles for adiabatic operation.



Analysis: Part (d): For the adiabatic case, the maximum temperature, which is the exit temperature, is higher than the other three exchange systems, and the selectivity is the lowest with $\tilde{S}_{C/D} = 700$. At this high temperature, the occurrence of unwanted side reactions certainly is a concern.

Overall Analysis Parts (a) to (d): Suppose the maximum temperature in each of these cases is outside the safety limit of 750 K for this system. **Problem P12-1A (i)** asks how you can keep the maximum temperature below 750 K.

12.7 RADIAL AND AXIAL TEMPERATURE VARIATIONS IN A TUBULAR REACTOR

In the previous sections, we have assumed that there were no radial variations in velocity, concentration, temperature, or reaction rate in the tubular and packed-bed reactors so that the axial profiles could be determined using an ordinary differential equation (ODE) solver. However, we consider both radial and axial variations in our mole and energy balance, we obtain partial differential equations (PDEs), which cannot be solved with Polymath and Wolfram. Consequently, it was decided to move this discussion on radial variation to Chapter 18 where we use the PDE solver COMSOL to explore two-dimensional problems of this type.

12.8 AND NOW... A WORD FROM OUR SPONSOR—SAFETY 12 (AWFOS–S12 SAFETY STATISTICS)[†]

[†] Also see <http://umich.edu/~safeche>.

12.8.1 The Process Safety Across the Chemical Engineering Curriculum Web site

The Process Safety Across the Chemical Engineering Curriculum Web site (<http://umich.edu/~safeche/index.html>)

provides a safety module for every core course in chemical engineering. A module consists of viewing a Chemical Safety Board (CSB) video, carrying out a safety analysis of the incident and doing a calculation related to a specific course. The Web site includes tutorials on a number of safety algorithms such as the BowTie Diagram (Section 6.7), the NFPA Diamond (Section 2.7), and the process Safety Pyramid (Section 9.5). This Web site was developed by the author of this text and the tutorials are also given at the end of the various chapters in a section titled “**A Word From Our Sponsor—Safety.**” The CRE safety modules include the explosions at Monsanto, Synthron, and T2 Laboratories. The CRE and safety Web sites are open to all as they have no passwords or other to be accessed.

12.8.2 Safety Statistics

Scaling up exothermic chemical reactions can be very tricky. Tables 12-5 and 12-6 give reactions that have resulted in accidents and their causes, respectively.⁷ The reader should review the case histories of these reactions to learn how to avoid similar accidents.

⁷ Courtesy of J. Singh, *Chemical Engineering*, 92 (1997) and B. Venugopal, *Chemical Engineering*, 54 (2002).

TABLE 12-5 INCIDENCE OF BATCH PROCESS ACCIDENTS

<i>Process Type</i>	<i>Number of Incidents in United Kingdom, 1962–1987</i>
Polymerization	64
Nitration	15
Sulfurization	13
Hydrolysis	10
Salt formation	8
Halogenation	8
Alkylation (Friedel-Crafts)	5
Amination	4
Diazolization	4
Oxidation	2
Esterification	1
Total:	134

Source: Courtesy of J. Singh, Chemical Engineering, 92 (1997).

TABLE 12-6 CAUSES OF BATCH REACTOR ACCIDENTS IN TABLE 12-5

<i>Cause</i>	<i>Contribution, %</i>
--------------	------------------------

Lack of knowledge of reaction chemistry	20
Problems with material quality	9
Temperature-control problems	19
Agitation problems	10
Mis-charging of reactants or catalyst	21
Poor maintenance	15
Operator error	5

Source: B. Venugopal, Chemical Engineering, 54 (2002).

Runaway reactions are the most dangerous in reactor operation, and a thorough understanding of how and when they could occur is part of the chemical reaction engineer's responsibility. The reaction in **Example 12-7** could be thought of as running away. Recall that as we moved down the length of the reactor, none of the cooling arrangements could keep the reactor from reaching an extremely high temperature (e.g., 800 K). In **Chapter 13**, we study case histories of two runaway reactions. One is the nitroaniline explosion discussed in **Example E13-2** and the other is **Example E13-6**, concerning the explosion at T2 Laboratories. See **Example 13-7** and videos on T2 Laboratories' explosion and what caused it to happen (<https://www.csb.gov/t2-laboratories-inc-reactive-chemical-explosion/> and <https://www.youtube.com/watch?v=C561PCq5E1g>).

There are many resources available for additional information on reactor safety and the management of chemical reactivity hazards. Guidelines for managing chemical reactivity hazards and other fire, explosion, and toxic release hazards are developed and published by the **Center for Chemical Process Safety (CCPS)** of the American Institute of Chemical Engineers. CCPS books and other resources are available at

www.aiche.org/ccps. For example, the book *Essential Practices for Managing Chemical Reactivity Hazards*, written by a team of industry experts, is also provided free of charge by CCPS on the site at <https://app.knovel.com/web/toc.v/cid:kpEPMCRH02/viewerType:toc/>. A concise and easy-to-use software program that can be used to determine the reactivity of substances or mixtures of substances, the Chemical Reactivity Worksheet, is provided by the National Oceanic and Atmospheric Administration (NOAA) for free on its Web site, www.noaa.gov.

12.8.3 Additional Resources CCPS and SACHe

The **Safety and Chemical Engineering Education (SACHe)** program was formed in 1992 as a cooperative effort between the AIChE, CCPS, and engineering schools to provide teaching materials and programs that bring elements of process safety into the education of undergraduate and graduate students studying chemical and biochemical products and processes. The **SACHe Web site** (www.sache.org) has a great discussion of reactor safety with examples as well as information on reactive materials. These materials are also suitable for training purposes in an industrial setting.

The following instruction modules are available on the SACHe Web site (www.sache.org).

1. *Chemical Reactivity Hazards*: This Web-based instructional module contains about 100 Web pages with extensive links, graphics, videos, and supplemental slides. It can be used either for classroom presentation or as a self-paced tutorial. The module is designed to supplement a junior or senior chemical engineering course by showing how uncontrolled chemical reactions in industry can lead to serious harm, and by introducing key concepts for avoiding unintended reactions and controlling intended reactions.
2. *Runaway Reactions: Experimental Characterization and Vent Sizing*: This instruction module describes the ARSST and its operation, and illustrates how this instrument can easily be used to experimentally determine the transient characteristics of runaway reactions, and how the resulting data can be analyzed and used to size the relief vent for such systems. The theory along with an example behind the **ARSST** is given on the CRE Web site under *Additional Material for Chapter 13* and the LEPs for *Chapter 13*, that is, PRS Example R13-1.
3. *Rupture of a Nitroaniline Reactor*: This case study demonstrates the concept of runaway reactions and how they are characterized and controlled to prevent major losses.
4. *Seveso Accidental Release Case History*: This presentation describes a widely discussed case history that illustrates how minor engineering errors

can cause significant problems; problems that should not be repeated. The accident was in Seveso, Italy, in 1976. It was a small release of a dioxin that caused many serious injuries.

Note: Access is restricted to SChE members and universities.

Membership in SChE is required to view these materials. Virtually all U.S. universities and many non-U.S. universities are members of SChE—contact your university SChE representative, listed on the SChE Web site, or your instructor or department chair to learn your university's username and password. Companies can also become members—see the SChE Web site for details.

Certificate Program

SChE also offers several certificate programs that are available to all chemical engineering students. Students can study the material, take an online test, and receive a certificate of completion. The following two certificate programs are of value for reaction engineering:

1. *Runaway Reactions*: This certificate focuses on managing chemical reaction hazards, particularly runaway reactions.
2. *Chemical Reactivity Hazards*: This is a Web-based certificate that provides an overview of the basic understanding of chemical reactivity hazards.

Many students are taking the certificate test online and put the fact that they successfully obtained the certificate on their résumés.

More information on safety is given in the *Summary Notes* and *Professional Reference Shelf* on the Web. Particularly study the use of the ARSST to detect potential problems. These will be discussed in *Chapter 13 Professional Reference Shelf R13.1* on the CRE Web site.

Closure. Virtually all reactions that are carried out in industry involve heat effects. This chapter provides the basis to design reactors that operate at steady state and involve heat effects. To model these reactors, we simply add another step to our algorithm; this step is the energy balance. Here, it is important to understand how the energy balance was applied to each reactor type so that you will be able to describe what would happen if you changed some of the operating conditions (e.g., the initial or entering temperature, T_0) in order to determine whether those changes result in unsafe conditions such as a runaway reaction. The *Living Example Problems* (especially T12-2) and the ICG module will help you achieve a high level of understanding of reactors and reactions with *heat effects*. Another major goal after studying this chapter is to

be able to design reactors that have multiple reactions taking place under nonisothermal conditions. Work through Problem 12-26_C to make sure you have achieved this goal. An industrial example that provides a number of practical details is included as an appendix to this chapter. We close with a brief discussion on safety and list some resources where you can obtain more information.

SUMMARY

1. For single reactions, the energy balance on a PFR/PBR in terms of *molar flow rate* is

$$\frac{dT}{dV} = \frac{(r_A)[\Delta H_{Rx}(T)] - Ua(T - T_a)}{\Sigma F_i C_{P_i}} = \frac{Q_g - Q_r}{\Sigma F_i C_{P_i}} \quad (\text{S12-1})$$

In terms of *conversion*

$$\frac{dT}{dV} = \frac{(r_A)[\Delta H_{Rx}(T)] - Ua(T - T_a)}{F_{A0}(\Sigma \Theta_j C_{P_j} + X \Delta C_p)} = \frac{Q_g - Q_r}{F_{A0}(\Sigma \Theta_j C_{P_j} + X \Delta C_p)} \quad (\text{S12-2})$$

2. The temperature dependence of the specific reaction rate is given in the form

$$k(T) = k(T_1) \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] = k(T_1) \exp \left[\frac{E}{R} \left(\frac{T - T_1}{TT_1} \right) \right] \quad (\text{S12-3})$$

3. The temperature dependence of the equilibrium constant is given by van't Hoff's equation for $\Delta C_p = 0$

$$K_P(T) = K_P(T_2) \exp \left[\frac{\Delta H_{Rx}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right) \right] \quad (\text{S12-4})$$

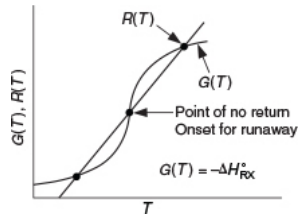
4. Neglecting changes in potential energy, kinetic energy, and viscous dissipation, and for the case of no work done on or by the system, large coolant flow rates (m_c), and all species entering at the same temperature, the steady-state CSTR energy balance for single reactions is

$$\frac{UA}{F_{A0}}(T_a - T) - X[\Delta H_{Rx}^\circ(T_R) + \Delta C_p(T - T_R)] = \Sigma \Theta_j C_{P_j}(T - T_{i0}) \quad (\text{S12-5})$$

5. Multiple steady states

$$G(T) = (-\Delta H_{Rx}^\circ) \left(\frac{-r_A V}{F_{A0}} \right) = (-\Delta H_{Rx}^\circ)(X) \quad (\text{S12-6})$$

$$R(T) = C_{P0}(1 + \kappa)(T - T_c) \quad (\text{S12-7})$$



where $\kappa = \frac{UA}{C_{p0}F_{A0}}$ and $T_c = \frac{\kappa T_a + T_0}{1 + \kappa}$

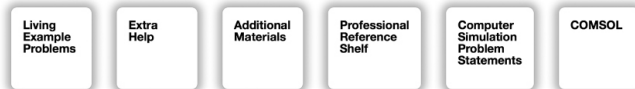
6. When q multiple reactions are taking place and there are m species

$$\frac{dT}{dV} = \frac{\sum_{i=1}^q (r_{ij}) [\Delta H_{Rij}(T)] - Ua(T - T_a)}{\sum_{j=1}^m F_j C_{pj}} = \frac{Q_g - Q_r}{\sum_{j=1}^m F_j C_{pj}} \quad (\text{S12-8})$$

CRE WEB SITE MATERIALS

([HTTP://WWW.UMICH.EDU/~ELEMENTS/6E/12CHAP/OBJ.HTML](http://www.umich.edu/~elements/6e/12chap/obj.html)
#/)

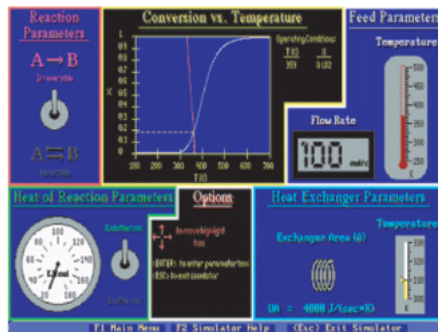
Useful Links



Evaluation

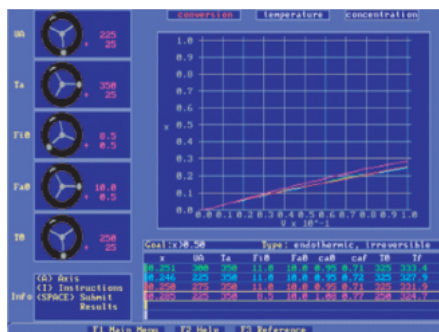


Interactive Computer Games that Talk to Each Other



Heat Effects I

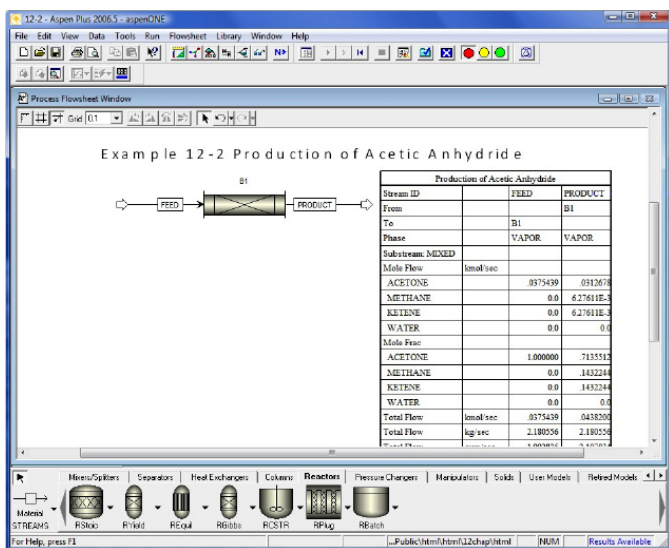
(<http://www.umich.edu/~elements/6e/icm/heatfx1.html>)



Heat Effects II

(<http://www.umich.edu/~elements/6e/icm/heatfx2.html>)

The derivation of the user-friendly energy balances are color coded and derived in the tutorials in Heat Effects I and Heat Effects II. Here you see animation of the various terms as they move around the screen and *talk to each other* to arrive at the final form of the balance equation.



A step-by-step AspenTech tutorial is given on the CRE Web site.

See [Example 12-2](#)

(<http://www.umich.edu/~elements/6e/software/aspen-example12-2.html>). Formulated in AspenTech: Download AspenTech directly from the CRE Web site.

QUESTIONS, SIMULATIONS, AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

A = ● B = ■ C = ◆ D = ◆◆

In each of the questions and problems, rather than just drawing a box around your answer, write a sentence or two describing how you solved the problem, the assumptions you made, the reasonableness of your answer, what you learned, and any other facts that you want to include. See Preface Section G.2 for additional generic parts (x), (y), and (z) to the home problems.

Before solving the problems, state or sketch qualitatively the expected results or trends.

Questions

Q12-1_A QBR (*Question Before Reading*). Before reading this chapter, identify the differences in applying the energy balance for co-current heat exchange and counter current heat exchange.

Q12-2_A i>clicker. Go to the Web site (http://www.umich.edu/~elements/6e/12chap/iclicker_ch12_q1.html) and view five i>clicker questions. Choose one that could be used as is, or a variation thereof, to be included on the next exam. You also could consider the opposite case: explaining why the question should *not* be on the next exam. In either case, explain your reasoning.

Q12-3_A Review Figure 12-13. Use this figure to write a few sentences (or at least draw an analogy) explaining why, when you strike the head of a safety match slowly on its pumice with little pressure, it may heat up a little, but does not ignite, yet when you put pressure on it and strike it rapidly, it does ignite. Thanks to Oscar Piedrahita, Medellín, Colombia.



Q12-4_A Read over the problems at the end of this chapter.

Make up an original problem that uses the concepts presented in this chapter. To obtain a solution:

- (a) Make up your data and reaction.
 - (b) Use a real reaction and real data. See Problem P5-1_A for guidelines.
 - (c) Prepare a list of safety considerations for designing and operating chemical reactors. (See www.sache.org.)
- The August 1985 issue of *Chemical Engineering Progress* may be useful for part (c).

Q12-5_A Go to the LearnChemE screencast link for Chapter 12

(<http://www.umich.edu/~elements/6e/12chap/learn-cheme-videos.html>). View one or more of the screencast 5- to 6-minute videos and write a two-sentence evaluation. What would you suggest changing in the video to increase the comment from Recommended to Highly Recommended?

Q12-6_A What did the section *And Now... A Word From Our Sponsor* point out or emphasize that was not done in the other AWFOS sections? What were the top two takeaway points in Chapter 12's AWFOS?

Computer Simulations and Experiments

We will use the *Living Example* on the CRE Web site extensively to carry out simulations. **Why** carry out simulations to vary the parameters in the *Living Example Problems*? We do it in order to

- Get a more intuitive feel reactor system.
- Gain insight about the most sensitive parameters (e.g., E , K_C) and how they affect outlet conditions.
- Learn how reactors are affected by different operating conditions.
- Simulate dangerous situations such as potential runaway reactions.
- Compare the model and parameters with experimental data.
- Optimize the reaction system.

P12-1_B (a) **LEP Table 12-2: Exothermic Reaction with Heat Exchange**

Download the Polymath, MATLAB, Python, or Wolfram codes for the algorithm and data given in Table T12-2 for the exothermic gas phase reversible reaction



given on the Web in the Living Example Problems (LEPs).

Vary the following parameters in the ranges shown in parts (i) through (xi). Write a paragraph describing the trends you find for each parameter variation and why they look the way they do. Use the base case for parameters not varied. **The feedback from students** on this problem is that one should use Wolfram on the Web in the LEP T12-2 as much as possible to carry out the parameter variations. For each part, write two or more sentences describing the trends.

Wolfram and Python

(i) This is a **Stop and Smell the Roses Simulation**. View the base case X , X_e , and T profiles and explain why the conversion (X and X_e) and temperature profiles look the way they do.



(ii) The slider parameters Ua/ρ , Θ_1 , F_{A0} , and ΔH_{Rx} all can be moved to make the X and X_e profiles to come together and to separate. What is the reason these sliders affect the profiles similarly?

(iii) Starting with the base case, determine which parameters when changed only a small amount most dramatically affects the conversion and temperature profiles.

(iv) What parameters separate X and X_e the most?

(v) Finally, write at least three conclusions about what you found in your experiments (i) through (iv).

Polymath

(vi) Vary T_0 : $310 \text{ K} \leq T_0 \leq 350 \text{ K}$ and write a conclusion.

(vii) Vary T_a : $300 \text{ K} \leq T_a \leq 340 \text{ K}$ and write a conclusion.

Repeat **(i)** for countercurrent coolant flow.

Hint: In analyzing the trends it might be helpful to plot X , X_e , and p as a function of W on the same graph and T and T_a as a function of W on the same graph.

(viii) Repeat this problem for the case of constant T_a and adiabatic operation, and describe the most dramatic affect

you find.

(b) Example 12-1: Butane Isomerization

Wolfram and Python Co-Current

This is another **Stop and Smell the Roses Simulation**.

(i) Describe the differences of the X , X_e , and T profiles between the four cases of heat exchange, co-current, counter current, constant T_a , and adiabatic.



(ii) Explain why the temperature (T and T_a) and conversion (X and X_e) look the way they do, and explain what happens to the X , X_e , T , and T_a profiles as you move slider y_{A0} .

(iii) What parameter value brings T and T_a profiles close together?

(iv) What parameter when varied separates X and X_e the most?

(v) What parameter keeps the X and X_e profiles the closest together?

(vi) Write at least three conclusions about what you found in your experiments (i) through (v).

Polymath Co-Current

(vii) What is the entering value of the temperature T_{a0} of the heat exchanger fluid below which the reaction will never “ignite”?

(viii) Vary some of the other parameters and see whether you can find unsafe operating conditions.

(ix) Plot Q_r and T_a as a function of V necessary to maintain isothermal operation.

Wolfram and Python Countercurrent

(x) Explain why T , T_a , X , and X_e profiles look the way they do for the base case.

(xi) Vary Ua and T_{a0} and describe what you find.

(xii) Vary y_{A0} and then one of the other parameters and describe what you find.

(xiii) Describe how Q_r and Q_g and their intersection change when you vary the molar flow rates of coolant, inert and y_{A0} .

(xiv) Write at least three conclusions about what you found in your experiments (x) through (xiii).

Polymath Countercurrent

(xv) Describe and explain what happens to the X and X_e profiles as you vary ΔH_{Rx} .

(xvi) Describe what happens to the temperature profile T and T_a as you vary F_{A0} .

(xvii) Compare the variations in the profiles for X , X_e , T , and T_a when you change the parameter values for all four cases: adiabatic, countercurrent exchange, co-current exchange, and constant T_a . What parameters when changed only a small amount dramatically change the profiles?

(xviii) The heat exchanger is designed for a maximum temperature of 370 K. Which parameter will you vary so that at least 75% conversion is still achieved while maintaining temperature under a safe limit?

Wolfram and Python Constant T_a

(xix) Vary y_{A0} and one other parameter of your choice, and describe how the X , X_e , and T profiles change.

(xx) Vary Ua and T_a and describe what you find.

(xxi) Vary ΔH_{Rx}° and then one of the other parameters (e.g., y_{A0}) and describe what you find.

(xxii) Write at least three conclusions about what you found in your experiments (xix)–(xxi).

Wolfram and Python Adiabatic Operation

(xxiii) Why do the shape of the profiles change in the way they do as you change y_{A0} ?

(xxiv) Write a set of three conclusions, one of which compares adiabatic operation with the other three modes of heat transfer (e.g., co-current).

(c) Example 12-2: Production of Acetic Anhydride- Endothermic Reaction Wolfram and Python

Co-Current



- (i) Explain why the temperatures (T and T_a) and conversions (X and X_e) look the way they do for the base case slider values.
- (ii) What parameter value when increased or decreased causes the reaction to die out the most quickly near the reactor entrance?
- (iii) Which parameter, when varied most, drastically changes the profiles?

Adiabatic

- (iv) How does the conversion change as heat capacity of A is increased?

Constant T_a

- (v) You find that conversion has decreased after 6 months of operation. You checked the flow rate and material properties and found that these values have not changed. Which parameter would have changed?

Countercurrent

- (vi) Explain why the temperatures (T and T_a) and conversions (X and X_e) look the way they do for the base case slider values.
- (vii) Discuss the most profound differences between the four heat exchange modes (e.g., co-current, adiabatic) for this endothermic reaction.
- (viii) Write two conclusions of what you learned from your experiments (i) through (vii).

Polymath

- (ix) Let $Q_g = r_A \Delta H_{R_X}$ and $Q_r = Ua(T - T_a)$, and then plot Q_g and Q_r on the same figure as a function of V .
- (x) Repeat (vi) for $V = 5 \text{ m}^3$.
- (xi) Plot Q_g , Q_r , and $-r_A$ versus V for all four cases on the same figure and describe what you find.
- (xii) For each of the four heat exchanger cases, investigate the addition of an inert I with a heat capacity

of 50 J/mol · K, keeping F_{A0} constant and letting the other inlet conditions adjust accordingly (e.g., ϵ).

(xiii) Vary the inert molar flow rate (i.e., Θ_I , $0.0 < \Theta_I < 3.0$ mol/s). Plot X and analyze versus Θ_I .

(xiv) Finally, vary the heat-exchange fluid temperature T_{a0} ($1000 \text{ K} < T_{a0} < 1350 \text{ K}$). Write a paragraph describing what you find, noting interesting profiles or results.

(d) Example 12-2: AspenTech Formulation. Go to the Aspen LEP and repeat Example 12-2 using AspenTech.

(e) Example 12-3: Production of Propylene Glycol in a CSTR

Wolfram and Python

(i) Vary activation energy (E) and find the values of E for which there are at least two solutions.

(ii) Vary the flow rate of F_{B0} to find the temperature at which the conversion is 0.8.

(iii) What is the operating range of inlet temperatures such that at least one steady state solution exists while maintaining the reactor temperature below 640°R?

Describe how your answers would change if the molar flow rate of methanol were increased by a factor of 4.

(iv) Vary V and find the points of (1) tangency and (2) intersection of X_{EB} and X_{MB} .

(v) Write a set of conclusions based on your experiments (i) through (iv).

(f) Example 12-4: CSTR with a Cooling Coil

Wolfram and Python

(i) Explore how variations in the activation energy (E) and in the heat of reaction, at reference temperature (ΔH_{Rx}°), affect the conversions X_{EB} and X_{MB} .

(ii) What variables most affect the intersection of and the points of tangency of X_{EB} and X_{MB} ?

(iii) Find a value of E and of ΔH_{Rx}° that increase conversion to more than 80% while maintaining the constraint of 125°F maximum temperature.

(iv) Write two conclusions about what you found in your experiments (i) through (iii).

Polymath

(v) The space time was calculated to be 0.01 minutes. Is this realistic? Decrease v_0 and both reaction rate constants

by a factor of 100 and describe what you find.

(vi) Use Figure E12-3.2 and Equation (E12-4.4) to plot X versus T to find the new exit conversion and temperature.

(vii) Other data on the Jofostan chemical engineering Web site show $\Delta H_{R_x}^\circ = -38700$ Btu/lb-mol and $\Delta C_p = 29$ Btu/lb-mol/°F. How would these values change your results?

(viii) Make a plot of conversion as a function of heat exchanger area. [$0 < A < 200$ ft²] and write a conclusion.

(g) Example 12-5: Parallel Reactions in a PFR with Heat Effects

Wolfram and Python

(i) Vary the sliders for the rate constants k_{1A0} and k_{2A0} and describe what you find.

(ii) What should be the initial concentration of A so that the company can produce equal flow rates of B and C?

(iii) Describe how the profiles for T , F_A , F_B , and F_C change as you move the sliders. Comment specifically on the drastic changes that occur when you change the overall heat transfer coefficient.

(iv) What set of conditions give you the greatest selectivity, $\tilde{S}_{B/C}$ at the exit and what is the corresponding conversion.

(v) Write at least three conclusions about what you found in your experiments (i) through (iv).

Polymath

(vi) Why is there a maximum in temperature? How would your results change if there is a -pressure drop with $\alpha = 1.05$ dm⁻³?

(vii) What if the reaction is reversible with $K_C = 10$ at 450 K?

(viii) How would the selectivity change if Ua is increased? Decreased?

(h) Example 12-6: Multiple Reactions in a CSTR (Use the LEP)

Wolfram and Python

(i) What is the minimum value of T_0 that causes the reactor temperature to jump to the single, upper steady-state value?

(ii) What is the operating range for the entering temperature T_0 for which there are only three steady

states?

(iii) Vary UA between 10,000 and 80,000, and describe how the number of steady-state solutions changes.

(iv) Write a set of conclusions from carrying out experiments (i) through (iii).

(i) Example 12-7: Complex Reactions with Heat Effects in a PFR—Safety

Wolfram and Python

(i) Co-current: Explore the effect of the coolant flow rate \dot{m}_c on the reactant temperature and coolant temperature profiles, and describe what you find.

(ii) Co-current: Explore the effect of Ua on the selectivity and describe what you find.

(iii) Constant T_a : How does the overall heat transfer coefficient affect the product flow rate distribution? Should it be kept minimum or maximum? Explain.

(iv) Constant T_a : Which are the variables that have virtually no effect on the profiles? Explain the reason.

(v) Adiabatic: You want to save capital cost by using a smaller volume reactor, that is, 5 dm³ instead of 10 dm³. Which parameters will you vary to achieve exit reactant and product flow rates same as base case?

(vi) Describe how the selectivity, $\tilde{S}_{C/D}$ changes as you change the parameters and operating conditions. What two variable slider(s) affect $\tilde{S}_{C/D}$ the most?

(vii) Write a set of conclusions of what you learned in experiments (i) through (vi).

Polymath

(viii) Plot Q_g and Q_r as a function of V . How can you keep the maximum temperature below 700 K? Would adding inerts help, and if so what should the flow rate be if $C_{p_i} = 10$ cal/mol/K?

(ix) Look at the figures. What happened to species D? What conditions would you suggest to make more species D?

(x) Make a table of the temperature (e.g., maximum T , T_a) and molar flow rates at two or three volumes, comparing the different heat-exchanger operations.

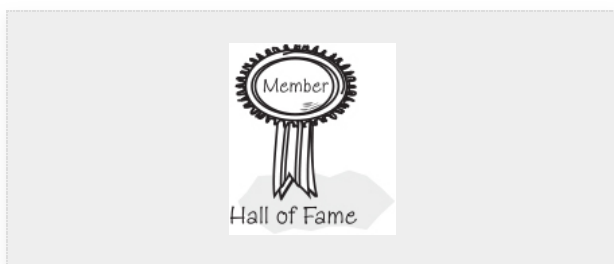
(xi) Why do you think the molar flow rate of C does not go through a maximum? Vary some of the parameters to learn whether there are conditions where it goes through a maximum. Start by increasing F_{A0} by a factor of 5.

(xii) Include pressure in this problem. Vary the pressure-drop parameter ($0 < \alpha p_b < 0.0999 \text{ dm}^{-3}$) and describe what you find and write a conclusion.

(j) Review the steps and procedure by which we derived Equation (12-5) and then, by analogy, derive Equation (12-35).

(k) CRE Web site SO₂ Example PRS-R12.4-1.

Download the SO₂ oxidation **LEP R12-1**. How would your results change if (1) the catalyst particle diameter were cut in half? (2) The pressure were doubled? At what particle size does pressure drop become important for the same catalyst weight, assuming the porosity doesn't change? (3) You vary the initial temperature and the coolant temperature? Write a paragraph with at least two conclusions describing what you find.



(l) SACHe. Go to the SACHe Web site, www.sache.org. Your instructor or department chair should have the username and password to enter the SACHe Web site in order to obtain the modules with the problems. On the left-hand menu, select "SACHe Products." Select the "All" tab and go to the module titled, "Safety, Health and the Environment" (S, H & E). The problems are for KINETICS (i.e., CRE). There are some example problems marked "K" and explanations in each of the above S, H & E selections. Solutions to the problems are in a different section of the site. Specifically look at: *Loss of Cooling Water* (K-1), *Runaway Reactions* (HT-1), *Design of Relief Values* (D-2), *Temperature Control and Runaway* (K-4) and (K-5), and *Runaway and the Critical Temperature Region* (K-7). Go through the K problems and write a paragraph on what you have learned.

**P12-2_B (a) Example 12-2 Production of Acetic Anhydride
Endothermic Reaction**

Case 1 Adiabatic

- (i) Vary inlet flow rate of inert and observe the conversion and temperature profiles. Describe what you find.
- (ii) Find inlet temperature, T_0 , for which the reaction rate at $V = 0.001 \text{ m}^3$ is 0.1 times the rate at inlet. Note the conversion at the reactor exit for this temperature.
- (iii) After varying two other parameters, write a set of conclusions from your experiments in (i) and (ii).

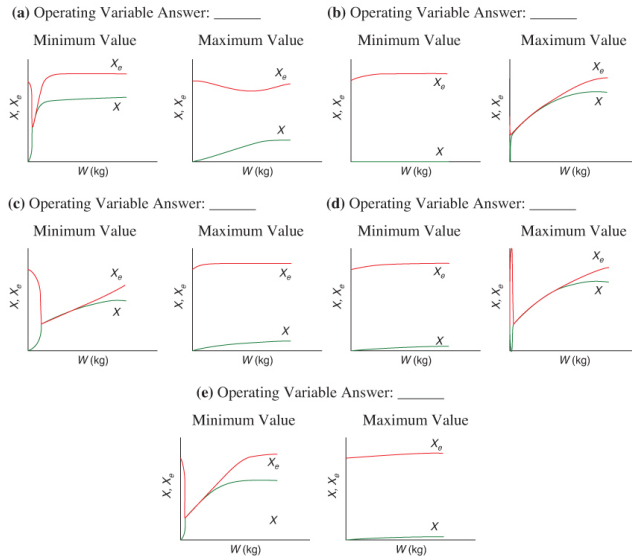
Case 2 Constant T_a

- (iv) To reduce operating cost, the inlet temperature of heating fluid can be reduced. Can you find a minimum temperature of heating fluid at which exit conversion is virtually 100% for constant T_a .
- (v) Find maximum value of the inlet concentration for which the conversion at exit is virtually 100% constant T_a .
- (vi) Write a set of conclusions from your experiments in (iv) and (v).

P12-3_B OEQ (Old Exam Question). Computer Experiments on a PFR for Reaction in Table 12-2.2. In order to develop a greater understanding of the temperature effects in PFRs, download the Living Example Problem Table 12-2, **LEP T12-2**, from the Web site to learn how changing the different parameters changes the conversion and temperature profiles.

This is a Sherlock Holmes Problem. Starting with the base case, one, and only one, parameter was varied between its maximum and minimum values to give the following figures. You need to decide what operating variable (e.g., T_0) property value (e.g., C_{PA}), or engineering variable (e.g., $\frac{U_a}{\rho_b}$) was varied. Choose from the following:

$$k_1, E, R, C_{T0}, T_a, T_0, T_1, T_2, K_{C2}, \Theta_B, \Theta_1, \Delta H_{Rx}^\circ, C_{PA}, C_{PB}, C_{PC}, U_a, \rho_a$$



Interactive Computer Games

P12-4A Download the Interactive Computer Games (ICG)

from the CRE Web site. Play the game, and then record your performance number for the module, which indicates your mastery of the material. *Note:* For simulation (b), only do the first three reactors, as reactors 4 and above do not work because of the technician tinkering with them.



(a) ICG Heat Effects Basketball 1 Performance # _____.

(b) ICG Heat Effects Simulation 2 Performance # _____.

Before attempting to play the ICG/Interactive Computer Games simulations, be sure to first go through the reviews to see the equations *talking* to each other.



Problems

P12-5_C OEQ (Old Exam Question). Safety Problem.

The following is an excerpt from *The Morning News*,
Wilmington, Delaware (August 3, 1977):

“Investigators sift through the debris from blast in quest for the cause [that destroyed the new nitrous oxide plant]. A company spokesman said it appears more likely that the [fatal] blast was caused by another gas—ammonium nitrate—used to produce nitrous oxide.” An 83% (wt) ammonium nitrate and 17% water solution is fed at 200°F to the CSTR operated at a temperature of about 510°F. Molten ammonium nitrate decomposes directly to produce gaseous nitrous oxide and steam. It is believed that pressure fluctuations were observed in the system and, as a result, the molten ammonium nitrate feed to the reactor may have been shut off approximately 4 min prior to the explosion.

Assume that at the time the feed to the CSTR stopped, there was 500 lb_m of ammonium nitrate in the reactor. The conversion in the reactor is believed to be virtually complete at about 99.99%.

Additional information (approximate but close to the real case):

$$\Delta H_{\text{Rx}}^{\circ} = -336 \text{ Btu/lb}_m \text{ ammonium nitrate at } 500^{\circ}\text{F (constant)}$$

$$C_P = 0.38 \text{ Btu/lb}_m \text{ ammonium nitrate} \cdot ^{\circ}\text{F}$$

$$C_P = 0.47 \text{ Btu/lb}_m \text{ of steam} \cdot ^{\circ}\text{F}$$

$$-r_A V = k C_A V = k \frac{M}{V} V = k M (\text{lb}_m/\text{h})$$

where M is the mass of ammonium nitrate in the CSTR (lb_m) and k is given by the relationship below.

$T (^{\circ}\text{F})$	510	560
$k (\text{h}^{-1})$	0.307	2.912

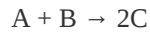
The enthalpies of water and steam are

$$H_w(200^{\circ}\text{F}) = 168 \text{ Btu/lb}_m$$

$$H_g(500^{\circ}\text{F}) = 1202 \text{ Btu/lb}_m$$

- (a) Can you explain the cause of the blast? *Hint:* See Problem P13-3_B.
- (b) If the feed rate to the reactor just before shutoff was 310 lb_m of solution per hour, what was the exact temperature in the reactor just prior to shutdown? *Hint:* Plot Q_r and Q_g as a function of temperature on the same plot.
- (c) How would you start up or shut down and control such a reaction? *Hint:* See Problem P13-2_B.
- (d) Explore this problem and describe what you find. For example, add a heat exchanger $UA(T - T_a)$, choose values of UA and T_a , and then plot $R(T)$ versus $G(T)$?
- (e) Discuss what you believe to be the point of the problem. The idea for this problem originated from an article by Ben Horowitz.

P12-6_B OEQ (*Old Exam Question*)—*Taken from California Professional Engineer's Exam. The endothermic liquid-phase elementary reaction*



proceeds, substantially, to completion in a single steam-jacketed, continuous-stirred reactor (Table P12-6_B). From the following data, calculate the steady-state reactor temperature:

Reactor volume: 125 gal

Steam jacket area: 10 ft²

Jacket steam: 150 psig (365.9°F saturation temperature)

Overall heat-transfer coefficient of jacket, U : 150 Btu/h · ft² · °F

Agitator shaft horsepower: 25 hp

Heat of reaction, $\Delta H_{R,x}^\circ = +20000$ Btu/lb-mol of A (independent of temperature)

TABLE P12-6_B FEED CONDITIONS AND PROPERTIES

Component			
A	B	C	
Feed (lb-mol/hr)			
	10.0	10.0	0
Feed temperature (°F)			
	80	80	—
Specific heat (Btu/lb-mol·°F)*			
	51.0	44.0	47.5
Molecular weight			
	128	94	111
Density (lb _m /ft ³)			
	63.0	67.2	65.0

* Independent of temperature. (**Ans:** $T = 199^\circ\text{F}$)

(Courtesy of the California Board of Registration for Professional & land surveyors.)

P12-7_B OEQ (Old Exam Question). Use the data in Problem P11-4_A for the following reaction. The elementary, irreversible, organic liquid-phase reaction



is carried out in a flow reactor. An equal molar feed in A and B enters at 27°C , and the volumetric flow rate is $2 \text{ dm}^3/\text{s}$ and $C_{A0} = 0.1 \text{ kmol/m}^3$.

Additional information:

$$H_A^\circ(273\text{K}) = -20\text{kcal/mol}, \quad H_B^\circ(273\text{K}) = -15\text{kcal/mol}, \quad H_C^\circ(273\text{K}) = -41\text{kcal/mol}$$

$$C_{PA} = C_{PB} = 15 \text{ cal/mol} \cdot \text{K} \quad C_{PC} = 30 \text{ cal/mol} \cdot \text{K}$$

$$k = 0.01 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \text{ at } 300 \text{ K} \quad E = 10000 \text{ cal/mol}$$

$$Ua = 20 \text{ cal/m}^3 \cdot \text{s/K} \quad \dot{m}_C = 50 \text{ g/s}$$

$$T_{a0} = 450\text{K} \quad C_{PCool} = 1\text{cal/g/K}$$

(a) Calculate the conversion when the reaction is carried out adiabatically in one 500-dm^3 CSTR and then compare the results with the two adiabatic 250-dm^3 CSTRs in series.

The reversible reaction (part **(d)** of Problem P11-4_A) is now carried out in a PFR with a heat exchanger. Plot and then analyze X , X_e , T , T_a , Q_r , Q_g , and the rate, $-r_A$, for the following cases:

- (b) Constant heat-exchanger temperature T_a
- (c) Co-current heat exchanger T_a (**Ans:** At $V = 10 \text{ m}^3$ then $X = 0.36$ and $T = 442 \text{ K}$)
- (d) Countercurrent heat exchanger T_a (**Ans:** At $V = 10 \text{ m}^3$ then $X = 0.364$ and $T = 450 \text{ K}$)
- (e) Adiabatic operation
- (f) Make a table comparing all your results (e.g., X , X_e , T , T_a). Write a paragraph describing what you find.
- (g) Plot Q_r and T_a as a function of V necessary to maintain isothermal operation.

P12-8_A The gas-phase reversible reaction as discussed in Problem P11-7_B



is now carried out under high pressure in a packed-bed reactor with pressure drop. The feed consists of both inerts I and species A with the ratio of inerts to the species A being 2 to 1. The entering molar flow rate of A is 5 mol/min at a temperature of 300 K and a concentration of 2 mol/dm³.

Work this problem in terms of volume. *Hint:*

$$V = W/\rho_B, r_A = \rho_B r'_A$$

Additional information:

$F_{A0} = 5.0 \text{ mol/min}$	$T_0 = 300K$	$\Delta H_{Rx} = -20000 \text{ cal/mol}$	$\alpha \rho_b = 0.02 \text{ dm}^{-3}$
$C_{A0} = 2 \text{ mol/dm}^3$	$T_1 = 300K$	$K_C = 1000 \text{ at } 300 \text{ K}$	<u>Coolant</u>
$C_1 = 2C_{A0}$	$k_1 = 0.1 \text{ min}^{-2} \text{ at } 300 \text{ K}$	$C_{PB} = 160 \text{ cal/mol/K}$	$\dot{m}_C = 50 \text{ mol/min}$
$C_{Pi} = 18 \text{ cal/mol/K}$	$Ua = 150 \text{ cal/dm}^3/\text{min/K}$	$p_B = 1.2 \text{ kg/dm}^3$	$C_{P_{Cool}} = 20 \text{ cal/mol/K}$
$C_{PA} = 160 \text{ cal/mol/K}$	$T_{a0} = 300K$		
$E = 10000 \text{ cal/mol}$	$V = 40 \text{ dm}^3$		

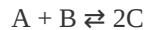
Plot and then analyze X , X_e , T , T_a , and the rate ($-r_A$) profiles in a PFR for the following cases. In each case, explain why the curves look the way they do.

- (a) Co-current heat exchange
- (b) Countercurrent heat exchange (**Ans:** When $V = 20 \text{ dm}^3$ then $X = 0.86$ and $X_e = 0.94$)
- (c) Constant heat-exchanger temperature T_a

- (d) Compare and contrast each of the above results and the results for adiabatic operation (e.g., make a plot or a table of X and X_e obtained in each case).
- (e) Vary some of the parameters, for example, ($0 < \Theta_1 < 10$) and describe what you find.
- (f) Plot Q_r and T_a as a function of V necessary to maintain isothermal operation.

P12-9_A Algorithm for reaction in a PBR with heat effects and pressure drop

The elementary gas-phase reaction



in Problem P11-8_B is now continued and carried out in packed-bed reactor. The entering molar flow rates are $F_{A0} = 5 \text{ mol/s}$, $F_{B0} = 2F_{A0}$, and $F_I = 2F_{A0}$ with $C_{A0} = 0.2 \text{ mol/dm}^3$. The entering temperature is 325 K and a coolant fluid is available at 300 K.

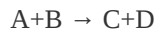
Additional information:

$$\begin{aligned} C_{P_A} = C_{P_B} = C_{P_C} &= 20 \text{ cal/mol/K} & k &= 0.0002 \frac{\text{dm}^6}{\text{kg}\cdot\text{mol}\cdot\text{s}} @ 300\text{K} \\ C_{P_A} &= 18 \text{ cal/mol/K} & \alpha &= 0.00015 \text{ kg}^{-1} & Ua &= 320 \frac{\text{Cal}}{\text{s}\cdot\text{m}^3\cdot\text{K}} \\ E &= 25 \frac{\text{kcal}}{\text{mol}} & \dot{m}_C &= 18 \text{ mol/s} & \rho_b &= 1400 \frac{\text{kg}}{\text{m}^3} \\ \Delta H_{R_x} &= -20 \frac{\text{kcal}}{\text{mol}} @ 298 \text{ K} & C_{P_{\text{Cool}}} &= 18 \text{ cal/mol (coolant)} \\ & & K_C &= 1000 @ 305\text{K} \end{aligned}$$

Plot X , X_e , T , T_a , and $-r_A$ down the length of the PFR for the following cases:

- (a) Co-current heat exchange
- (b) Countercurrent heat exchange
- (c) Constant heat-exchanger temperature T_a
- (d) Compare and contrast your results for (a), (b), and (c) along with those for adiabatic operation and write a paragraph describing what you find.

P12-10_B Use the data and reaction in Problems P11-4_A and P12-7_B for the following reaction:



- (a) Plot and then analyze the conversion, Q_r , Q_g , and temperature profiles up to a PFR reactor volume of 10 dm^3 for the case when the reaction is reversible with $K_C = 10$

m^3/kmol at 450 K. Plot and then analyze the equilibrium conversion profile.

(b) Repeat **(a)** when a heat exchanger is added, $Ua = 20 \text{ cal/m}^3\text{/s/K}$, and the coolant temperature is constant at $T_a = 450 \text{ K}$.

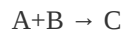
(c) Repeat **(b)** for both a co-current and a countercurrent heat exchanger. The coolant flow rate is 50 g/s, $C_{p_c} = 1 \text{ cal/g} \cdot \text{K}$, and the inlet coolant temperature is $T_{a0} = 450 \text{ K}$. Vary the coolant rate ($10 < \dot{m}_c < 1000 \text{ g/s}$).

(d) Plot Q_r and T_a as a function of V necessary to maintain isothermal operation.

(e) Compare your answers to **(a)** through **(d)** and describe what you find. What generalizations can you make?

(f) Repeat **(c)** and **(d)** when the reaction is irreversible but endothermic with $\Delta H_{\text{Rx}}^\circ = 6000 \text{ cal/mol}$. Choose $T_{a0} = 450 \text{ K}$.

P12-11_B OEQ (Old Exam Question). Use the reaction data in Problems P11-4_A and P12-7_B for the case when heat is removed by a heat exchanger jacketing the reactor. The flow rate of coolant through the jacket is sufficiently high that the ambient exchanger temperature is constant at $T_a = 50^\circ\text{C}$.



(a) (1) Plot and then analyze the temperature conversion, Q_r , and Q_g profiles for a PBR with where

$$\frac{Ua}{\rho_b} = 0.08 \frac{\text{J}}{\text{s} \cdot \text{kg-cat} \cdot \text{K}}$$

where

ρ_b = bulk density of the catalyst (kg/m^3)

a = heat-exchange area per unit volume of reactor (m^2/m^3)

U = overall heat transfer coefficient ($\text{J/s} \cdot \text{m}^2 \cdot \text{K}$)

(2) How would the profiles change if Ua/ρ_b were increased by a factor of 3000?

(3) If there is a pressure drop with $\alpha = 0.019 \text{ kg}^{-1}$?

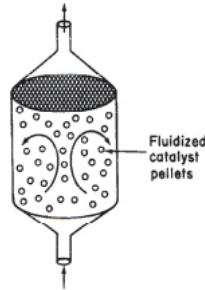
(b) Repeat part **(a)** for co-current and countercurrent flow and adiabatic operation with $\dot{m}_c = 0.2 \text{ kg/s}$, $C_{p_c} = 5000 \text{ J/kg K}$ and an entering coolant temperature of 50°C .

(c) Find X and T for a “fluidized” CSTR with 80 kg of catalyst.

$$UA = 500 \frac{\text{J}}{\text{s}\cdot\text{K}}, \quad \rho_b = 1 \text{ kg/m}^3$$

(d) Repeat parts (a) and (b) for $W = 80.0 \text{ kg}$, assuming a reversible reaction with a reverse specific reaction rate of

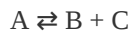
$$k_r = 0.2 \exp \left[\frac{E_r}{R} \left(\frac{1}{450} - \frac{1}{T} \right) \right] \left(\frac{\text{dm}^6}{\text{kg-cat}\cdot\text{mol}\cdot\text{s}} \right); \quad E_r = 51.4 \text{ kJ/mol}$$



Vary the entering temperature, T_0 , and describe what you find.

(e) Use or modify the data in this problem to suggest another question or calculation. Explain why your question requires either critical thinking or creative thinking. See Preface Section G and <http://www.umich.edu/~scps>.

P12-12C Derive the energy balance for a packed-bed membrane reactor. Apply the balance to the reaction in Problem P11-5A



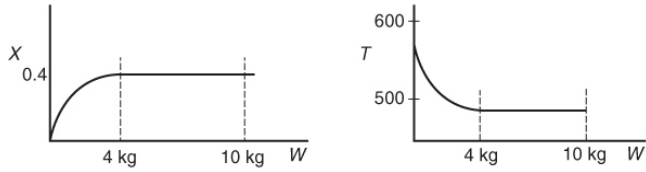
for the case when it is reversible with $K_C = 1.0 \text{ mol/dm}^3$ at 300 K. Species C diffuses out of the membrane with $k_C = 1.5 \text{ s}^{-1}$.

(a) Plot and then analyze the concentration profiles for different values of K_C when the reaction is carried out adiabatically.

(b) Repeat part (a) when the heat transfer coefficient is $Ua = 30 \text{ J/s}\cdot\text{kg-cat}\cdot\text{K}$ with $T_a = 50^\circ\text{C}$.

P12-13B OEQ (Old Exam Question). Circle the correct answer.

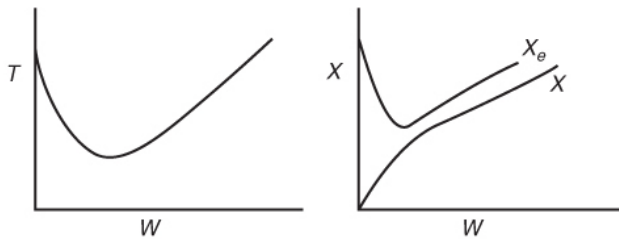
(a) The elementary reversible isomerization of A to B was carried out in a packed-bed reactor. The following profiles were obtained:



If the total entering volumetric flow rate remains constant, the addition of inerts to the feed stream will most likely

- A) Increase conversion.
- B) Decrease conversion.
- C) Have no effect.
- D) Insufficient information to tell

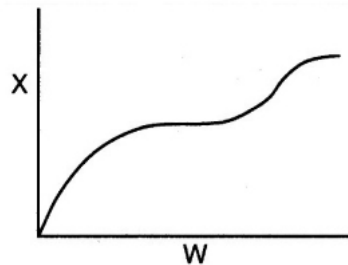
(b)



Which of the following statements are true?

- A) The above reaction could be adiabatic.
- B) The above reaction could be exothermic with constant cooling temperature.
- C) The above reaction could be endothermic with constant heating temperature.
- D) The above reaction could be second order.

(c) The conversion is shown below as a function of catalyst weight down a PBR.



Which of the following statements are false?

- A) The reaction could be first-order endothermic and carried out adiabatically.

B) The reaction could be first-order endothermic and reactor is heated along the length with T_a being constant.

C) The reaction could be second-order exothermic and cooled along the length of the reactor with T_a being constant.

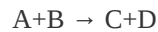
D) The reaction could be second-order exothermic and carried out adiabatically.

E) The reaction could be irreversible.

To view more conceptual problems similar to (a)–(c) above go to

http://www.umich.edu/~elements/6e/12chap/iclicker_ch12_q1.html.

P12-14_A OEQ (Old Exam Question). The irreversible reaction



is carried out adiabatically in a CSTR. The “heat generated” $G(T)$ and the “heat removed” $R(T)$ curves are shown in Figure P12-14_A.

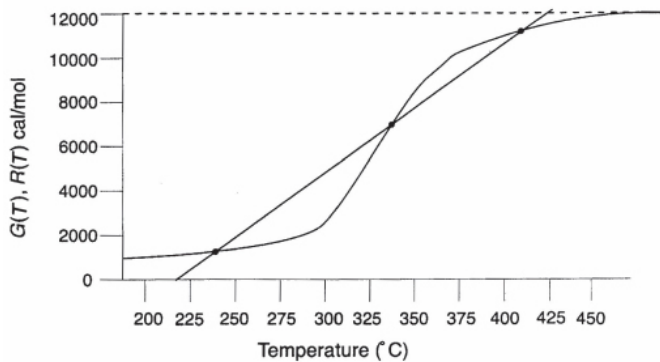


Figure P12-14_A Heat removed $R(T)$ and heat “generated” $G(T)$ curves.

- What is the ΔH_{R_x} of the reaction?
- What are the inlet ignition and extinction temperatures?
- What are all the temperatures in the reactor corresponding to the inlet ignition and extinction temperatures?
- What are the conversions at the ignition and extinction temperatures?

P12-15_B The first-order, irreversible, exothermic liquid-phase reaction



is to be carried out in a jacketed CSTR. Species A and an inert I are fed to the reactor in equimolar amounts. The molar feed rate of A is 80 mol/min.

Additional information:

Heat capacity of the inert: $30 \text{ cal/mol} \cdot ^\circ \text{C}$ $\tau = 100 \text{ min}$

Heat capacity of A and B: $20 \text{ cal/mol} \cdot ^\circ \text{C}$ $\Delta H_{\text{Rx}}^\circ = -7500 \text{ cal/mol}$

UA: $8000 \text{ cal/min} \cdot ^\circ \text{C}$ $k = 6.6 \times 10^{-3} \text{ min}^{-1}$ at 350 K

Ambient temperature, T_a : 300 K $E = 40000 \text{ cal/mol} \cdot \text{K}$

(a) What is the reactor temperature for a feed temperature of 450 K?

(b) Plot and then analyze the reactor temperature as a function of the feed temperature.

(c) To what inlet temperature must the fluid be preheated for the reactor to operate at a high conversion? What are the corresponding temperature and conversion of the fluid in the CSTR at this inlet temperature?

(d) Suppose that the fluid inlet temperature is now heated 5°C above the reactor temperature in part (c) and then cooled 20°C , where it remains. What will be the conversion?

(e) What is the inlet extinction temperature for this reaction system? (**Ans:** $T_0 = 87^\circ \text{C}$)

P12-16B The elementary reversible liquid-phase reaction



takes place in a CSTR with a heat exchanger. Pure A enters the reactor.

(a) Derive an expression (or set of expressions) to calculate $G(T)$ as a function of the heat of reaction, equilibrium constant, temperature, and so on. Show a sample calculation for $G(T)$ at $T = 400 \text{ K}$.

(b) What are the steady-state temperatures? (**Ans:** 310, 377, 418 K)

(c) Which steady states are locally stable?

(d) What is the conversion corresponding to the upper steady state?

(e) Vary the ambient temperature T_a and make a plot of the reactor temperature as a function of T_a , identifying the ignition and extinction temperatures.

(f) If the heat exchanger in the reactor suddenly fails (i.e., $UA = 0$), what would be the conversion and the reactor temperature when the new upper steady state is reached?

(Ans: 431 K)

(g) What heat exchanger product, UA , will give the maximum conversion?

(h) Write a question that requires critical thinking and then explain why your question requires critical thinking.
Hint: See Preface Section G.

(i) What is the adiabatic blowout flow rate, v_0 ?

(j) Suppose that you want to operate at the lower steady state. What parameter values would you suggest to prevent runaway, for example, the upper SS?

Additional information:

$$\begin{array}{ll}
 UA = 3600 \text{ cal/min} \cdot K & E/R = 20000K \\
 C_{P_A} = C_{P_B} = 40 \text{ cal/mol} \cdot K & V = 10 \text{ dm}^3 \\
 \Delta H_{R_x}^\circ = -80000 \text{ cal/mol A} & v_0 = 1 \text{ dm}^3/\text{min} \\
 K_C = 100 \text{ at } 400\text{k} & F_{A0} = 10 \text{ mol/min} \\
 k = 1 \text{ min}^{-1} \text{ at } 400 \text{ K} & \\
 \text{Ambient temperature, } T_a = 37^\circ & \text{Feed temperature, } T_0 = 37^\circ C
 \end{array}$$

P12-17_B OEQ (Old Exam Question). The reversible liquid-phase reaction



is carried out in a 12-dm³ CSTR with heat exchange. Both the entering temperature, T_0 , and the heat exchange fluid, T_a , are at 330 K. An equal molar mixture of inerts and A enter the reactor.

(a) Choose a temperature, T , and carry out a calculation to find $G(T)$ to show that your calculation agrees with the corresponding $G(T)$ value on the curve shown in **Figure P12-17_B** at the temperature you choose.

(b) Find the exit conversion and temperature from the CSTR. $X = \underline{\hspace{1cm}}$ $T = \underline{\hspace{1cm}}$ Answers

(c) What entering temperature T_0 would give you the maximum conversion? $T_0 = \underline{\hspace{1cm}}$ $X = \underline{\hspace{1cm}}$

(d) What would the exit conversion and temperature be if the heat-exchange system failed (i.e., $U = 0$)?

(e) Can you find the inlet ignition and extinction temperatures? If yes, what are they? If not, go on to the next problem.

(f) Use Preface Section G to ask another question.

Additional information:

The $G(T)$ curve for this reaction is shown in Figure P12-17B.

$$C_{P_A} = C_{P_B} = 100 \text{ cal/mol/K}, C_{P_I} = 150 \text{ cal/mol/K} \quad k = 0.001 \text{ h}^{-1} \text{ at } 300 \text{ K with } E = 30000 \text{ cal/mol}$$

$$F_{A0} = 10 \text{ mol/h}, C_{A0} = 1 \text{ mol/dm}^3, v_0 = 10 \text{ dm}^3/\text{h} \quad K_C = 5,000,000 \text{ at } 300 \text{ K}$$

$$\Delta H_{R_x} = -42000 \text{ cal/mol} \quad UA = 5000 \text{ cal/h/K}$$

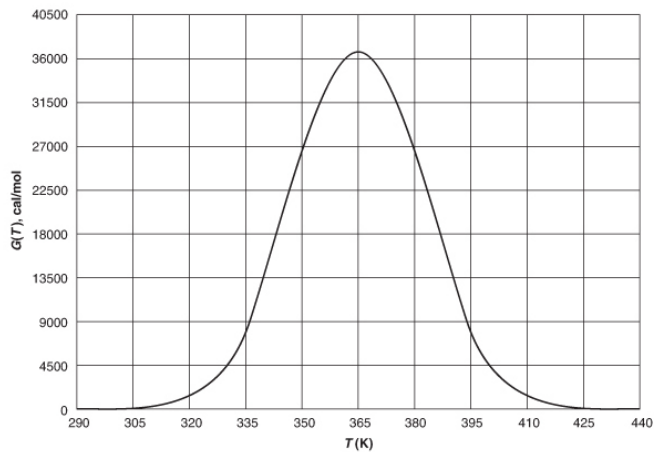
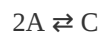


Figure P12-17B Heat removed curve, $G(T)$, for a reversible reaction.

P12-18C The elementary gas-phase reaction



is carried out in a packed-bed reactor. Pure A enters the reactor at a 450-K flow rate of 10 mol/s, and a concentration of 0.25 mol/dm³. The PBR contains 90 kg of catalyst and is surrounded by a heat exchanger for which cooling fluid is available at 500 K. Compare the conversion achieved for the four types of heat exchanger operation: adiabatic, constant T_a , co-current flow, and countercurrent flow.

Additional information:

$$\alpha = 0.019/\text{kg-cat} \quad C_{P_C} = 20 \text{ J/mol/K}$$

$$Ua/\rho_b = 0.8 \text{ J/kg-cat} \cdot \text{s} \cdot \text{K} \quad F_{A0} = 10 \text{ mol/h}$$

$$\Delta H_{R_x} = -20000 \text{ J/mol} \quad C_{A0} = 1 \text{ mol/dm}^3$$

$$C_{P_A} = 10 \text{ J/mol} \cdot \text{K} \quad v_0 = 10 \text{ dm}^3/\text{h}$$

P12-19C A reaction is to be carried out in the packed-bed reactor shown in Figure P12-19C.

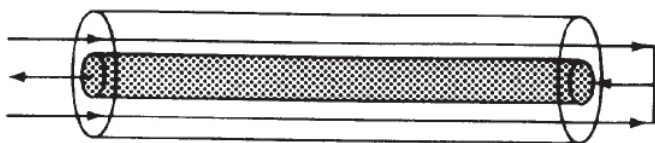


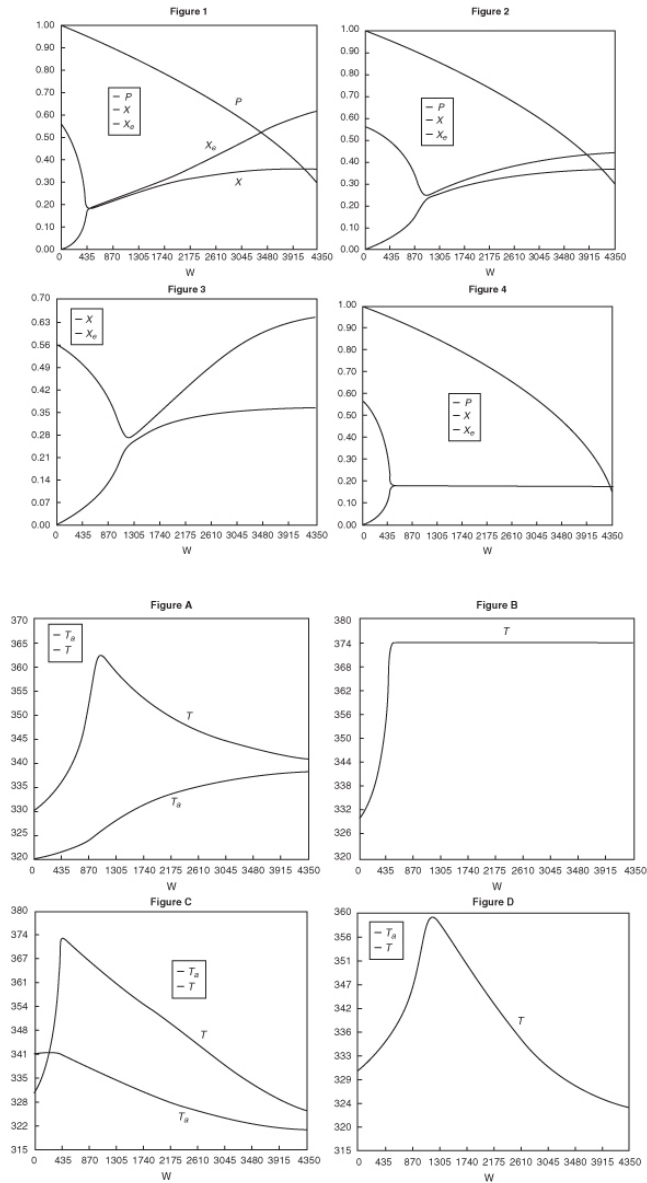
Figure P12-19_C PFR with heat exchange.

The reactants enter the annular space between an outer insulated tube and an inner tube containing the catalyst. No reaction takes place in the annular region. Heat transfer between the gas in this packed-bed reactor and the gas flowing countercurrently in the annular space occurs along the length of the reactor. The overall heat-transfer coefficient is $5 \text{ W/m}^2 \cdot \text{K}$. Plot the conversion and temperature as a function of reactor length for the data given in Problem P12-7_B.

P12-20_B OEQ (*Old Exam Question*). The reaction



is carried out in a packed-bed reactor. Match the following temperature and conversion profiles for the four different heat-exchange cases: adiabatic, constant T_a , co-current exchange, and countercurrent exchange.



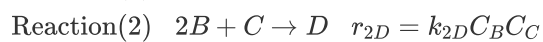
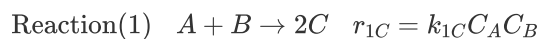
(a) Figure 1 matches Figure ____

(b) Figure 2 matches Figure ____

(c) Figure 3 matches Figure ____

(d) Figure 4 matches Figure ____

P12-21_B OEQ (Old Exam Question). Also Hall of Fame Problem. The irreversible liquid-phase reactions



are carried out in a PFR with heat exchange. The temperature profiles shown in Figure P12-21_B were obtained for the reactor and the coolant stream:

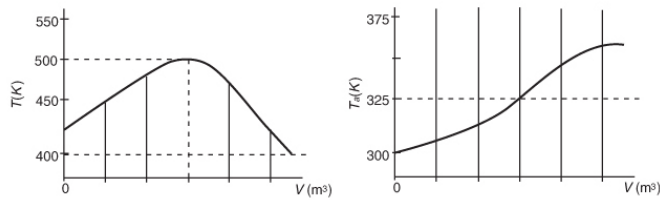


Figure P12-21B Reactant temperature T and coolant temperature T_c profiles.

The concentrations of A, B, C, and D were measured at the point down the reactor where the liquid temperature, T , reached a maximum, and they were found to be $C_A = 0.1$, $C_B = 0.2$, $C_C = 0.5$, and $C_D = 1.5$, all in mol/dm^3 . The product of the overall heat transfer coefficient and the heat-exchanger area per unit volume, Ua , is $10 \text{ cal/s} \cdot \text{dm}^3 \cdot \text{K}$. The entering molar flow rate of A is 10 mol/s .

Additional information:

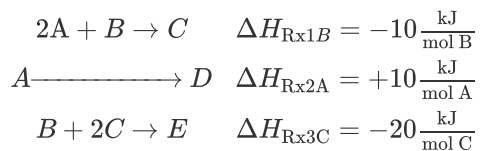
$$C_{P_A} = C_{P_B} = C_{P_C} = 30 \text{ cal/mol/K} \quad C_{P_D} = 90 \text{ cal/mol/K}, \quad C_{P_I} = 100 \text{ cal/mol/K}$$

$$\Delta H_{\text{Rx1A}}^\circ = -50000 \text{ cal/molA} \quad k_{1C} = 0.043 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \text{ at } 400 \text{ K}$$

$$\Delta H_{\text{Rx2B}}^\circ = +5000 \text{ cal/molB} \quad k_{2D} = 0.4 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \text{ at } 500 \text{ K, with } \frac{E}{R} = 5000 \text{ K}$$

(a) What is the activation energy for Reaction (1)?

P12-22B The following elementary reactions are to be carried out in a PFR with a heat exchange with constant T_c :



The reactants all enter at 400 K . Only A and B enter the reactor. The entering concentration of A and B are 3 molar and 1 molar at a volumetric flow rate of $10 \text{ dm}^3/\text{s}$.

Additional information:

$$Ua = 100 \text{ J/dm}^3/\text{S/K} \quad C_{P_A} = 10 \text{ J/mol/K}$$

$$k_{1A} \left(400 \text{ K} \right) = 1.0 \left(\frac{\text{dm}^3}{\text{mol}} \right)^2 / \text{S} \quad C_{P_B} = 20 \text{ J/mol/K}$$

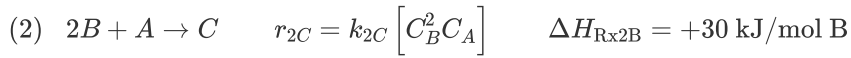
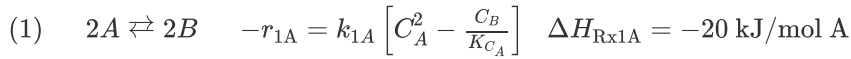
$$k_{2A} (400 \text{ K}) = 1.333 \text{ s}^{-1} \quad C_{P_C} = 40 \text{ J/mol/K}$$

$$k_{3B} \left(400 \text{ K} \right) = 2 \left(\frac{\text{dm}^3}{\text{mol}} \right)^2 / \text{S} \quad C_{P_D} = 20 \text{ J/mol/K}$$

$$C_{P_E} = 100 \text{ J/mol/K}$$

What constant coolant temperature, T_a , is necessary such that at the reactor entrance, that is, $V = 0$, $\frac{dT}{dV} = 0$?

P12-23B The complex gas-phase reactions are elementary



and carried out in a PFR with a heat exchanger. Pure A enters at a rate of 5 mol/min, a concentration of 0.2 mol/dm³, and temperature 300 K. The entering temperature of an available coolant is 320 K.

Additional information:

$$k_{1A1} = 50 \text{ dm}^3/\text{mol} \cdot \text{min} @ 305 \text{ K with } E_1 = 8000 \text{ J/mol}$$

$$k_{2C2} = 4000 \text{ dm}^9/\text{mol}^3 \cdot \text{min} @ 310 \text{ K with } E_2 = 4000 \text{ J/mol}$$

$$K_{CA} = 10 \text{ dm}^3/\text{mol} @ 315 \text{ K}$$

Note: This is the equilibrium constant with respect to A in reaction 1 when using van't Hoff's equation, that is, (S12-4),

$$Ua = 200 \frac{\text{J}}{\text{dm}^3 \cdot \text{min} \cdot \text{K}} \quad C_{P_{\text{Cool}}} = 10 \text{ J/mol/K} \quad C_{P_B} = 80 \text{ J/mol/K} \quad C_{P_C} = 100 \text{ J/mol/K}$$

$$\dot{m}_C = 50 \text{ g/min} \quad C_{P_A} = 20 \text{ J/mol/K} \quad R = 8.31 \text{ J/mol/K}$$

The reactor volume is 10 dm³.

(a) Plot (F_A , F_B , F_C) on one graph and (T and T_a) on another along the length of the reactor for adiabatic operation, heat exchange with constant T_a , and co-current and countercurrent heat exchange with variable T_a . Only turn in a copy of your code and output for co-current exchange.

Adiabatic operation

(b) What is the maximum temperature and at what reactor volume is it reached?

(c) At what reactor volume is the flow rate of B a maximum, and what is $F_{B\text{max}}$ at this value?

Constant T_a

(d) What is the maximum temperature and at what reactor volume is it reached?

(e) At which reactor volume is the flow rate of B a maximum, and what is $F_{B\text{max}}$ at this volume?

Co-current exchange

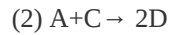
(f) At what reactor volume does T_a become greater than T ? Why does it become greater?

Countercurrent exchange

(g) At what reactor volume does T_a become greater than T ?

Hint: Guess T_a at entrance around 350 K.

P12-24_B The elementary liquid-phase reactions



are carried out adiabatically in a 10 dm³ PFR. After streams A and B mix, species A enters the reactor at a concentration of $C_{A0} = 2$ mol/dm³ and species B at a concentration of 4 mol/dm³. The entering volumetric flow rate is 10 dm³/s.

Assuming you could vary the entering temperature between 300 K and 600 K, what entering temperature would you recommend to maximize the concentration of species C exiting the reactor? ($\pm 25^\circ\text{K}$). Assume all species have the same density.

Additional information:

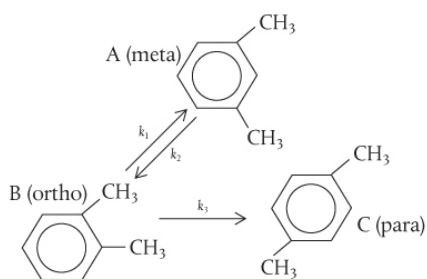
$$C_{P_A} = C_{P_B} = 20 \text{ cal/mol/K}, C_{P_C} = 60 \text{ cal/mol/K}, C_{P_D} = 80 \text{ cal/mol/K}$$

$$\Delta H_{R_{x1A}} = 20000 \text{ cal/mol A}, \Delta H_{R_{x2A}} = -10000 \text{ cal/mol A}$$

$$k_{1A} = 0.001 \frac{\text{dm}^6}{\text{mol}^2 \cdot \text{s}} \text{ at } 300 \text{ K with } E = 5000 \text{ cal/mol}$$

$$k_{2A} = 0.001 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \text{ at } 300 \text{ K with } E = 7500 \text{ cal/mol}$$

P12-25_C OTHEQ (*Old Take Home Exam Question*). **Multiple reactions with heat effects.** Xylene has three major isomers, *m*-xylene (A), *o*-xylene (B), and *p*-xylene (C). When *m*-xylene (A) is passed over a Cryotite catalyst, the following elementary reactions are observed. The reaction to form *p*-xylene is irreversible:



Application
Pending
for Problem
Hall of
Fame

The feed to the reactor is pure *m*-xylene (A). For a total feed rate of 2 mol/min and the reaction conditions below, plot the temperature and the molar flow rates of each species as a function of catalyst weight up to a weight of 100 kg.

- Plot the concentrations of each of xylenes down the length (i.e., V) of a PBR.
- Find the lowest concentration of *o*-xylene achieved in the reactor.
- Find the maximum concentration of *o*-xylene in the reactor.
- Repeat part (a) for a pure feed of *o*-xylene (B). What is the maximum concentration of meta-xylene and where does it occur in the reactor?
- Vary some of the system parameters and describe what you learn.
- What do you believe to be the point of this problem?

Additional information⁸

⁸ Obtained from inviscid pericosity measurements.

All heat capacities are virtually the same at 100 J/mol · K.

$$C_{T0} = 2 \text{ mol/dm}^3$$

$$\Delta H_{R\text{x}10}^\circ = -1800 \text{ J/mol } o\text{-xylene}$$

$$\Delta H_{R\text{x}30}^\circ = -1100 \text{ J/mol } o\text{-xylene}$$

$$k_1 = 0.5 \exp \left[2 \left(1 - 320/T \right) \right] \text{ dm}^3/\text{kg-cat} \cdot \text{min}, (T \text{ is in K})$$

$$k_3 = 0.005 \exp \left\{ \left[4.6 \left(1 - (460/T) \right) \right] \right\} \text{ dm}^3/\text{kg-cat} \cdot \text{min}$$

$$K_C = 10 \exp [4.8 (430/T - 1.5)]$$

$$T_0 = 330 \text{ K} \quad T_a = 500 \text{ K}$$

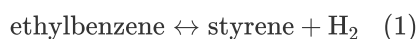
$$k_2 = k_1/K_C$$

$$Ua/\rho_b = 16 \text{ J/kg-cat} \cdot \text{min} \cdot ^\circ \text{C}$$

$$W = 100 \text{ kg}$$

P12-26_C OTHEQ (Old Take Home Exam Question).

Comprehensive problem on multiple reactions with heat effects. Styrene can be produced from ethylbenzene by the following reaction:

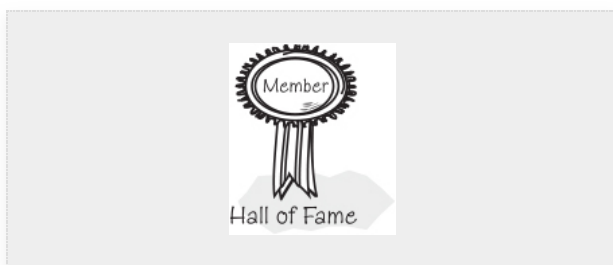


However, several irreversible side reactions also occur:



(J. Snyder and B. Subramaniam, *Chem. Eng. Sci.*, 49, 5585 (1994)). Ethylbenzene is fed at a rate of 0.00344 kmol/s to a 10.0-m³ PFR (PBR), along with inert steam at a total pressure of 2.4 atm. The steam/ethylbenzene molar ratio is initially, that is, parts (a) to (c), 14.5:1 but can be varied.

Given the following data, find the exiting molar flow rates of styrene, benzene, and toluene along with $\tilde{S}_{\text{St/BT}}$ for the following inlet temperatures when the reactor is operated adiabatically:



(a) $T_0 = 800 \text{ K}$

(b) $T_0 = 930 \text{ K}$

(c) $T_0 = 1100 \text{ K}$

(d) Find the ideal inlet temperature for the production of styrene for a steam/ethylbenzene ratio of 58:1. *Hint:* Plot the molar flow rate of styrene versus T_0 . Explain why your curve looks the way it does.

(e) Find the ideal steam/ethylbenzene ratio for the production of styrene at 900 K. *Hint:* See part (d).

(f) It is proposed to add a countercurrent heat exchanger with $Ua = 100 \text{ kJ/m}^3/\text{min/K}$, where T_a is virtually constant at 1000 K. For an entering stream to ethylbenzene ratio of 20, what would you suggest as an entering temperature? Plot the molar flow rates and $\tilde{S}_{\text{St/BT}}$.

(g) What do you believe to be the major points of this problem?

(h) Ask another question or suggest another calculation that can be made for this problem.

Note: Whenever I teach Chemical Reaction Engineering, I always assign this problem.

Additional information

Heat capacities	
Methane	68 J/mol · K
Ethylene	90 J/mol·K
Benzene	201 J/mol · K
Toluene	249 J/mol · K
Styrene	273 J/mol · K
Ethylbenzene	299 J/mol·K
Hydrogen	30 J/mol · K
Steam	40 J/mol · K

$$\rho = 2137 \text{ kg/m}^3 \text{ of pellet}$$

$$\phi = 0.4$$

$$\Delta H_{\text{Rx1EB}}^\circ = 118000 \text{ kJ/kmol ethylbenzene}$$

$$\Delta H_{\text{Rx2EB}}^\circ = 105200 \text{ kJ/kmol ethylbenzene}$$

$$\Delta H_{\text{Rx3EB}}^\circ = 53900 \text{ kJ/kmol ethylbenzene}$$

$$K_{\text{P1}} = \exp \left\{ b_1 + \frac{b_2}{T} + b_3 \ln(T) + [(b_4 T + b_5)T + b_6] T \right\} \text{ atm with}$$

$$b_1 = -17.34$$

$$b_4 = 2.314 \times 10^{-10} K^{-3}$$

$$b_2 = 1.302 \times 10^4 K$$

$$b_5 = 1.302 \times 10^{-6} K^{-2}$$

$$b_3 = 5.051$$

$$b_6 = -4.931 \times 10^{-3} K^{-1}$$

The kinetic rate laws for the formation of styrene (St), benzene (B), and toluene (T), respectively, are as follows (EB = ethylbenzene).

$$r_{1\text{St}} = \rho \left(1 - \phi \right) \exp \left(-0.08539 - \frac{10925 K}{T} \right) \left(P_{\text{EB}} - \frac{P_{\text{St}} P_{\text{H}_2}}{K_{\text{pl}}} \right) \quad (\text{kmol/m}^3 \cdot \text{s})$$

$$r_{2\text{B}} = \rho \left(1 - \phi \right) \exp \left(13.2392 - \frac{25000 K}{T} \right) (P_{\text{EB}}) \quad (\text{kmol/m}^3 \cdot \text{s})$$

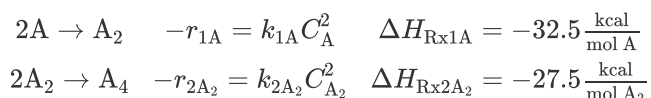
$$r_{3\text{T}} = \rho \left(1 - \phi \right) \exp \left(0.2961 - \frac{11000 K}{T} \right) (P_{\text{EB}} P_{\text{H}_2}) \quad (\text{kmol/m}^3 \cdot \text{s})$$

The temperature T is in Kelvin and P_i is in atm.

P12-27_B OTHEQ (*Old Take Home Exam Question*). The liquid-phase, dimer-quadmer series addition reaction



can be written as



and is carried out in a 10-dm³ PFR. The mass flow rate through the heat exchanger surrounding the reactor is sufficiently large so that the ambient temperature of the exchanger is constant at $T_a = 315$ K. The reactants enter at a temperature T_0 , of 300 K. Pure A is fed to the reactor at a volumetric flow rate of 50 dm³/s and a concentration of 2 mol/dm³.

(a) Plot, compare, and analyze the profiles F_A , F_{A_2} , and F_{A_4} down the length of the reactor up to 10 dm³.

(b) The desired product is A_2 and it has been suggested that the current reactor may be too large. What reactor volume would you recommend to maximize F_{A_2} ?

(c) What operating variables (e.g., T_0 , T_a) would you change and how would you change them to make the reactor volume as small as possible and to still maximize F_{A_2} ? Note any opposing factors in maximum production of A_2 . The ambient temperature and the inlet temperature must be kept between 0°C and 177°C.

Additional information:

$$k_{1A} = 0.6 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \text{ at } 300 \text{ K with } E_1 = 4000 \frac{\text{cal}}{\text{mol}}$$

$$k_{2A_2} = 0.35 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \text{ at } 320 \text{ K with } E_2 = 5000 \frac{\text{cal}}{\text{mol}}$$

$$C_{P_A} = 25 \frac{\text{cal}}{\text{mol} \cdot \text{K}}, C_{P_{A_2}} = 50 \frac{\text{cal}}{\text{mol} \cdot \text{K}}, C_{P_{A_4}} = 100 \frac{\text{cal}}{\text{mol} \cdot \text{K}}$$

$$Ua = 1000 \frac{\text{cal}}{\text{dm}^3 \cdot \text{s} \cdot \text{K}}$$

Turn in your recommendation of reactor volume to maximize and the molar flow rate at this maximum.

SUPPLEMENTARY READING

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2. Safety

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DANIEL A. CROWL and JOSEPH F. LOUVAR, *Chemical
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2011.

G. A. MELHEM and H. G. FISHER, *International
Symposium on Runaway Reactions and Pressure
Relief Design*. New York: Center for Chemical
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of Chemical Engineers (AIChE) and The
Institution of Chemical Engineers, 1995.

See the Center for Chemical Process Safety (CCPS)
Web site, www.aiche.org/ccps.

3. A number of example problems dealing with
nonisothermal reactors may or may not be found in
THORNTON W. BURGESS, *The Adventures of Jerry
Muskrat*. New York: Dover Publications, Inc.,
1914.

G. F. FROMENT and K. B. BISCHOFF, *Chemical
Reactor Analysis and Design*, 3rd ed. New York:
Wiley, 2010.

S. M. WALAS, *Chemical Reaction Engineering
Handbook of Solved Problems*. Amsterdam:
Gordon and Breach, 1995. See the following
solved problems: Problem 4.10.1, page 444;
Problem 4.10.08, page 450; Problem 4.10.09,
page 451; Problem 4.10.13, page 454; Problem
4.11.02, page 456; Problem 4.11.09, page 462;
Problem 4.11.03, page 459; Problem 4.10.11,
page 463.

4. A review of the multiplicity of the steady state and
reactor stability is discussed by
D. D. PERLMUTTER, *Stability of Chemical Reactors*.
Upper Saddle River, NJ: Prentice Hall, 1972.
5. The heats of formation, ($H_i^\circ T$), Gibbs free energies,
($G_i^\circ T_R$), and the heat capacities of various
compounds can be found in

DON W. GREEN and ROBERT H. PERRY, *Perry's Chemical Engineers' Handbook*, 8th ed. (Chemical Engineers Handbook). New York: McGraw-Hill, 2008.

DAVID R. LIDE, *CRC Handbook of Chemistry and Physics*, 90th ed. Boca Raton, FL: CRC Press, 2009.

13. Unsteady-State Nonisothermal Reactor Design

Chemical engineers are not gentle people, they like high temperatures and high pressures.

—Prof. Steven LeBlanc

Overview. Up to now we have focused on the steady-state operation of nonisothermal reactors. In this chapter, the unsteady-state energy balance will be developed and then applied to CSTRs, as well as well-mixed batch and semibatch reactors. We will use the difference between the rate of “heat generated,” \dot{Q}_g , and the rate of “heat removed,” \dot{Q}_r , to arrive at the **user-friendly form** of the energy balance

$$\frac{dT}{dt} = \frac{\dot{Q}_g - \dot{Q}_r}{\sum N_i C_{Pi}}$$

- Section 13.1 shows how to arrange the general energy balance (Equation (11-9)) in a more simplified form for unsteady-state operation.
- Section 13.2 discusses the application of the energy balance to the operation of batch reactors and discusses reactor safety and the reasons for the explosion of an industrial batch reactor.
- Section 13.3 discusses the startup of a CSTR and how to avoid exceeding the practical stability limit.
- Section 13.4 shows how to apply the energy balance to semi-batch reactor in which the ambient temperature varies.
- Section 13.5 discusses a case study of the T2 Laboratory explosion involving multiple reactions in a batch reactor.
- Section 13.6 closes the chapter with a continuing discussion of **Safety**, which is another focus of this chapter. The example problems and homework problems were chosen to emphasize the hazards of *runaway* reactions.

13.1 THE UNSTEADY-STATE ENERGY BALANCE

We start by deriving the user-friendly form of the energy balance that can be easily used in making reactor calculations. As I have stated before, the reason I derive the equations rather

than just giving the final result is (1) the reader can see what assumptions are used at what points along the way in the derivation to the user-friendly energy balance, and (2) it is my experience that if the reader goes line-by-line through the derivation, they will be less likely to insert the incorrect numbers into symbols in the equation when making a calculation.

We begin by recalling the unsteady-state form of the energy balance developed in Chapter 11.

$$\dot{Q} - \dot{W}_s + \sum_{i=1}^m F_i H_i \Big|_{\text{in}} - \sum_{i=1}^m F_i H_i \Big|_{\text{out}} = \left(\frac{d\hat{E}_{\text{sys}}}{dt} \right) \quad (11-9)$$

We shall first concentrate on evaluating the change in the total energy of the system wrt time, $\left(d\hat{E}_{\text{sys}}/dt \right)$. The total energy of the system is the sum of the products of specific energies, E_i (e.g., J/mol i), of the various species in the system volume and the number of moles, N_i (mol i), of that species

$$\hat{E}_{\text{sys}} = \sum_{i=1}^m N_i E_i = N_A E_A + N_B E_B + N_C E_C + N_D E_D + N_I E_I \quad (13-1)$$

In evaluating \hat{E}_{sys} , as before we neglect changes in the potential and kinetic energies and substitute for the internal energy U_i in terms of the enthalpy H_i

$$\hat{E}_{\text{sys}} = \sum_{i=1}^m N_i E_i = \sum_{i=1}^m N_i U_i = \left[\sum_{i=1}^m N_i (H_i - PV_i) \right]_{\text{sys}} = \sum_{i=1}^m N_i H_i - P \underbrace{\sum_{i=1}^m N_i \tilde{V}_i}_{\substack{\text{Neglect} \\ V}} \quad (13-2)$$

We note the last term on the right-hand side of Equation (13-2) is just the total pressure times the total volume, that is, PV , and this term is virtually always smaller than the other terms in Equation (13-2), and thus will be neglected.[†] For brevity, we shall write all summations as

[†] Marat Orazov while a student at University of California, Berkeley, pointed out that the last term in Equation (13-2) need not be neglected for the *special case*

of an ideal gas with a constant total number of moles. The denominator on the r.h.s. of Equation (13-9) in this case is just $\sum N_i (C_{P_i} - R)$.

$$\Sigma = \sum_{i=1}^m$$

unless otherwise stated.

When no spatial variations are present in the system volume, and time variations in the product of the total pressure and volume (PV) are neglected, the energy balance, after substitution of Equation (13-2) into (11-9), gives

$$\dot{Q} - \dot{W}_S + \sum F_{i0} H_{i0} \Big|_{\text{in}} - \sum F_i H_i \Big|_{\text{out}} = \left[\sum N_i \frac{dH_i}{dt} + \sum H_i \frac{dN_i}{dt} \right]_{\text{sys}} \quad (13-3)$$

Recalling Equation (11-19)

$$H_i = H_i^o(T_R) + \int_{T_R}^T C_{P_i} dT \quad (11-19)$$

and differentiating with respect to time, we obtain

$$\frac{dH_i}{dt} = C_{P_i} \frac{dT}{dt} \quad (13-4)$$

Then, substituting Equation (13-4) into (13-3) gives

$$\dot{Q} - \dot{W}_S + \sum F_{i0} H_{i0} - \sum F_i H_i = \sum N_i C_{P_i} \frac{dT}{dt} + \sum H_i \frac{dN_i}{dt} \quad (13-5)$$

The mole balance on species i is

$$\boxed{\frac{dN_i}{dt} = -v_i r_A V + F_{i0} - F_i} \quad (13-6)$$

Using Equation (13-6) to substitute for dN_i/dt , Equation (13-5) becomes

$$\begin{aligned} \dot{Q} - \dot{W}_s + \sum F_{i0} H_{i0} - \sum F_i H_i \\ = \sum N_i C_{P_i} \frac{dT}{dt} + \sum \nu_i H_i (-r_A V) + \sum F_{i0} H_i - \sum F_i H_i \end{aligned} \quad (13-7)$$

Rearranging, and recalling $\sum \nu_i H_i = \Delta H_{R_x}$, we have

This form of the energy balance should be used when there is a phase change.

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s - \sum F_{i0}(H_i - H_{i0}) + (-\Delta H_{Rx})(-r_A V)}{\sum N_i C_{P_i}} \quad (13-8)$$

Substituting for H_i and H_{i0} for the case of **no phase change** gives us

Energy balance on a transient CSTR or semibatch reactor

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s - \sum F_{i0} C_{P_i} (T_i - T_{i0}) + [-\Delta H_{Rx}(T)](-r_A V)}{\sum N_i C_{P_i}} \quad (13-9)$$

Equation (13-9) applies to a semibatch reactor, as well as to the unsteady-state operation of a CSTR, and is also shown in Table 11-1 as Equation (T11-1.I).

For liquid-phase reactions where ΔC_p is usually small and can be neglected and thus the following approximation is often made

C_{P_s} : Heat capacity of solution

$$\sum N_i C_i \cong \sum N_{i0} C_{P_i} = N_{A0} \overbrace{\sum \Theta_i C_{P_i}}^{C_{P_s}} = N_{A0} C_{P_s}$$

where C_{P_s} is the heat capacity of the solution. The units of the batch term ($N_{A0} C_{P_s}$) are (cal/K) or (J/K) or (Btu/°R), and analogously for the flow term

$$\sum F_{i0} C_{P_i} = F_{A0} C_{P_s}$$

the units are (J/s · K) or (cal/s · K) or (Btu/h · °R).¹ With this approximation and assuming that every species enters the reactor at the same temperature T_0 , we have

¹ If the heat capacities were given in terms of mass (i.e., $C_{p_{sm}} = \text{J/g} \cdot \text{K}$), then both F_{A0} and N_{A0} would have to be converted to mass

for batch

$$m_{A0} C_{Psm} = N_{A0} C_{Ps}$$

$$\left(\text{g} \right) \left(\text{J/g} \cdot \text{K} \right) = \left(\text{mol} \right) \frac{\text{J}}{\left(\text{mol} \cdot \text{K} \right)} = \frac{\text{J}}{\text{K}}$$

and for flow

$$\dot{m}_{A0} C_{Psm} = F_{A0} C_{Ps}$$

$$\left(\text{g/s} \right) \left(\text{J/g} \cdot \text{K} \right) = \left(\frac{\text{mol}}{\text{s}} \right) \left(\text{J/mol} \cdot \text{K} \right) = \frac{\text{J}}{\text{K} \cdot \text{s}}$$

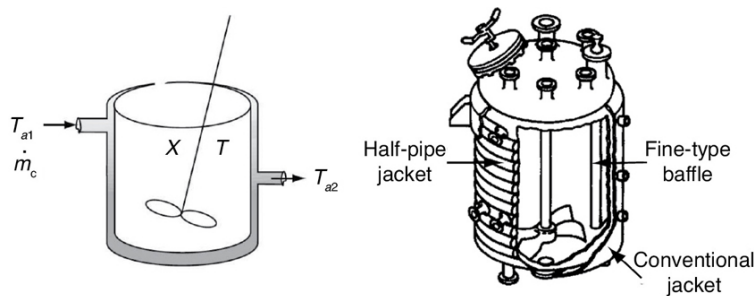
However, we note that the units of the product of mass flow rate and mass heat capacities would still be the same as the product of molar flow and molar heat capacities (e.g., cal/s · K), respectively.

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s - F_{A0} C_{Ps} (T - T_0) + [-\Delta H_{Rx}(T)](-r_A V)}{N_{A0} C_{Ps}} \quad (13-10)$$

$$C_{Ps} = \sum \Theta_i C_{Pi}$$

13.2 ENERGY BALANCE ON BATCH REACTORS (BRS)

A batch reactor is usually well mixed, so that we may neglect spatial variations in the temperature and species concentrations.



The energy balance on batch reactors (BR) is found by setting the inlet and outlet flows to zero, that is, $F_{i0} = F_i = 0$, in Equation (13-9)

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s + (-\Delta H_{Rx})(-r_A V)}{\sum N_i C_{Pi}} \quad (13-11)$$

Next we use the energy balance on the heat exchanger to obtain, \dot{Q} , Equation (12-19), and realize that the heat “added” to the batch reactor, \dot{Q} , is just the negative of the heat “removed” from the batch reactor, \dot{Q}_{rb} , that is, $\dot{Q} = -\dot{Q}_{rb}$. Neglecting shaft work (recall we could not do this in Problem P12-6B) we get

$$\boxed{\frac{dT}{dt} = \frac{\dot{Q}_{gb} - \dot{Q}_{rb} - \cancel{\dot{W}_s}}{\sum N_i C_{P_i}} \quad \text{Neglect}}$$

$$\boxed{\frac{dT}{dt} = \frac{\dot{Q}_{gb} - \dot{Q}_{rb}}{\sum N_i C_{T_i}} \quad (13-12)}$$

where the terms for heat generated, \dot{Q}_{gb} , and heat removed, \dot{Q}_{rb} , for a batch system are

$$\boxed{\dot{Q}_{gb} = (-\Delta H_{Rx})(-r_A V) \quad (13-13)}$$

$$\boxed{\dot{Q}_{rb} = m\dot{C}_{P_C} \left(T - T_{a1} \right) \left[1 - \exp \left(-\frac{UA}{m\dot{C}_{P_C}} \right) \right] \quad (13-14)}$$

with an added bonus we obtained in Equation (12-17)

$$\boxed{T_{a2} = T - \left(T - T_{a1} \right) \left[\exp \left(-\frac{UA}{m\dot{C}_{P_C}} \right) \right] \quad (13-15)}$$

Equations (13-12) and (13-13) are the preferred form of the energy balance when the number of moles, N_i , is used in the mole balance, rather than the conversion, X .

To write the energy balance in terms of conversion, recall that the number of moles of species i at any X is

$$N_i = N_{A0} (\Theta_i + \nu_i X)$$

Consequently, in terms of conversion, the **user-friendly form** of the energy balance becomes

Reminder: The sign convention**Heat Added**

$$\dot{Q} = +10 \text{ J/s}$$

Heat Removed

$$\dot{Q} = -10 \text{ J/s}$$

Work Done by System

$$\dot{W}_s = +10 \text{ J/s}$$

Work Done on System

$$\dot{W}_s = -10 \text{ J/s}$$

Batch reactor energy balance

$$\frac{dT}{dt} = \frac{\dot{Q}_{gb} - \dot{Q}_{rb}}{N_{A0}(\sum \Theta_i C_{Pi} + \Delta C_P X)} \quad (13-16)$$

Equation (13-12) must be coupled with the mole balance

Batch reactor mole balance

$$N_{A0} \frac{dX}{dt} = -r_A V \quad (2-6)$$

13.2.1 Adiabatic Operation of a Batch Reactor

Batch reactors operated adiabatically are often used to determine the reaction orders, activation energies, and specific reaction rates of exothermic reactions by monitoring the temperature–time trajectories for different initial conditions. In the steps that follow, we will derive the temperature–conversion relationship for adiabatic operation.

For adiabatic operation ($\dot{Q} = 0$) of a batch reactor ($F_{i0} = 0$) and when the work done by the stirrer can be neglected ($\dot{W}_s \cong 0$), Equation (13-10) can be written as

$$\frac{dT}{dt} = \frac{(-\Delta H_{Rx})(-r_A V)}{\sum N_i C_{Pi}} \quad (13-17)$$

It is shown in the *Summary Notes of Chapter 13* on the CRE Web site

(<http://www.umich.edu/~elements/6e/13chap/RelationshipBetweenXandT.pdf>) that if we combine Equation (13-17) with Equation (2-6), we can do a lot of rearranging and integrating to arrive at the following **user-friendly** equation for an adiabatic batch reactor.

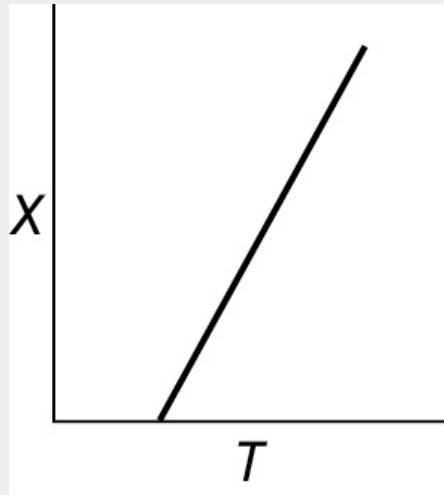
$$X = \frac{\sum \Theta_i C_{P_i} (T - T_0)}{-\Delta H_{Rx}(T)} \quad (13-18)$$

$$T = T_0 + \frac{[-\Delta H_{Rx}(T_0)]X}{\sum \Theta_i C_{P_i} + X \Delta C_P} \quad (13-19)$$

We note that for *adiabatic* conditions, the relationship between temperature and conversion is the same for BRs, CSTRs, PBRs, and PFRs. Once we have T as a function of X for a batch reactor, we can construct a table similar to [Table E11-3.1](#) and use techniques analogous to those discussed in [Section 11.3.2](#) to evaluate the following design equation that determines the time necessary to achieve a specified conversion.

$$t = N_{A0} \int_0^X \frac{dX}{-r_A V} \quad (2-9)$$

However, if you do not have *that much time on your hands* to form a table and use [Chapter 2](#) integration techniques, then use a software package such as Poly-math, Wolfram, Python, or MATLAB to solve the coupled differential forms of mole balance equation (2-6) and the energy balance equation (13-19) simultaneously.



Temperature–conversion relationship for *any* reactor operated adiabatically

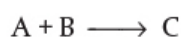
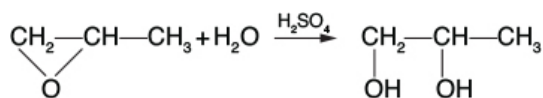


#TimeOnYourHands

$$N_{A0} \frac{dX}{dt} = -r_A V \quad (2-6)$$

Example 13–1 Batch Reactor with an Exothermic Reaction

It is still winter, and although you were hoping for a transfer to the plant in the tropical southern coast of Florida, you unfortunately are still the engineer of the CSTR from [Example 12-3](#), in charge of the production of propylene glycol.



You are considering the installation of a new, attractive-looking, glass-lined 1000-dm³ CSTR, and you decide to make a quick check of the reaction kinetics and maximum adiabatic temperature. You have a stylish, nicely decorated and instrumented 40-dm³ (~10 gal) stirred batch reactor you ordered from a company. You charge (i.e., fill) this reactor with 4 dm³ (~1 gal) of ethylene oxide, 4 dm³ (~1 gal) of methanol, and 10 dm³ (~2.5 gal) of water containing 0.1 wt % H₂SO₄. For safety reasons, the reactor is located on a boating pier on the banks of Lake Walloon (you don't want the entire plant to be destroyed if the reactor explodes). At this time of year in northern Michigan, the initial temperature of all materials is 276 K (3°C). We have to be careful here! If the reactor temperature increases above 350 K (77°C), a secondary, more exothermic reaction will take over, causing runaway and subsequent explosion, similar to what happened in the T2 Laboratory plant explosion in Florida (see [page 717](#)).

Although you requested obtaining the data for this reaction from the Jofostan national research laboratory, the purchasing department decided to save money and buy it off the Internet. The values it purchased are

$$E = 1800 \text{ cal/mol}, \Delta H_{\text{Rx}}^0 = 20202 \text{ cal/mol}, C_{\text{P}_A} = 35 \text{ cal/mol/K},$$

$$C_{\text{P}_B} = 18 \text{ cal/mol/K}, C_{\text{P}_C} = 46 \text{ cal/mol/K}, \text{ and } C_{\text{P}_M} = 19.5 \text{ cal/mol/K}$$

Prof. Dr. Sven Köttlov objected to this Internet purchase and said that it should be recorded that he is skeptical of these parameter values. The initial concentrations of pure ethylene oxide and methanol are 13.7 and 24.7 mol/dm³, respectively. Consequently, the initial number of moles added to the reactor are

$$\begin{aligned} \text{A: Ethylene oxide: } N_{A0} &= (13.7 \text{ mol/dm}^3) (4 \text{ dm}^3) = 54.8 \text{ mol} \\ \text{B: Water: } N_{B0} &= (55.5 \text{ mol/dm}^3) (10 \text{ dm}^3) = 555 \text{ mol} \\ \text{M: Methanol: } N_M &= (24.7 \text{ mol/dm}^3) (4 \text{ dm}^3) = 98.8 \text{ mol} \end{aligned}$$

The sulfuric acid catalyst takes up negligible space, so the total volume is 18 dm³, while the data and the reaction-rate law are given in Example 12-3. We are going to carry out two scenarios: (1) to learn how fast the temperature rises and how long it takes to reach 350 K for adiabatic operation, and (2) how long would it take to reach 345 K if we added a heat exchanger.

- 1. Adiabatic Operation:** Plot conversion and temperature X and T as a function of time for adiabatic operation. How many minutes should it take the mixture inside the reactor to reach a conversion of 51.5%? What is the corresponding adiabatic temperature?
- 2. Heat Exchange:** Plot the temperature and conversion as a function of time when a heat exchanger is added. The product of the overall heat transfer coefficient and exchange surface area is $UA = 10 \text{ cal/s/K}$ with $T_{a1} = 290 \text{ K}$ and the coolant rate is 10 g/s, and it has a heat capacity of 4.16 cal/g/K.

Solution

The initial temperature is 3°C, and if the reactor temperature increases to above 77°C, a dangerous exothermic side reaction can occur, as was reported in *Jofostan Journal of Chemical Safety*, Vol. 19, p. 201 (2009).

As before, there is approximately a 10°C (18°F) rise in temperature immediately after mixing.



1. **Mole Balance**, Chapter 2, rearranging Equation (2-6) we have

$$\frac{dX}{dt} = \frac{-r_A V}{N_{A0}} \quad (\text{E13-1.1})$$

2. **Rate Law**: Apparent first order

$$-r_A = kC_A \quad (\text{E13-1.2})$$

3. **Stoichiometry**:

$$N_A = N_{A0}(1 - X) \quad (2-4)$$

Recall that for a liquid-phase batch reaction $V = V_0$

$$C_A = \frac{N_A}{V} = \frac{N_A}{V_0} = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1 - X) \quad (\text{E13.1.3})$$

4. **Combining** Equations (E13-1.1), (E13-1.2), and (2-4) above, we have

$$\frac{dX}{dt} = k(1 - X) \quad (\text{E13-1.4})$$

Changing the data in Example 12-3 from English units to mks units, we have

$$k = (4.71 \times 10^9) \exp\left[\left(\frac{E}{R}\right)\frac{1}{T}\right] s^{-1} \quad (\text{E13-1.5})$$

$$\text{With } \frac{E}{R} = 9059 K$$

Choosing 297 K as a reference temperature for k , and putting Equation (E13-1.5) in the form of Equation (3-21), we get

$$k = \left(2.73 \times 10^{-4}\right) \exp \left[9059 \text{ K} \left(\frac{1}{297} - \frac{1}{T}\right) s^{-1}\right] \quad (\text{E13-1.6})$$

5. Energy Balance:

Part (a) Adiabatic Operation.

Recalling Equation (13-12)

$$\frac{dT}{dt} = \frac{\dot{Q}_{gb} - \dot{Q}_{rb}}{\Sigma N_i C_{p_i}} = \frac{\dot{Q}_{gb}}{\Sigma N_i C_{p_i}} = \frac{(-\Delta H_{\text{Rx}})(-r_A V)}{\Sigma N_i C_{p_i}} \quad (13-17)$$

with

$$\dot{Q}_{gb} = (-\Delta H_{\text{Rx}})(-r_A V)$$

we could couple this ODE, Equation (13-17), with the mole balance ODE, Equation (E13-1.1), and solve these two equations simultaneously to obtain X and T as a function of t . However, for adiabatic operation we can use the explicit relationship, Equation (13-19), directly to couple with the mole balance that is

$$T = T_0 + \frac{[-\Delta H_{\text{Rx}}(T_0)]X}{\Sigma \Theta_i C_{P_i} + \Delta C_P X} \quad (\text{E13-1.7})$$

6. Parameters:

$$C_{P_S} = \sum \Theta_i C_{P_i} = C_{P_A} + C_{P_B} \Theta_B + C_{P_M} \Theta_M \quad (\text{E13-1.8})$$

$$\begin{aligned} C_{P_S} &= 35 + 18\left(\frac{55.5}{54.8}\right) + 19.5\left(\frac{98.8}{54.8}\right) \\ &= 35 + 182.3 + 35.2 = 252.5 \frac{\text{cal}}{\text{mol} \cdot \text{K}} \end{aligned}$$

The lumped heat capacity of the solution, C_{P_S} is

$$C_{P_S} = 252.2 \frac{\text{cal}}{\text{mol} \cdot \text{K}}$$

In the equation for the heat of reaction (i.e., Eq. (E13-1.9) below), we are going to neglect the second term on the right-hand side, that is,

$$\Delta H_{\text{Rx}}(T) = \Delta H_{\text{Rx}}^{\circ}(T_{\text{R}}) + \cancel{\Delta C_{\text{P}}(T - T_{\text{R}})} \xrightarrow{\text{Neglect}} \quad (\text{E13-1.9})$$

We can do this because ΔC_{P} is -7 cal/mol/K and for a 50-K temperature difference, $\Delta C_{\text{P}}(T - T_{\text{R}}) = 350$ cal/mol, which is negligible with respect to the heat of reaction of -20202 cal/mol

$$\Delta H_{\text{Rx}}(T) = \Delta H_{\text{Rx}}^{\circ} = -20202 \text{ cal/mol} \quad (\text{E13-1.10})$$

In calculating the inlet temperature after mixing, T_0 , we must include the temperature rise 10°C (18°F) resulting from the heat of mixing the two solutions that are initially at 3°C

$$T_0 = 276 + 10 = 286 \text{ K}$$

$$T = T_0 + \frac{X(-\Delta H_{\text{Rx}})}{C_{\text{P}_s}} = 286 \text{ K} + \frac{X(-1(-20,202)) \frac{\text{cal}}{\text{mol}}}{252.5 \text{ cal/mol}\cdot\text{K}}$$

$$T = 286 + 80X \quad (\text{E13-1.11})$$

Adiabatic energy balance

A summary of the heat and mole balance equations is given in Table E13-1.1.

TABLE E13-1.1 SUMMARY FOR FIRST-ORDER
ADIABATIC BATCH REACTION

$$\frac{dX}{dt} = k(1 - X) \quad (\text{E13-1.4})$$

$$k = (2.73 \times 10^{-4}) \exp \left[9059 \text{ K} \left(\frac{1}{297} - \frac{1}{T} \right) \right] \text{ s}^{-1} \quad (\text{E13-1.6})$$

$$T = 286 + 80X \quad (\text{E13-1.11})$$

where T is in K and t is in seconds.

A table similar to that used in [Example 11-3](#) can now be constructed or one can make better use of his or her time using Polymath.

The software package Polymath will be used to combine Equations (E13-1.4), (E13-1.6), and (E13-1.11) to determine conversion and temperature as a function of time. [Table E13-1.2](#) shows the program, and [Figures E13-1.1](#) and [E13-1.2](#) show the solution results.

TABLE E13-1.2 POLYMATH PROGRAM

Differential equations

$$1 \quad d(X)/d(t) = k*(1-X)$$

Explicit equations

$$1 \quad T = 286 + 80*X$$

$$2 \quad k = .000273 * \exp(9059 * (1/297 - 1/T))$$

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	k	8.446E-05	0.0858013
2	T	286.	366.
3	t	0	2500.
4	X	0	1.

The Polymath equations do not include the runaway reaction that “ignites” at 350 K. A switching technique, SW , can be used to prevent the temperature from numerically going to infinity and could be used here as described in detail in [Example 13-6](#).

We note for the initial temperature of 286 K that the reaction starts off relatively slowly then at approximately 1200 sec (20 minutes) “ignites” and the temperature rises rapidly to 370 K, at which point we reach complete conversion.

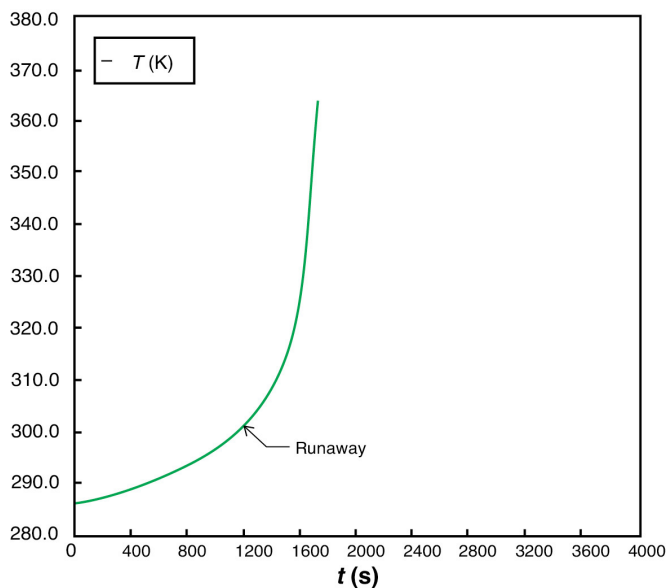
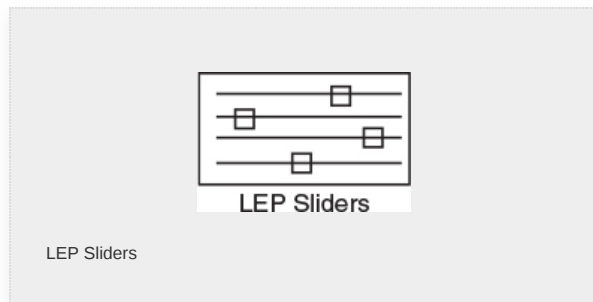


Figure E13-1.1 Temperature–time trajectory.

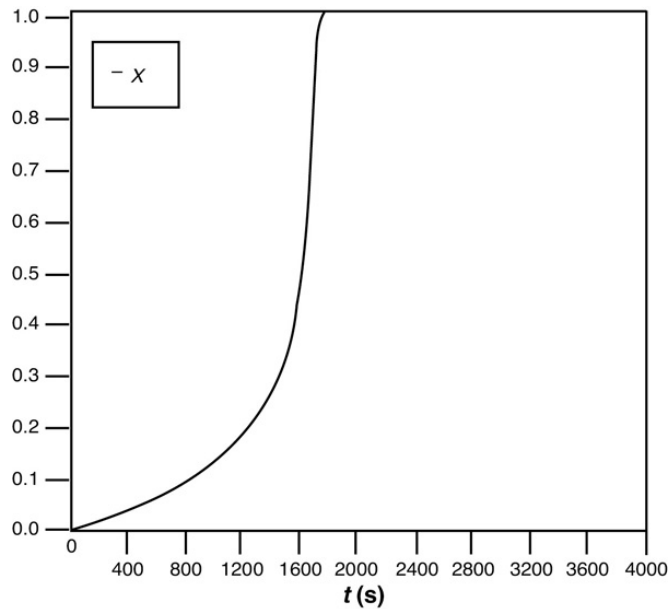


Figure E13-1.2 Conversion–time trajectory.

Part (b) Heat Exchanger in a Batch Reactor.

We now consider the case where a heat exchanger is added to the batch reactor. The coolant enters at 290 K and the flow rate, \dot{m}_c , through the exchanger is 10 g/s. The mole balance, Equation (E13-1.1), and the physical properties, Equations (E13-1.2)–(E13-1.6) and (E13-1.8), remain the same.

$$\frac{dX}{dt} = \frac{-r_A V}{N_{A0}} \quad (\text{E13-1.1})$$

Neglecting ΔC_p the energy balance is

$$\frac{dX}{dt} = \frac{\dot{Q}_{gb} - \dot{Q}_{rb}}{N_{A0} C_{Ps}} \quad (\text{E13-1.12})$$

with

$$\dot{Q}_{rb} = \dot{m}_c C_{Pc} \left\{ (T - T_{a1}) \left[1 - \exp \left(\frac{-UA}{\dot{m}_c C_{Pc}} \right) \right] \right\} \quad (\text{E13-1.13})$$

$$\dot{Q}_{rb} = (-r_A V) (-\Delta H_{Rx}^\circ) \quad (\text{E13-1.14})$$

$$-r_A V = N_{A0} k (1 - X) \quad (\text{E13-1.15})$$

The Polymath Program is shown in Table E13-1.3 with **parameters**

$$C_{P_S} = \sum \Theta_i C_{P_i} = 252.5 \text{ cal/mol/K} \quad C_{P_C} = 4.16 \text{ cal/g/K} \quad \dot{m}c = 10 \text{ g/s}$$

$$N_{A0} = 54.8 \text{ mol, UA} = 10 \text{ cal/K/S}$$

$$T_{al} = 290 \text{ K, } T_0 = 286 \text{ K}$$

Mole balance

Energy balance

and the other terms remain the same as in **Part (a)**.

Parameters

Polymath solution

TABLE E13-1.3 POLYMATH PROGRAM

Differential equations

$$1 \quad d(T)/d(t) = (Q_g - Q_r)/C_{ps}/N_{ao}$$

$$2 \quad d(X)/d(t) = k^*(1-X)$$

Explicit equations

$$1 \quad UA = 10$$

$$2 \quad \Delta H = -20202$$

$$3 \quad T_{a1} = 290$$

$$4 \quad C_{pc} = 4.18$$

$$5 \text{ Cps} = 252.5$$

$$6 \text{ mc} = 10$$

$$7 \text{ R} = 1.987$$

$$8 \text{ E} = 18000$$

$$9 \text{ k} = .000273 * \exp((\text{E}/\text{R}) * (1/297 - 1/\text{T}))$$

$$10 \text{ Ta2} = \text{T} - (\text{T} - \text{Ta1}) * \exp(-\text{UA}/\text{mc}/\text{Cpc})$$

$$11 \text{ Qr} = \text{mc} * \text{Cpc} * (\text{T} - \text{Ta1}) * (1 - \exp(-\text{UA}/\text{mc}/\text{Cpc}))$$

$$12 \text{ Nao} = 54.8$$

$$13 \text{ Qg} = \text{Nao} * \text{k} * (1 - \text{X}) * (-\text{DeltaH})$$

$$14 \text{ DeltaQ} = \text{Qr} - \text{Qg}$$

Calculated values of DEQ variables

	Variable	Initial value	Final value
--	----------	---------------	-------------

1	Cpc	4.18	4.18
2	Cps	252.5	252.5
3	DeltaH	-2.02E+04	-2.02E+04
4	DeltaQ	-129.0845	155.5059
5	E	1.8E+04	1.8E+04
6	k	8.447E-05	0.0007724
7	mc	10.	10.
8	Nao	54.8	54.8
9	Qg	93.50939	0.0004296
10	Qr	-35.57509	155.5063
11	R	1.987	1.987
12	T	286.	307.4849

13	t	0	4000.
14	Ta1	290.	290.
15	Ta2	289.1489	293.7202
16	UA	10.	10.
17	X	0	0.9999995

One notes after comparing [Figures E13-1.1](#) and [E13-1.3](#) that the temperature profiles are not as steep as the adiabatic case. As expected the temperature of this exothermic reaction first increases as $(\dot{Q}_{gb} > \dot{Q}_{rb})$, goes through a maximum and then as the reactants have been consumed the temperature decreases because the heat “removed” is greater than the heat “generated,” that is, $(\dot{Q}_{rb} > \dot{Q}_{gb})$. As a result the specific reaction-rate constant goes through a maximum as the fluid becomes heated at first and then later cooled. [Figure E13-1.4](#) shows the LEP slider variable while [Figure E13-1.5](#) shows the trajectories of the “heat generated,” Q_{gb} , and “heat removed,” Q_{rb} . A plot of Q_{gb} and Q_{rb} as a function of time can often be useful in understanding the reaction dynamics. Whenever $(\dot{Q}_{gb} > \dot{Q}_{rb})$ the reacting mixture temperature will **increase** and whenever $(\dot{Q}_{rb} > \dot{Q}_{gb})$ the temperature will **decrease**.

$$\frac{dT}{dt} = \frac{\dot{Q}_{gb} - \dot{Q}_{rb}}{N_{A0} \sum \Theta_i C_{P_i}} \quad (\text{E13-1.16})$$

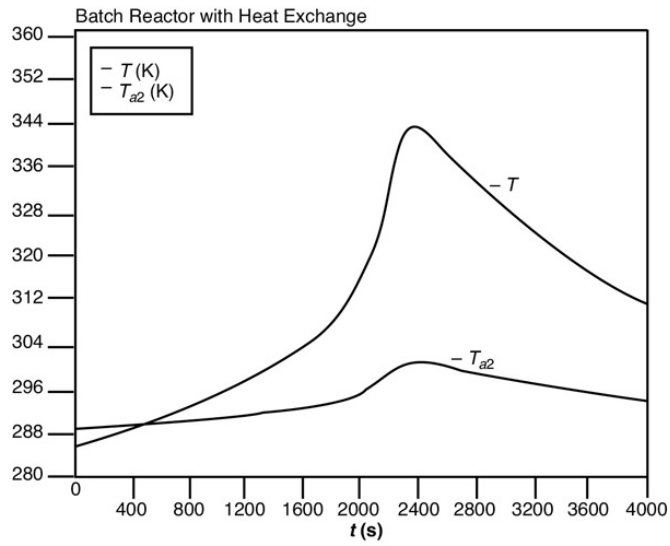


Figure E13-1.3 Polymath temperature–time trajectory.

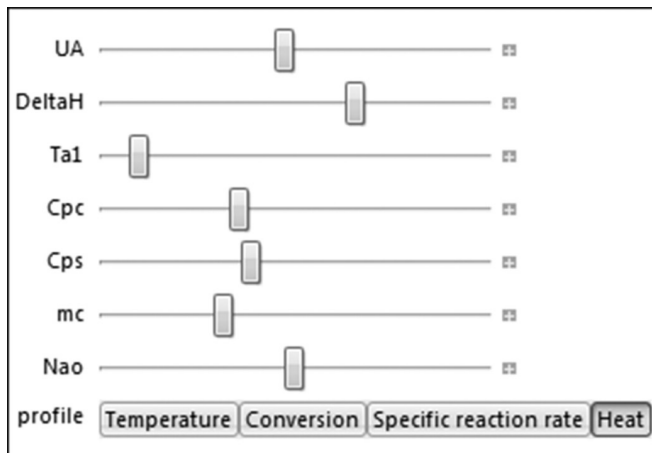
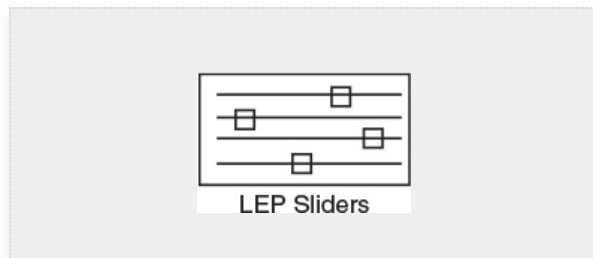


Figure E13-1.4 LEP sliders.



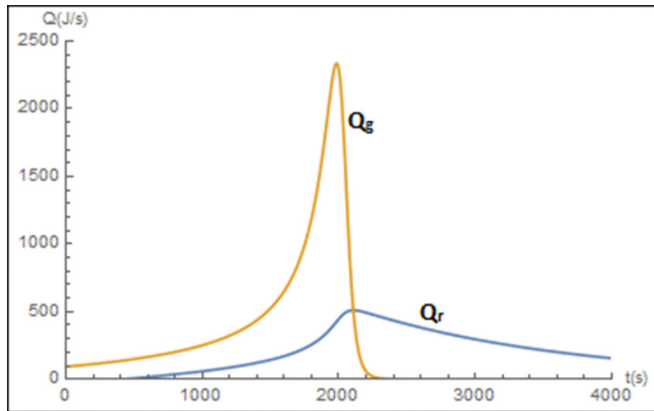


Figure E13-1.5 Wolfram heat-generated as heat-removed trajectories.

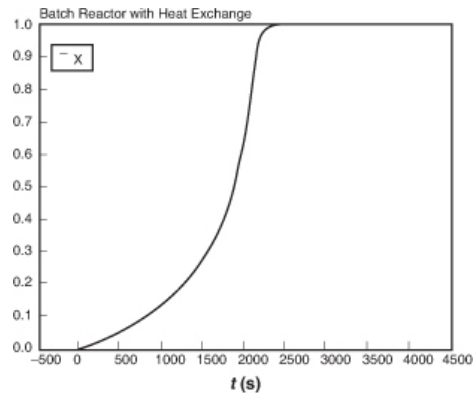


Figure E13-1.6 Polymath conversion–time trajectory.

Analysis:

(a) Adiabatic. The initial temperature is rather low, so the reaction is slow at first. However, as the exothermic reaction proceeds, it heats up and becomes virtually autocatalytic as it goes from a small conversion at 1600 seconds to complete conversion just a few seconds later. As seen in [Figure E13-1.6](#), the conversion reaches $X = 1.0$ and the temperature reaches its maximum value, where it remains.

(b) Heat Exchange. Because the temperature is maintained at a lower value in the heat exchange case than in the adiabatic case, there will be less conversion for the parameter values UA , T_{ai} , T_0 , \dot{m}_c , and so on,

given in the problem statement. However, if you change these values as suggested in **LEP** Problem P13-1_B (a), you will find situations where the conversion remains very low and other cases where the temperature curve is extremely steep.

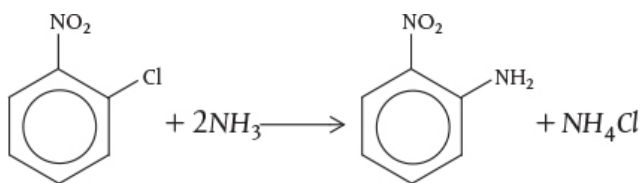
13.2.2 Case History of a Batch Reactor with Interrupted Isothermal Operation Causing a **Runaway Reaction**

In Chapters 5 and 6 we discussed the design of reactors operating isothermally. This operation may be achieved by efficient control of a heat exchanger. The following example shows what can happen when the heat exchanger suddenly fails.

Example 13–2 Safety in Chemical Plants with Exothermic Runaway Reactions²

² Adapted from the problem by Ronald Willey, *Seminar on a Nitroaniline Reactor Rupture*. Prepared for SACHE, Center for Chemical Process Safety, American Institute of Chemical Engineers, New York (1994). Also see *Process Safety Progress*, vol. 20, no. 2 (2001), pp. 123–129. The values of ΔH_{RX} and UA were estimated from the plant data of the temperature–time trajectory in the article by G. C. Vincent, *Loss Prevention*, 5, 46–52.

A serious accident occurred at the Monsanto plant in Sauget, Illinois, on August 8, 1969, at 12:18 A.M. (see Figure E13-2.1). (Sauget (pop. 200) is the home of the 1988 Mon-Clar League Softball Champions.) The blast was heard as far as 10 mi away in Belleville, Illinois, where people were awakened from a deep sleep. The explosion occurred in a batch reactor that was used to produce nitroaniline from ammonia and *o*-nitrochlorobenzene (ONCB):



This reaction is normally carried out isothermally at 175°C and about 500 psi over a 24-hour period. The ambient temperature of the cooling water in the heat exchanger is 25°C. By adjusting the coolant flow rate, the reactor temperature could be maintained at 175°C. At the maximum coolant rate, the ambient temperature is 25°C throughout the heat exchanger. Also review the T2 Laboratories Safety Modules ([http://umich.edu/~safeche/assets/pdf/courses/Problem/s/344ReactionEngrModule\(1\)PS-T2.pdf](http://umich.edu/~safeche/assets/pdf/courses/Problem/s/344ReactionEngrModule(1)PS-T2.pdf)).

Let me tell you something about the operation of this reactor. Over the years, the heat exchanger would fail from time to time, but the technicians would be “Johnny on the Spot” and run out and get it up and running within 10 minutes or so, and there was never any problem. It is believed that one day someone in

management looked at the reactor and said, “It looks as if your reactor is only a third full and you still have room to add more reactants and to make more product and more money. How about filling it up to the top so we could triple production?” They did, and started the reactor up at 9:45 P.M. Around midnight the reactor exploded and the aftermath is shown in Figure E13-2.1.

On the day of the accident, two changes in normal operation occurred.

1. The reactor was charged with 9.044 kmol of ONCB, 33.0 kmol of NH_3 , and 103.7 kmol of H_2O . Normally, the reactor is charged with 3.17 kmol of ONCB, 103.6 kmol of H_2O , and 43 kmol of NH_3 .

A decision was made to triple production.

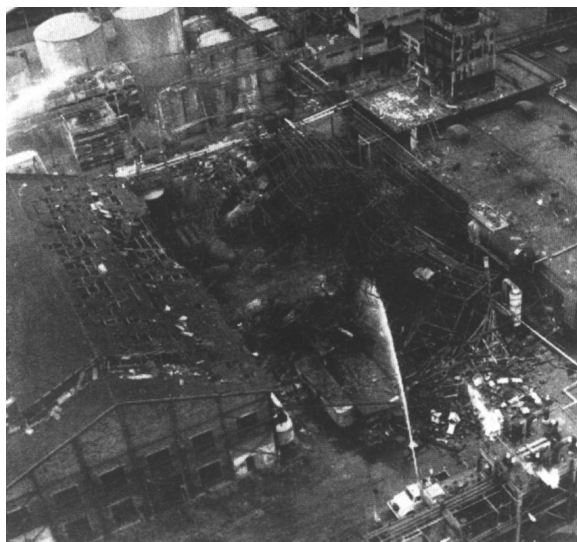


Figure E13-2.1 Aftermath of the explosion. (St. Louis *Globe/Democrat* photo by Roy Cook. Courtesy of St. Louis Mercantile Library.)

2. The reaction is normally carried out isothermally at 175°C over a 24-hour period. However, approximately 45 minutes after the reaction was started, cooling to the reactor failed, but only for 10 minutes, after which cooling was again up and running at the 55-minute mark. Cooling may have been halted for 10 minutes

or so on previous occasions when the normal charge of 3.17 kmol of ONCB was used and no ill effects occurred.

The reactor had a rupture disk designed to burst when the pressure exceeded approximately 700 psi. If the disk would have ruptured, the pressure in the reactor would have dropped, causing the water to vaporize, and the reaction would have been cooled (quenched) by the latent heat of vaporization.

1. Plot and analyze the temperature–time trajectory up to a period of 120 minutes after the reactants were mixed and brought up to 175°C (448K).
2. Show that *all* of the following three conditions had to have been present for the explosion to occur: (1) increased ONCB charge, (2) cooling stopped for 10 minutes at a time early in the reaction, and (3) relief-system failure.

Additional information:

Rate law: $-r_{\text{ONCB}} = kC_{\text{ONCB}}C_{\text{NH}_3}^3$

with $k = 0.00017 \frac{\text{m}^3}{\text{kmol} \cdot \text{min}}$ at 188°C (461 K) and $E = 11273 \text{ cal/mol}$

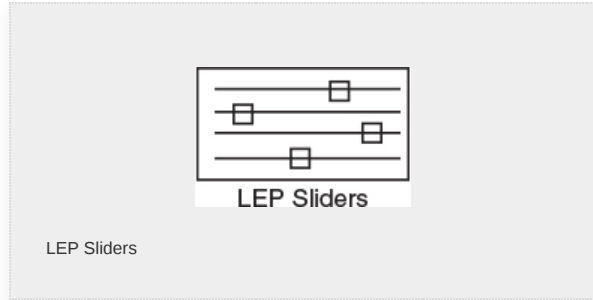
The reaction volume for the new charge of 9.0448 kmol of ONCB

$$V = V_{\text{aqNH}_3} = V_{\text{ONCB}}$$

Because ammonia is soluble in water, the aqueous ammonia volume will not change much as ammonia is added, and thus we will assume the volume is constant at 3.9 m^3 (i.e., $V_{\text{aqNH}_3} \equiv V_{\text{aqam}} = 3.9 \text{ m}^3$) for both cases. The volume of ONCB is

$$V_{\text{ONCB}} = \frac{N_{\text{ONCB}} \cdot MW_{\text{ONCB}}}{\rho_{\text{ONCB}}} = \frac{(0.94 \text{ kmol}) \left(157.5 \frac{\text{kg}}{\text{kmol}} \right)}{1199 \frac{\text{kg}}{\text{m}^3}} = 1.19 \text{ m}^3$$

The total volume for the increased charge to the reactor is



The total volume for the increased charge to the reactor is

$$V = 3.9 \text{ m}^3 + 1.19 \text{ m}^3 = 5.1 \text{ m}^3$$

Case history

The reaction volume for the previous 3.17 kmol ONCB charge was Assume that

$$V = 3.9 \text{ m}^3 + 0.42 \text{ m}^3 = 4.32 \text{ m}^3$$

$$\Delta H_{\text{Rx}} = -5.9 \times 10^5 \text{ kcal/kmol}$$

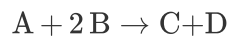
$$C_{\text{P}_{\text{ONCB}}} = C_{\text{P}_{\text{A}}} = 40 \text{ cal/mol} \cdot \text{K}$$

$$C_{\text{P}_{\text{H}_2\text{O}}} = c_{\text{P}_{\text{W}}} = 18 \text{ cal/mol} \cdot \text{K} \quad C_{\text{P}_{\text{NH}_3}} = C_{\text{P}_{\text{B}}} = 8.38 \text{ cal/mol} \cdot \text{K}$$

Assume that $\Delta C_p \approx 0$

$$UA = \frac{35.85 \text{ kcal}}{\text{min}^\circ\text{C}} \text{ with } T_a = 298 \text{ K}$$

Solution



Mole Balance:

$$\frac{dX}{dt} = -r_{\text{A}} \frac{V}{N_{\text{A}0}} = \frac{-r_{\text{A}}}{C_{\text{A}0}} \quad (\text{E13-2.1})$$

Rate Law:

$$-r_A = kC_A C_B \quad (\text{E13-2.2})$$

Stoichiometry (liquid phase):

$$C_A = C_{A0} (1 - X) \quad (\text{E13-2.3})$$

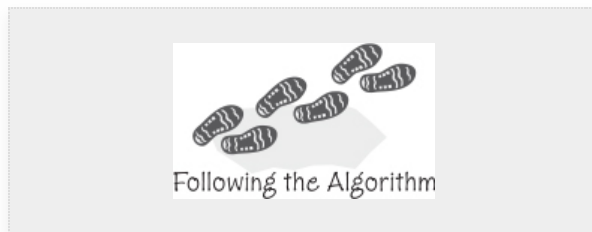
with

$$C_B = C_{A0} (\Theta_B - 2X) \quad (\text{E13-2.4})$$

$$\Theta_B = \frac{N_{B0}}{N_{A0}}$$

Combine:

$$-r_A = kC_{A0}^2 (1 - X) (\Theta_B - 2X) \quad (\text{E13-2.5})$$



Substituting our parameter values into Equation (3-21)

$$k = k(T_0) \exp \left[\frac{E}{R} \left(\frac{1}{T_0} - \frac{1}{T_1} \right) \right] \quad (3-21)$$

We obtain

$$k = 0.00017 \exp \left[\frac{11273}{1.987} \left(\frac{1}{461} - \frac{1}{T} \right) \right] \frac{\text{m}^3}{\text{kmol} \cdot \text{min}}$$

Energy Balance:

$$\frac{dT}{dt} = \frac{Q_g - Q_r}{\Sigma N_i C_{P_i}} \quad (\text{E13-2.6})$$

For $\Delta C_P = 0$,

$$\Sigma N_i C_{P_i} = N C_P = N_{A0} C_{P_A} + N_{B0} C_{P_B} + N_w C_{P_w} \quad (\text{E13-2.7})$$

Parameter evaluation for day of explosion:

$$NC_P = (9.04)(40) + (103.7)(18) + (33)(8.38)$$

$$NC_P = 2505 \text{ kcal/K}$$

Substituting for $\sum N_i C_{P_i}$, \dot{Q}_g , and \dot{Q}_r in Equation (E13-2.6) one obtains

$$\frac{dT}{dt} = \frac{\overbrace{(r_A V)(\Delta H_{Rx})}^{Q_g} - \overbrace{UA(T - T_a)}^{Q_r}}{N_{A0}C_{P_A} + N_{B0}C_{P_B} + N_W C_{P_W}} \quad (\text{E13-2.8})$$

$$Q_g = (r_A V)(\Delta H_{Rx})$$

$$Q_r = UA(T - T_a)$$

A. Isothermal Operation up to 45 Minutes

The reaction takes place isothermally at 175°C (448 K) up to the time the heat exchanger fails and cooling stops at 45 minutes. We will calculate the conversion, X , the temperature, T , as well as Q_r and Q_g at the point that the heat exchanger fails. Next we calculate T , X , Q_r , and Q_g again 10 minutes later at the point when cooling is restored, and then again compare Q_g and Q_r .

Combining Equations (E13-2.1) with (E13-2.5) and canceling yields

$$\frac{dX}{dt} = kC_{A0}(1 - X)(\Theta_B - 2X) \quad (\text{E13-2.9})$$

$$\Theta_B = \frac{33}{9.04} = 3.64$$

Integrating Equation (E13-2.9) gives us

$$t = \left[\frac{V}{kN_{A0}} \right] \left(\frac{1}{\Theta_B - 2} \right) \ln \left[\frac{\Theta_B - 2X}{\Theta_B(1 - X)} \right] \quad (\text{E13-2.10})$$

At 175°C = 448 K, $k = 0.000119 \text{ m}^3/\text{kmol} \cdot \text{min}$.

Substituting for k and the other parameter values

$$45 \text{ min} = \left[\frac{5.119 \cdot \text{m}^3}{0.0001167 \text{ m}^3/\text{kmol} \cdot \text{min} (9.044 \text{ kmol})} \right] \times \left(\frac{1}{1.64} \right) \ln \left[\frac{3.64 - 2X}{3.64(1-X)} \right]$$

The calculation and results can also be obtained from the Polymath output.

Solving for X , we find that at $t = 45 \text{ min}$, then $X = 0.034$.

We can now calculate the rate of generation, Q_g , at this temperature and conversion and compare it with the maximum rate of heat removal, Q_r , that is available for a constant coolant temperature of $T_a = 298 \text{ K}$. The rate of generation, Q_g , is

$$Q_g = r_A V \Delta H_{Rx} = k \frac{N_{A0}(1-X)N_{A0}[(N_{B0}/N_{A0}) - 2X]V(-\Delta H_{Rx})}{V^2} \quad (\text{E13-2.11})$$

Comparing Q_r and Q_g at the Time Cooling Stops

At this time (i.e., $t = 45 \text{ min}$, $X = 0.034$, $T = 175^\circ\text{C}$), we calculate k , then Q_r and Q_g . At 175°C , $k = 0.000119 \text{ m}^3/\text{min} \cdot \text{kmol}$.

$$Q_g = (0.000119) \frac{(9.044)^2(1-0.034)}{5.1} \left[\frac{33}{9.044} - 2(0.034) \right] 5.9 \times 10^5$$

\$

$$Q_g = 3904 \text{ kcal/min}$$

The corresponding maximum cooling rate is

$$\begin{aligned} Q_r &= UA(T - 298) \\ &= 35.85(448 - 298) \end{aligned} \quad (\text{E13-2.12})$$

$$Q_r = 5378 \text{ kcal/min}$$

Therefore

$$Q_r > Q_g \quad (\text{E13-2.13})$$

The reaction can be controlled. There would have been no explosion had the cooling not failed.

B. Adiabatic Operation for 10 Minutes

Unexpectedly, the cooling failed from 45 to 55 minutes after the reaction was started. We will now use the conditions at the end of the period of isothermal operation as our initial conditions for the adiabatic operation period between 45 and 55 minutes

$$t = 45 \text{ min} \quad X = 0.034 \quad T = 448 \text{ K}$$

Between $t = 45$ and $t = 55$ minutes, $Q_r = 0$. The Polymath program was modified to account for the time of adiabatic operation by using an “*if statement*” for Q_r in the program, that is,

$$Q_r = \text{if } (t > 45 \text{ and } t < 55) \text{ then } (0) \text{ else } (UA(T - 298))$$

A similar “*if statement*” is used for isothermal operation between $t = 0$ and $t = 45$ minutes, that is, $(dT/dt) = 0$ and as shown in the Polymath and Wolfram Program.

Comparing Q_r and Q_g after 10 minutes of Adiabatic Operation

For the 45- to 55-minute period without cooling, the temperature rose from 448 K to 468 K, and the conversion increased from 0.034 to 0.0432. Using this temperature and conversion in Equation (E13-2.11), we calculate the rate of generation Q_g at 55 minutes and see that it has increased to

$$Q_g = 6638 \text{ kcal / min}$$

The maximum rate of cooling at this reactor temperature is found from Equation (E13-2.12) to be

$$Q_r = 6101 \text{ kcal/min}$$

Everything is OK.

Interruptions in the cooling system have happened before with no ill effects.

$\dot{Q}_g > \dot{Q}_r$ Oh no, looks like we may be in trouble.

We can also use the **LEP** Polymath Program to find these values for X , T , Q_r , and Q_g . In addition we note that by changing the run time from $t = 45$ to $t = 55$ minutes and by including an “if statement,” we can include the complete calculation of trajectory temperature and conversion versus time. The “if” statement will include the time of isothermal operation up to 45 minutes,

$$\frac{dT}{dt} = \text{if } (t < 45) \text{ then } (0) \text{ else } ((Q_g - Q_r)/NC_p)$$

and adiabatic operation between 45 and 55 and heat exchange thereafter.

$$Q_r = \text{if } (45 < t < 55) \text{ then } (0) \text{ else } (UA(T - 298))$$

Here, we see that at the end of the 10-minute down time, the heat exchange system is now operating again, but now

$$Q_g > Q_r \quad (\text{E13-2.14})$$

and the temperature will continue to increase. *We have a Runaway Reaction!!* The **point of no return** has been passed and the temperature will continue to increase, as will the rate of reaction until the explosion occurs.

C. Batch Operation with Heat Exchange

Return of the cooling occurs at 55 minutes after startup. The values at the end of the period of adiabatic operation ($T = 468$ K, $X = 0.0433$) become the initial conditions for the period of restored operation with the heat exchange. The cooling is turned on at its maximum capacity, $Q_r = UA(T - 298)$, at 55 minutes. Table E13-2.1 gives the Poly-math program to determine the temperature–time trajectory. (Note that one can change N_{A0} and N_{B0} to 3.17 and 43 kmol in the program and show that, if the cooling is shut off for 10 minutes, at the end of that 10 minutes, Q_r will still be greater than Q_g and no explosion will occur and one should really do that calculation.)

The point of no return

TABLE E13-2.1 POLYMATH PROGRAM

Differential equations

$$1 \quad d(T)/d(t) = \text{if } (t < t_1) \text{ then } (0) \text{ else } ((Q_g - Q_r)/NC_p)$$

$$2 \quad d(X)/d(t) = (-r_a) * V / N_{A0}$$

Explicit equations

$$1 \quad N_{A0} = 9.044 \text{ \#kmol}$$

$$2 \quad N_{B0} = 33 \text{ \#kmol}$$

$$3 \quad N_W = 103.7 \text{ \#kmol}$$

$$4 \quad m_{A0} = N_{A0} * 157.55 \text{ \#kg}$$

$$5 \quad m_{B0} = N_{B0} * 17.03 \text{ \#kg}$$

$$6 \quad m_W = N_W * 18.03 \text{ \#kg}$$

$$7 \quad NC_p = N_{A0} * 40 + N_W * 18 + N_{B0} * 8.38 \text{ \#kcal/K}$$

$$8 \text{ } V_a = m_{ao}/1199 \text{ \#m}^3$$

$$9 \text{ } V_{aqam} = (m_{bo} + m_w)/\rho_{oaqam} \text{ \#m}^3$$

$$10 \text{ } V = V_a + V_{aqam} \text{ \#m}^3$$

$$11 \text{ } \Delta H_{rx} = -590000 \text{ \#kcal/kmol}$$

$$12 \text{ } k = .00017 * \exp(11273 / (1.987) * (1/461 - 1/T)) \text{ \#m}^3 / (\text{kmol} \cdot \text{min})$$

$$13 \text{ } t_2 = 55 \text{ \#min}$$

$$14 \text{ } U_A = 35.85 \text{ \#kcal}/(\text{min } ^\circ\text{C})$$

$$15 \text{ } t_1 = 45 \text{ \#min}$$

$$16 \text{ } Q_r = \text{if}(t > t_1 \text{ and } t < t_2) \text{ then } (0) \text{ else } (U_A * (T - 298)) \text{ \#kcal/min}$$

$$17 \text{ } \theta_{eata} = N_{bo}/N_{ao}$$

$$18 \text{ } r_a = -k * n_{ao}^2 * (1 - X) * (\theta_{eata} - 2 * X) / V^2 \text{ \#kmol}/(\text{m}^3 \cdot \text{min})$$

$$19 \text{ } Q_g = r_a * V * \Delta H_{rx} \text{ \#kcal/min}$$

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	DeltaHrx	-5.9E+05	-5.9E+05
2	k	0.0001189	2.900631
3	mao	1424.882	1424.882
4	mbo	561.99	561.99
5	mw	1869.711	1869.711
6	Nao	9.044	9.044
7	Nbo	33.	33.

8	NCp	2504.9	2504.9
9	Nw	103.7	103.7
10	Qg	4116.257	1.356334
11	Qr	5377.5	6.87E+04
12	ra	-0.0013711	-4.518E-07
13	t	0	122.
14	T	448.	2214.403
15	t1	45.	45.
16	t2	55.	55.
17	Theata	3.648828	3.648828
18	UA	35.85	35.85
19	V	5.088392	5.088392
20	Va	1.188392	1.188392
21	Vaqam	3.9	3.9
22	X	0	1.

The complete temperature–time trajectory is shown in Figure E13-2.2. One notes the long plateau after the cooling is turned back on. Using the values of Q_g and Q_r at 55 minutes and substituting into Equation (E13-2.8), we find that

$$\frac{dT}{dt} = \frac{(6638 \text{ kcal/min} - (6101 \text{ kcal/min}))}{2505 \text{ kcal/}^\circ\text{C}} = 0.2^\circ\text{C/min}$$

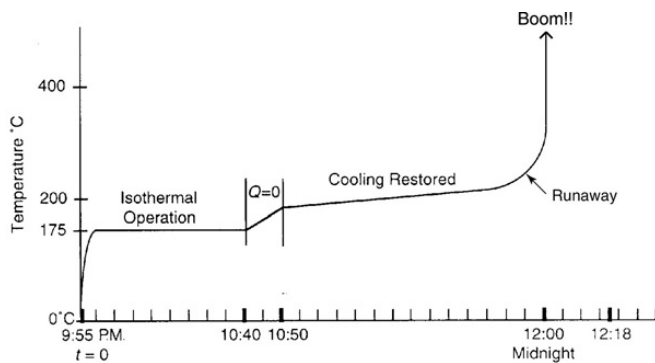


Figure E13-2.2 Temperature–time trajectory.

Consequently, even though (dT/dt) is positive, the temperature increases very slowly at first, $0.2^\circ\text{C}/\text{min}$. By 11:45, the temperature has reached 240°C and both the “heat generated” and the temperature begin to increase more rapidly. This rapid increase is a result of the Arrhenius temperature dependence, which causes the temperature to increase exponentially. The reaction is **running away**! One observes in [Figure E13-2.2](#) that 119 minutes after the batch reaction was started, the temperature increases sharply and the reactor explodes at approximately midnight. If the mass and heat capacity of the stirrer and reaction vessel had been included, the NC_p term would have increased by about 5% and extended the time until the explosion occurred by 15 or so minutes, which would predict the actual time the explosion occurred, at 12:18 A.M.

When the temperature reached 300°C , a secondary reaction, the decomposition of nitroaniline to noncondensable gases such as CO , N_2 , and NO_2 , occurred, releasing even more energy. The total energy released was estimated to be $6.8 \times 10^9 \text{ J}$, which is enough energy to lift the entire 2500-ton building 300 m (the length of three football fields) straight up. In Problem **P13-1B (b)** you are asked to use the Wolfram sliders to explore this example, that is, E13-2, and find such things as the value of amount of reactant fed below which **no explosion** would have occurred.

D. Safety Disk Rupture Failure

We note that the pressure-safety-relief disk should have ruptured when the temperature reached 265°C (ca. 700 psi) but did not and the temperature continued to rise. If it had ruptured and all the water had vaporized, then 10^6 kcal would have been drawn from the reacting solution, thereby lowering its temperature and quenching the runaway reaction.

If the disk had ruptured at 265°C (700 psi), we know from fluid mechanics that the maximum mass flow

rate, \dot{m}_{vap} , out of the 2-in. orifice to the atmosphere (1 atm) would have been 830 kg/min at the time of rupture. The corresponding heat removed would have been

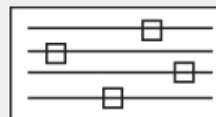


LEP Sliders

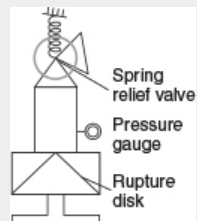
The explosion occurred shortly after midnight.



Runaway Reaction



LEP Sliders



$$\begin{aligned}
 Q_r &= \dot{m}_{\text{vap}} \Delta H_{\text{vap}} + UA(T - T_a) \\
 &= 830 \frac{\text{kg}}{\text{min}} \times 540 \frac{\text{kcal}}{\text{kg}} + 35.83 \frac{\text{kcal}}{\text{min} \cdot \text{K}} (538 - 298) \text{K} \\
 &= 4.48 \times 10^5 \frac{\text{kcal}}{\text{min}} + 8604 \frac{\text{kcal}}{\text{min}} \\
 &= 456604 \frac{\text{kcal}}{\text{min}}
 \end{aligned}$$

This value of Q_r is much greater than the “heat generated” Q_g

($Q_g = 26990 \text{ kcal/min}$), so that the reaction could have been easily quenched.

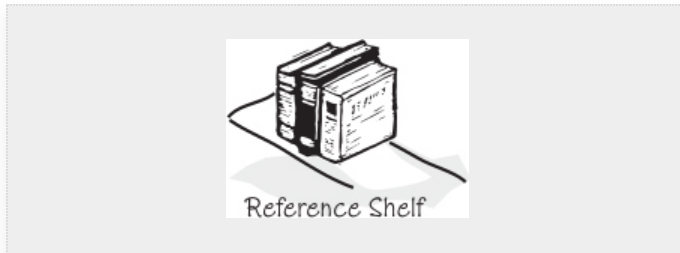
Analysis: Runaway reactions are the most deadly in the chemical industry. Elaborate safety measures are usually installed to prevent them from occurring. However, as we show in this example, the backup plan failed. *If any one of the following three things had **not** occurred, the explosion would **not** have happened.*

1. Tripled production
2. Heat-exchanger failure for 10 minutes early in the operation
3. Failure of the relieving device (rupture disk)

In other words, all the above had to happen to cause the explosion. If the relief valve had operated properly, it would not have prevented reaction runaway but it could have prevented the explosion. In addition to using rupture disks as relieving devices, one can also use pressure relief valves. In many cases, sufficient care is not taken to obtain data for the reaction at hand and to use it to properly size the relief device. This data can be obtained using a specially designed batch reactor called the *Advanced Reactor Safety Screening Tool* (ARSST) described in the Professional Reference Shelf

(http://www.umich.edu/~elements/6e/13chap/pdf/CD_ARSSST_ProfRef.pdf). You can now see this example on the Web site *Process Safety Across the Chemical Engineering Curriculum* (<http://umich.edu/~safeche>) and click on Chemical Reaction Engineering Course.

Another example of runaway reactions in CRE is Module 2, on the safety Web site, the Synthron explosion. This semibatch reactor shows a similar situation where reactants were added at a rate such that the heat generated \dot{Q}_g was greater than the heat removed \dot{Q}_r .



13.3 BATCH AND SEMIBATCH REACTORS WITH A HEAT EXCHANGER

In our past discussions of reactors with heat exchangers, we assumed that the ambient temperature T_a was spatially uniform throughout the exchangers. This assumption is a good one if the system is a tubular reactor with the external pipe surface exposed to the atmosphere, or if the system is a CSTR or BR where the coolant flow rate through the exchanger is so rapid that the coolant temperatures entering and leaving the exchanger are virtually the same.

We now consider the case where the coolant temperature varies along the length of the exchanger while the temperature in the reactor is spatially uniform. The coolant enters the exchanger at a mass flow rate, \dot{m}_c , at a temperature, T_{a1} , and leaves at a temperature, T_{a2} (see Figure 13-1). Figure 13-1 could represent a **CSTR** as shown, or for a **batch reactor (BR)** if the *inlet and outlet* flow rate were set to zero, that is, $F_A = F_{A0} = 0$, or for a **semibatch reactor (SBR)** if the *outlet* streams are set equal to zero, that is, $F_A = F_B = 0$.

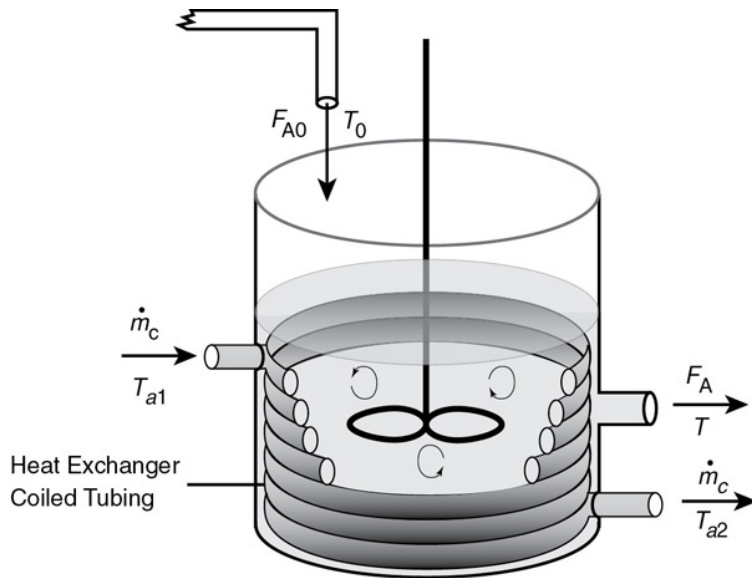


Figure 13-1 Tank reactor with heat exchanger.

As a first approximation, we assume a quasi-steady state for the coolant flow and neglect the accumulation term (i.e., $dT_c/dt = 0$). As a result, Equation (12-19) will give the rate of heat transfer *from* the exchanger *to* the reactor

$$\dot{Q} = \dot{m}_c C_{p_c} (T_{a1} - T) \left[1 - \exp(-UA/\dot{m}_c C_{p_c}) \right] \quad (12-19)$$

The energy balance on a semibatch reactor is

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s = \sum F_{i0} C_{p_i} (T - T_{i0}) - [\Delta H_{R_x}(T)](-r_A V)}{\sum N_i C_{p_i}} \quad (13-9)$$

Using a slight rearrangement of the heat exchanger energy balance equation, that is, Equation (12-9) and neglecting shaft work, \dot{W}_s

$$\frac{dT}{dt} = \frac{\dot{Q}_{gs} - \dot{Q}_{rs}}{\sum N_i C_{p_i}} \quad (13-20)$$

where the “heat generated,” \dot{Q}_{gs} , for a the semibatch reactor is the same as that for a BR,

$$\dot{Q}_{gs} = (r_A V) (\Delta H_{R_x}) \quad (13-21)$$

however, the “heat removed” for a semibatch reactor, \dot{Q}_{rs} , is

$$\dot{Q}_{rs} = \Sigma F_{i0} C_{P_i} (T - T_{i0}) + \dot{m} C_{P_C} [T - T_{a1}] \left[1 - \exp \left(\frac{-UA}{\dot{m} C_{P_C}} \right) \right] \quad (13-22)$$

Note: The subscript “s” in \dot{Q}_{rs} and \dot{Q}_{gs} means these equations only apply to a semibatch reactor.

For large coolant flow rates, we showed in [Section 12.4.1](#) that the exponent in Equation (13-22) could be expanded and therefore Equation (13-22) can be written as

$$\frac{dT}{dt} = \frac{\overbrace{(r_A V)(\Delta H_{Rx})}^{\dot{Q}_{gs}} - \overbrace{[\Sigma F_{i0}(T - T_{i0}) + UA(T - T_a)]}^{\dot{Q}_{rs}}}{\Sigma N_i C_{P_i}} \quad (13-23)$$

One added complexity for the semibatch reactor is that the heat-transfer area, A , could vary with time. For example, as the tank in [Figure 13-1](#) fills up, more of the reacting fluid comes in contact with the heat-exchanger area, consequently this area changes significantly as the fluid level rises. This change in area will depend on the reactor geometry, how the exchanger is placed in the reactor, and the initial and final fluid volumes in the reactor. In the semibatch reactor examples that follow, we will assume the surface area, A , remains virtually constant, although this assumption will be analyzed in Problem P13-1B (d) (vii).

13.3.1 Startup of a CSTR

In reactor startup, it is often very important *how* temperature and concentrations approach their steady-state values. For example, a significant overshoot in temperature may cause a reactant or product to degrade, or the overshoot may be unacceptable for safe operation, such as initiating a secondary reaction that causes runaway. If either case were to occur, we would say that the system exceeded its *practical stability limit*. The practical limit is specific to the specific reaction and conditions under which the reaction is carried out, and is usually determined by the reaction safety engineer. Although we can solve the unsteady temperature–time and

concentration–time equations numerically to see whether such a limit is exceeded, it is often more insightful to study the approach to steady state by using the *temperature–concentration phase plane*. To illustrate these concepts, we shall confine our analysis to a liquid-phase reaction carried out in a CSTR.

A qualitative discussion of how a CSTR approaches steady state is given in *PRS R13.5* on the CRE Web site (<http://www.umich.edu/~elements/6e/13chap/prof-steadystate.html>). This analysis, summarized in *Figure PRS13.5* in the Summary is developed to show the four different regions into which the phase plane is divided and how they allow one to sketch the approach to the steady state.

Startup of a CSTR



Example 13–3 Startup of a CSTR

Again, we consider the production of propylene glycol (C) in a CSTR with a heat exchanger in [Example 12-3](#). Initially there is only water, $C_{wi} = 55.3 \text{ kmol/m}^3$, at $T_i = 297 \text{ K}$ and 0.1 wt % H_2SO_4 in the 1.89 m^3 reactor. The feed stream consists of 36.3 kmol/h of propylene oxide (A), 453.6 kmol/h of water (B) containing 0.1 wt % H_2SO_4 , and 45.4 kmol/h of methanol $\text{A} + \text{B} \rightarrow \text{C}$ (M).

The water coolant flows through the heat exchanger at a rate of 2.27 kg/s (453.6 kmol/h). The molar densities of pure propylene oxide (A), water (B), and methanol (M) are $\rho_{A0} = 14.8 \text{ kmol/m}^3$, $\rho_{B0} = 55.3 \text{ kmol/m}^3$, and $\rho_{M0} = 24.7 \text{ kmol/m}^3$, respectively.

Plot the temperature and concentration of propylene oxide as a function of time, and also the concentration of A as a function of temperature for different entering temperatures and initial concentrations of A in the reactor to learn whether the practical stability limit of 355 K is exceeded.

Additional information:

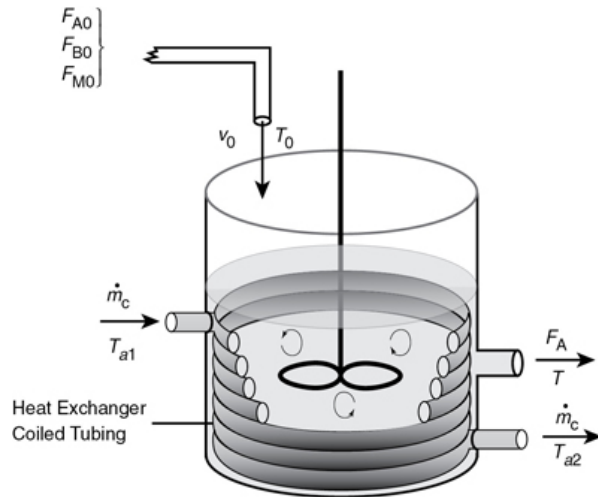
$$UA = 7262 \frac{\text{kcal}}{\text{h} \cdot \text{K}} \text{ with } T_{a1} = 288.7 \text{ K, with } C_{P_w} = 18 \text{ kcal/kmol} \cdot \text{K}$$

$$C_{P_A} = 35 \text{ kcal/kmol} \cdot \text{K}, C_{P_B} = 18 \text{ kcal/kmol} \cdot \text{K}$$

$$C_{P_C} = 46 \text{ kcal/kmol} \cdot \text{K}, C_{P_M} = 19.5 \text{ kcal/kmol} \cdot \text{K}$$

Is the practical stability limit exceeded?

Again, the temperature of the mixed reactant streams entering the CSTR is $T_0 = 297 \text{ K}$.



Solution



Mole Balances:

Initial Conditions

$$A: \frac{dC_A}{dt} = r_A + \frac{(C_{A0} - C_A)v_0}{V} \quad C_{Ai} = 0 \quad (\text{E13-3.1})$$

$$B: \frac{dC_B}{dt} = r_B + \frac{(C_{B0} - C_B)v_0}{V} \quad C_{Bi} = 55.3 \frac{\text{kmol}}{\text{m}^3} \quad (\text{E13-3.2})$$

$$C: \frac{dC_C}{dt} = r_C + \frac{-C_C v_0}{V} \quad C_{Ci} = 0 \quad (\text{E13-3.3})$$

$$M: \frac{dC_M}{dt} = \frac{v_0(C_{M0} - C_M)}{V} \quad C_{Mi} = 0 \quad (\text{E13-3.4})$$

Rate Law:

$$-r_A = kC_A \quad (\text{E13-3.5})$$

Stoichiometry:

$$-r_A = -r_B = r_C \quad (\text{E13.3.6})$$

Energy Balance:

$$\frac{dT}{dt} = \frac{\dot{Q}_{\text{gs}} - \dot{Q}_{\text{rs}}}{NC_P} \quad (\text{E13-3.7})$$

where

$$\dot{Q}_{gs} = (r_A V)(\Delta H_{Rx}) \quad (\text{E13.3.8})$$



using

$$\sum F_{i0} C_{P_i} = F_{A0} \sum \Theta_i C_{P_i} \quad (\text{E13-3.9})$$

the “heat removed” term from the unsteady startup of a CSTR is similar to that for the “heat removed” term from a semi batch reactor. Recalling Equations (12-12) and (12-19)

$$\dot{Q}_{rs} = \overbrace{F_{A0} \sum \Theta_i C_{P_i} (T - T_0)}^{\dot{Q}_{rs1}} + \overbrace{\dot{m}_c C_{P_c} (T - T_{a1}) \left[1 - \exp \left(\frac{-UA}{\dot{m}_c C_{P_c}} \right) \right]}^{\dot{Q}_{rs2}} \quad (\text{E13-3.10})$$

$$\dot{Q}_{rs} = \dot{Q}_{rs1} + \dot{Q}_{rs2}$$

\dot{Q}_{rs1} is the sensible heat removed by flow of material into the reactor and being heated while \dot{Q}_{rs2} is the heat removed by the heat exchanger.

$$T_{a2} = T - (T - T_{a1}) \exp \left(-\frac{UA}{\dot{m}_c C_{P_c}} \right) \quad (12-17)$$

Evaluation of Parameters:

$$\begin{aligned} NC_P &= \sum N_i C_{P_i} = C_{P_A} N_A + C_{P_B} N_B + C_{P_C} N_C + C_{P_M} N_M \quad (\text{E13-3.11}) \\ &= 35 (C_A V) + 18 (C_B V) + 46 (C_C V) + 19.5 (C_M V) \end{aligned}$$

$$\begin{aligned} \sum \Theta_i C_{P_i} &= C_{P_A} + \frac{F_{B0}}{F_{A0}} C_{P_B} + \frac{F_{M0}}{F_{A0}} C_{P_M} \quad (\text{E13-3.12}) \\ &= 35 + 18 \frac{F_{B0}}{F_{A0}} + 19.5 \frac{F_{M0}}{F_{A0}} \end{aligned}$$

$$v_0 = \frac{F_{A0}}{\rho_{A0}} + \frac{F_{B0}}{\rho_{B0}} + \frac{F_{M0}}{\rho_{M0}} = \left(\frac{F_{A0}}{14.8} + \frac{F_{B0}}{55.3} + \frac{F_{M0}}{24.7} \right) \frac{\text{m}^3}{\text{h}} \quad (\text{E13-3.13})$$

Neglecting because ΔC_p it changes the heat of reaction insignificantly over the temperature range of the reaction, the heat of reaction is assumed constant at its reference temperature

$$\Delta H_{\text{Rx}} = -20013 \frac{\text{kcal}}{\text{kmolA}}$$

The Polymath program is shown in [Table E13-3.1](#).

[Figures E13-3.1](#) and [E13-3.2](#) show the concentration of propylene oxide and reactor temperature as a function of time, respectively, for an initial temperature of $T_i = 297 \text{ K}$ and only water in the tank (i.e., $C_{Ai} = 0$). One observes that both the temperature and concentration oscillate around their steady-state values ($T = 331 \text{ K}$, $C_A = 0.658 \text{ kmol/m}^3$) as steady state is approached.

[Figure E13-3.3](#) combines [Figures E13-3.1](#) and [E13-3.2](#) into a phase plot of C_A versus T . The final steady-state operating concentration of A is 0.658 kmol/m^3 at a temperature of 331.5 K . The arrows on the phase-plane plots show the trajectories with increasing time. The maximum temperature reached during startup is 337.5 K , which is below the *practical stability limit* of 355 K .

Unacceptable startup

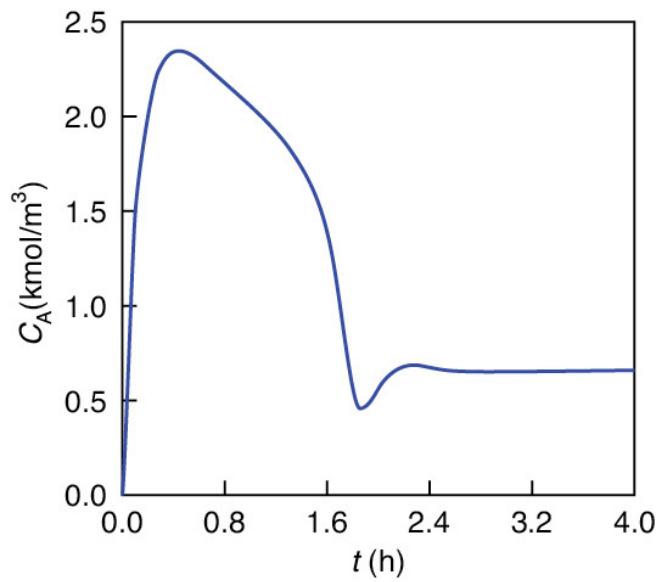


Figure E13-3.1 Propylene oxide concentration as a function of time for $C_{Ai} = 0$ and $T_i = 297$ K.

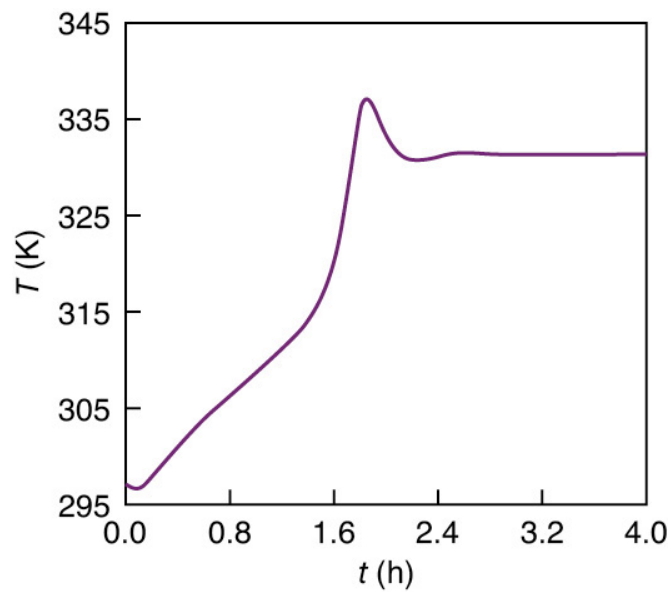


Figure E13-3.2 Temperature-time trajectory for CSTR startup for $C_{Ai} = 0$ and $T_i = 297$ K.

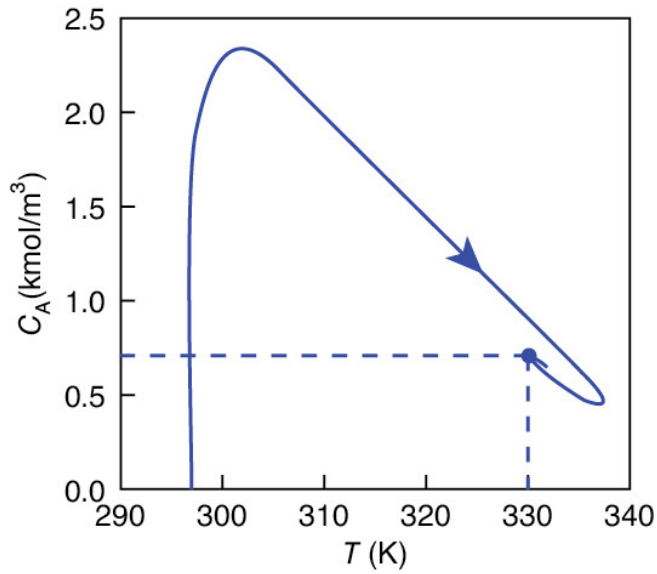


Figure E13-3.3 Concentration–temperature phase-plane trajectory using Figures E13-3.1 and E13-3.2.

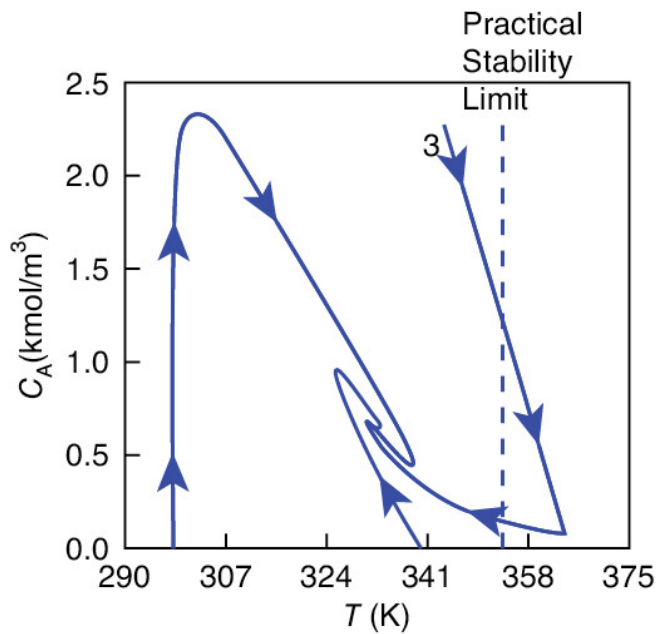


Figure E13-3.4 Concentration–temperature phase-plane for three different initial conditions.

Next, consider Figure E13-3.4, which shows three different phase-plane trajectories for three different sets of initial conditions:

$$(1) T_i = 297 \text{ K} \quad C_{Ai} = 0 \quad (\text{same as Figure E13-3.3})$$

$$(2) T_i = 339 \text{ K} \quad C_{Ai} = 0$$

$$(3) T_i = 344 \text{ K} \quad C_{Ai} = 2.26 \text{ kmol/m}^3$$

After 3 hours, the reaction is operating at steady state and all three trajectories converge on the final steady-state temperature of 331 K and the corresponding steady-state concentrations

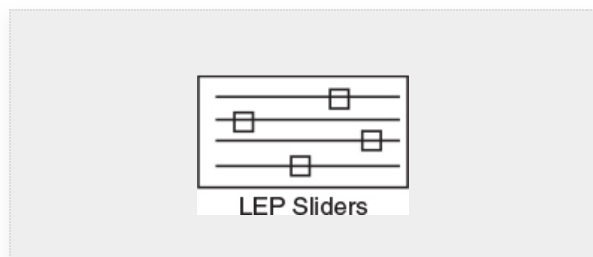
$$C_A = 0.658 \text{ kmol/m}^3 \quad C_C = 2.25 \text{ kmol/m}^3$$

$$C_B = 34 \text{ kmol/m}^3 \quad C_M = 3.63 \text{ kmol/m}^3$$

$$T = 331.5 \text{ K}$$

One can use the Wolfram sliders in the LEP for [Example 13-3](#) to observe how the parameters change the trajectories as the temperature and concentration approach steady state.

For this reaction system, the plant safety office believes that an upper temperature limit of 355 K should not be exceeded in the tank. This temperature is the practical stability limit. The **practical stability limit** represents a temperature above which it is undesirable to operate because of unwanted side reactions, safety considerations, damage to equipment, or secondary runaway reactions, such as in the T2 Explosion. Consequently, we see that if we started at an initial temperature of



Oops! The practical stability limit was exceeded.

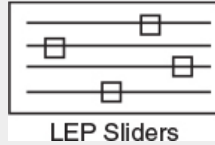


TABLE E13-3.1 POLYMATH PROGRAM FOR CSTR

STARTUP

Differential equations

$$1 \frac{d(C_a)}{d(t)} = 1/\tau(C_{a0} - C_a) + r_a$$

$$2 \frac{d(C_b)}{d(t)} = 1/\tau(C_{b0} - C_b) + r_b$$

$$3 \frac{d(C_c)}{d(t)} = 1/\tau(0 - C_c) + r_c$$

$$4 \frac{d(C_m)}{d(t)} = 1/\tau(C_{m0} - C_m)$$

$$5 \frac{d(T)}{d(t)} = (Q_g - Q_r)/NC_p$$

Explicit equations

$$1 Fa_0 = 36.3$$

$$2 T_0 = 297$$

$$3 V = 1.89$$

$$4 UA = 7262$$

$$5 dh = -20013$$

$$6 Ta_1 = 288.7$$

$$7 k = 16.96e12 \cdot \exp(-18012/1.987/(T))$$

$$8 \text{ Fb0} = 453.6$$

$$9 \text{ Fm0} = 45.4$$

$$10 \text{ mc} = 453.6$$

$$11 \text{ ra} = -k * \text{Ca}$$

$$12 \text{ rb} = -k * \text{Ca}$$

$$13 \text{ rc} = k * \text{Ca}$$

$$14 \text{ Nm} = \text{Cm} * \text{V}$$

$$15 \text{ Na} = \text{Ca} * \text{V}$$

$$16 \text{ Nb} = \text{Cb} * \text{V}$$

$$17 \text{ Nc} = \text{Cc} * \text{V}$$

$$18 \text{ ThetaCp} = 35 + \text{Fb0} / \text{Fa0} * 18 + \text{Fm0} / \text{Fa0} * 19.5$$

$$19 \text{ v0} = \text{Fa0} / 14.8 + \text{Fb0} / 55.3 + \text{Fm0} / 24.7$$

$$20 \text{ Ta2} = \text{T} - (\text{T} - \text{Ta1}) * \exp(-\text{UA} / (18 * \text{mc}))$$

$$21 \text{ Ca0} = \text{Fa0} / \text{v0}$$

$$22 \text{ Cb0} = \text{Fb0} / \text{v0}$$

$$23 \text{ Cm0} = \text{Fm0} / \text{v0}$$

$$24 \text{ Qr2} = \text{mc} * 18 * (\text{Ta2} - \text{Ta1})$$

$$25 \text{ tau} = \text{V} / \text{v0}$$

$$26 \text{ NCp} = \text{Na} * 35 + \text{Nb} * 18 + \text{Nc} * 46 + \text{Nm} * 19.5$$

$$27 \text{ Qr1} = \text{Fa0} * \text{ThetaCp} * (\text{T} - \text{T0})$$

$$28 \text{ Qr} = \text{Qr1} + \text{Qr2}$$

29 $Q_g = r_a \cdot V \cdot d_h$

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	Ca	0	0.658258
2	Ca0	2.905559	2.905559
3	Cb	55.3	34.06019
4	Cb0	36.30749	36.30749
5	Cc	0	2.247301
6	Cm	0	3.63395
7	Cm0	3.63395	3.63395
8	dh	-2.001E+04	-2.001E+04
9	Fa0	36.3	36.3
10	Fb0	453.6	453.6
11	Fm0	45.4	45.4
12	k	0.9420055	22.56758
13	mc	453.6	453.6
14	Na	0	1.244108
15	Nb	104.517	64.37375
16	Nc	0	4.2474
17	NCp	1881.306	1531.581
18	Nm	0	6.868166
19	Qg	0	5.619E+05
20	Qr	3.992E+04	5.619E+05
21	Qr1	0	3.56E+05
22	Qr2	3.992E+04	2.059E+05
23	ra	0	-14.85529
24	rb	0	-14.85529
25	rc	0	14.85529

26	T	297.	331.4976
27	t	0	4.
28	T0	297.	297.
29	Ta1	288.7	288.7
30	Ta2	293.5896	313.9124
31	tau	0.1512812	0.1512812
32	ThetaCp	284.314	284.314
33	UA	7262.	7262.
34	V	1.89	1.89
35	v0	12.49329	12.49329

$T_i = 344$ K and an initial concentration of 2.26 kmol/m^3 , **the practical stability limit of 355 K** would be exceeded as the reactor approached its steady-state temperature of 331 K. See the concentration–temperature trajectory in [Figure E13-3.4](#).

[Figures E13-3.1](#) through [E13-3.4](#) show the concentration and temperature–time trajectories for the start up of a CSTR for different initial conditions.

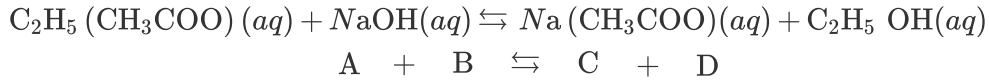
The reader is encouraged to use Wolfram to explore this problem to learn the answers to questions such as: (1) what parameter values lead to the greatest and smallest number of oscillations before steady state is reached (see Problem **P13-1B (c)**).

Analysis: One of the purposes of this example was to demonstrate the use of phase plots, for example, T versus C_A , in analyzing CSTR startup. Phase plots allow us to see how the steady state is approached for different sets of initial conditions and if the *practical stability limit* is exceeded causing a secondary, more exothermic reaction to set in.

13.3.2 Semibatch Operation

Example 13–4 Heat Effects in a Semibatch Reactor

The second-order saponification of ethyl acetate is to be carried out in a semibatch reactor shown schematically in Figure E13-4.1.



Aqueous sodium hydroxide is to be fed at a concentration of 1 kmol/m^3 , a temperature of 300 K , and a volumetric rate of $0.004 \text{ m}^3/\text{s}$ to an initial volume of 0.2 m^3 of water and ethyl acetate. The concentration of water in the feed, C_{W0} , is 55 kmol/m^3 . The initial concentrations of ethyl acetate and water in the reactor are 5 and 30.7 kmol/m^3 , respectively. The reaction is exothermic and it is necessary to add a heat exchanger to keep its temperature below 315 K . A super-shiny heat exchanger with $UA = 3000 \text{ J/s} \cdot \text{K}$ obtained from the downtown Sunday markets in Riça, Jofostan, is available and ready for use. The coolant enters at a mass flow rate of 100 kg/s and a temperature of 285 K .

1. Are the heat exchanger and coolant flow rate adequate to keep the reactor temperature below 315 K ?
2. Plot the reactor temperature, T , and the concentrations, C_A , C_B , and C_C as a function of time.

*Additional information:*³

³ Value for k from J. M. Smith, *Chemical Engineering Kinetics*, 3rd ed. New York: McGraw-Hill, 1981, p. 205. Note that ΔH_{Rx} and K_C were calculated from values given in *Perry's Chemical Engineers' Handbook*, 6th ed. New York: McGraw-Hill, 1984, pp. 3–147.

$$k = 0.39175 \exp \left[5472.7 \left(\frac{1}{273} - \frac{1}{T} \right) \right] \text{ m}^3/\text{kmol} \cdot \text{s}$$

$$K_C = 10^{3885.44/T}$$

$$\Delta H_{Rx}^\circ = -79,076 \text{ kJ/kmol} \cdot \text{K}$$

$$C_{PA} = 170.7 \text{ kJ/kmol} \cdot \text{K} = 170700 \text{ J/kmol} \cdot \text{K}$$

$$C_{PB} = C_{PC} = C_{PD} \cong C_{PW} = C_P = 75.24 \text{ kJ/kmol} \cdot \text{K} = 75246 \text{ J/kmol} \cdot \text{K}$$

Feed: $C_{W0} = 55 \text{ kmol/m}^3$ $C_{B0} = 1.0 \text{ kmol/m}^3$

Initially:

$C_{Wi} = 30.7 \text{ kmol/m}^3$ $C_{Ai} = 5 \text{ kmol/m}^3$ $C_{Bi} = 0$

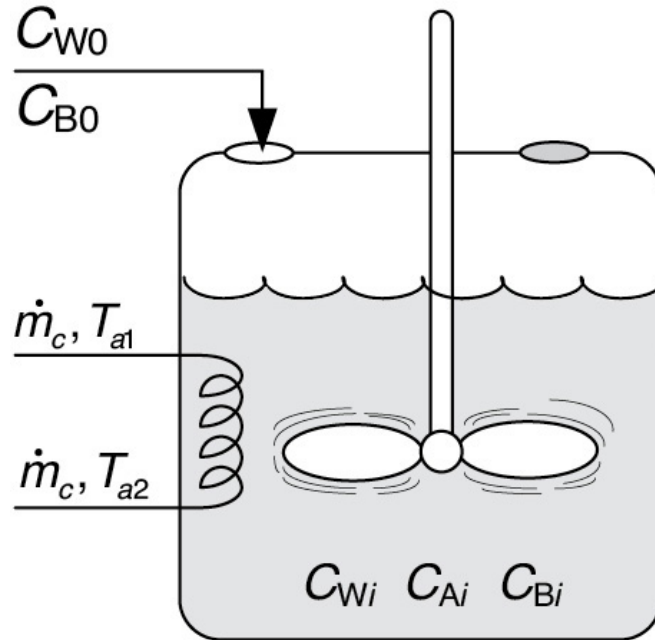


Figure E13-4.1 Semibatch reactor with heat exchange.

Solution

1. Mole Balances: (See Chapter 6.)

$$\frac{dC_A}{dt} = r_A - \frac{v_0 C_A}{V} \quad (\text{E13-4.1})$$

$$\frac{dC_B}{dt} = r_B + \frac{v_0 (C_{B0} - C_B)}{V} \quad (\text{E13-4.2})$$

$$\frac{dC_C}{dt} = r_C - \frac{C_C v_0}{V} \quad (\text{E13-4.3})$$

$$C_D = C_C$$

$$\frac{dN_W}{dt} = C_{w0} v_0 \quad (\text{E13-4.4})$$

Initially, the number of moles of water in the reactor is,

N_{Wi} ,

$$N_{Wi} = V_i C_{W0} = (0.2 \text{ m}^3)(30.7 \text{ kmol/m}^3) = 6.14 \text{ kmol}$$

2. Rate Law:

$$-r_A = k \left(C_A C_B - \frac{C_C C_D}{K_C} \right) \quad (\text{E13.4.5})$$

3. Stoichiometry:

$$-r_A = -r_B = r_C = r_D \quad (\text{E13-4.6})$$

$$N_A = C_A V \quad (\text{E13-4.7})$$

$$V = V_0 + v_0 t \quad (\text{E13-4.8})$$

4. Energy Balance:

The user-friendly energy balance is

$$\frac{dT}{dt} = \frac{\dot{Q}_{gs} - \dot{Q}_{rs}}{\sum N_i C_{P_i}} \quad (13-20)$$

$$\dot{Q}_{gs} = (r_A V) (\Delta H_{Rx}) \quad (13-21)$$

$$\dot{Q}_{rs} = \sum F_{i0} C_{P_i} (T - T_{i0}) + \dot{m}_c C_{P_w} [T - T_{a1}] \left[1 - \exp \left(\frac{-UA}{\dot{m}_c C_{P_w}} \right) \right] \quad (13-22)$$

Only species B (NaOH) and water flow into the reactor, so Equation (13-22) becomes

$$\dot{Q}_{rs} = \overbrace{(F_{B0} C_{P_B} + F_w C_{P_w}) (T - T_0)}^{\dot{Q}_{rs1}} + \overbrace{\dot{m}_c C_{P_w} [T - T_{a1}] \left[1 - \exp \left(\frac{-UA}{\dot{m}_c C_{P_w}} \right) \right]}^{\dot{Q}_{rs2}} \quad (\text{E13-4.9})$$

\dot{Q}_{rs1} is the heat removed by mass flow, and \dot{Q}_{rs2} is the heat removed through heat exchange.



TABLE E13-4.1 POLYMATH PROGRAM AND OUTPUT FOR SEMIBATCH REACTOR

Differential equations

1 $d(C_a)/d(t) = r_a - (v_0 \cdot C_a)/V$

2 $d(C_b)/d(t) = r_b + (v_0 \cdot (C_{b0} - C_b))/V$

3 $d(C_c)/d(t) = r_c - (C_c \cdot v_0)/V$

4 $d(T)/d(t) = (Q_g - Q_r)/NC_p$

5 $d(N_w)/d(t) = v_0 \cdot C_{w0}$

Explicit equations

1 $v_0 = 0.004$

2 $C_{b0} = 1$

3 $UA = 3000$

4 $c_p = 75240$

5 $T_0 = 300$

6 $dh = -7.9076e7$

7 $C_{w0} = 55$

8 $k = 0.39175 \cdot \exp(5472.7 \cdot ((1/273) - (1/T)))$

9 $C_d = C_c$

$$10 \ V_i = 0.2$$

$$11 \ K_c = 10^{(3885.44/T)}$$

$$12 \ c_{pa} = 170700$$

$$13 \ V = V_i + v_0 * t$$

$$14 \ F_{b0} = C_{b0} * v_0$$

$$15 \ r_a = -k * ((C_a * C_b) - ((C_c * C_d)/K_c))$$

$$16 \ N_a = V * C_a$$

$$17 \ N_b = V * C_b$$

$$18 \ F_w = C_{w0} * v_0$$

$$19 \ N_c = V * C_c$$

$$20 \ r_b = r_a$$

$$21 \ r_c = -r_a$$

$$22 \ Q_{r1} = ((F_{b0} * c_p) + (F_w * c_p)) * (T - T_0)$$

$$23 \ N_d = V * C_d$$

$$24 \ \text{rate} = -r_a$$

$$25 \ N_{Cp} = c_p * (N_b + N_c + N_d + N_w) + c_{pa} * N_a$$

$$26 \ C_{pc} = 18$$

$$27 \ T_{a1} = 285$$

$$28 \ m_c = 100$$

$$29 \ Q_{r2} = m_c * C_{pw} * (T - T_{a1}) * (1 - \exp(-UA/m_c/C_{pw}))$$

$$30 \ T_{a2} = T - (T - T_{a1}) * \exp(-UA/m_c/C_{pw})$$

$$31 \text{ } Q_r = Q_{r1} + Q_{r2}$$

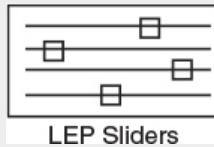
$$32 \text{ } Q_g = r_a * V * d_h$$

Calculated values of DEQ variables

	Variable	Initial value	Final value
--	----------	---------------	-------------

1	Ca	5.	3.981E-13
2	Cb	0	0.2682927
3	Cb0	1.	1.
4	Cc	0	0.6097561
5	Cd	0	0.6097561
6	Cp	7.524E+04	7.524E+04
7	cpa	1.707E+05	1.707E+05
8	Cpc	18.	18.
9	Cw0	55.	55.
10	dh	-7.908E+07	-7.908E+07
11	Fb0	0.004	0.004
12	Fw	0.22	0.22
13	k	2.379893	4.211077
14	Kc	8.943E+12	3.518E+12
15	mc	100.	100.
16	Na	1.	6.529E-13
17	Nb	0	0.44
18	Nc	0	1.
19	NCp	6.327E+05	6.605E+06
20	Nd	0	1.
21	Nw	6.14	85.34
22	Qg	0	6.19E-07
23	Qr	2.19E+04	1.993E+05
24	Qr1	0	1.633E+05

25	Qr2	2.19E+04	3.604E+04
26	ra	0	-4.773E-15
27	rate	0	4.773E-15
28	rb	0	-4.773E-15
29	rc	0	4.773E-15
30	t	0	360.
31	T	300.	309.6878
32	T0	300.	300.
33	Ta1	285.	285.
34	Ta2	297.1669	305.0248
35	UA	3000.	3000.
36	V	0.2	1.64
37	v0	0.004	0.004
38	Vi	0.2	0.2



In Jofostan we have the added bonus that we can ask Prof. Dr. Sven Köttlov to calculate the temperature of the heat-exchange fluid at its exit using Equation (12-17)

$$T_{a2} = T - \left(T - T_{a1} \right) \exp \left[\frac{-UA}{\dot{m}_c C_{P_w}} \right] \quad (12-17)$$

#AddedBonus

5. Evaluation of Parameters:

$$F_{B0} = \nu_0 C_{B0} = (0.004 \frac{\text{m}^3}{\text{s}}) (1 \frac{\text{kmol}}{\text{m}^3}) = 0.004 \frac{\text{kmol}}{\text{s}},$$

$$F_w = \nu_0 C_w = (0.004 \frac{\text{m}^3}{\text{s}}) (55 \frac{\text{kmol}}{\text{m}^3}) = 0.220 \frac{\text{kmol}}{\text{s}}$$

$$C_{PA} = 170700 \text{ J/kmol/K}, C_P = 75246 \text{ J/kmol/K}$$

We note the heat capacities for B, C, and water are essentially the same at C_P

$$NC_P = C_{PA}N_A + C_P (N_B + N_C + N_D + N_W)$$

The Polymath program is given in [Table E13-4.1](#), and the graphical output of the Polymath program—given in terms of temperatures T and T_a and concentrations (C_A , C_B , and C_C)—are shown in [Figures E13-4.2](#) and [E13-4.3](#).

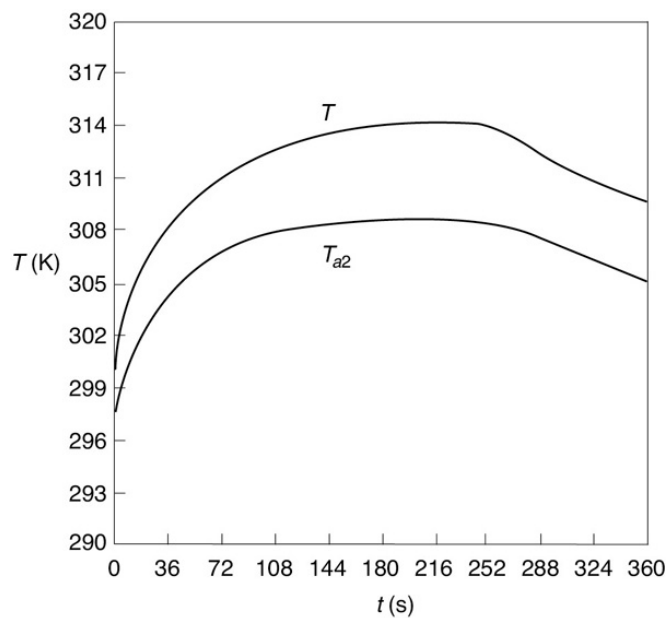


Figure E13-4.2 Temperature–time trajectories in a semibatch reactor.

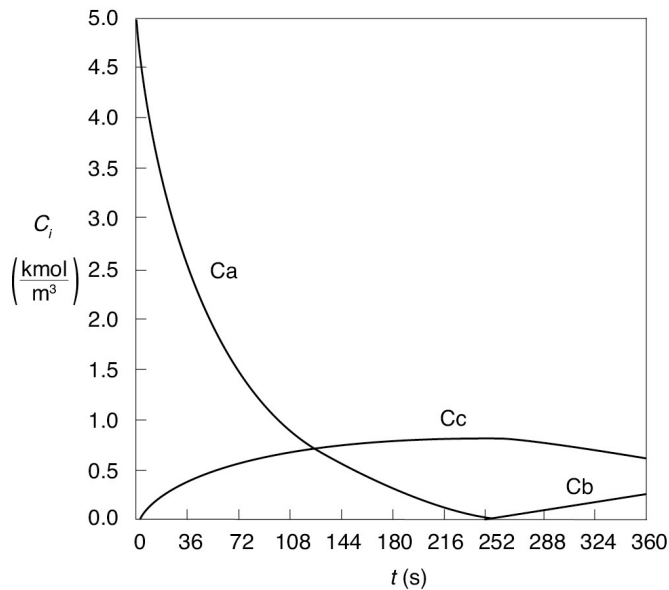
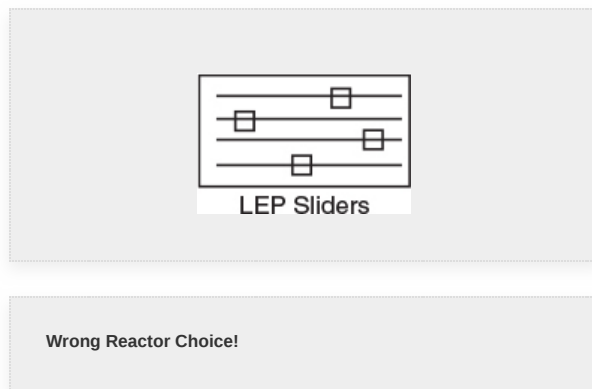
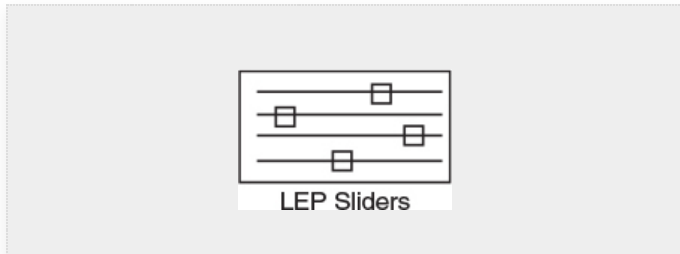


Figure E13-4.3 Concentration–time trajectories in a semibatch reactor.



Analysis: From Figure E13-4.3 we see that the concentration of species B is essentially zero, owing to the fact that it is consumed virtually as fast as it enters the reactor up to a time of 252 seconds. By the time we reach 252 seconds, all species A has been consumed, and the reaction rate is virtually zero and no more of species C or D is produced and no more B is consumed. Because species B continues to enter the reactor at a volumetric flow rate v_0 , after 252 seconds, the fluid volume continues to increase and the concentrations of C and D are diluted. The figure shows that before 252 seconds, $(\dot{Q}_{gs} > \dot{Q}_{rs})$, both the reactor temperature and the coolant temperature

increase. However, after 252 seconds, the reaction rate, and hence \dot{Q}_{rs} , are virtually zero so that $(\dot{Q}_{gs} > \dot{Q}_{rs})$ and the temperature decreases. Because of the impractical short reaction time (252 seconds), a semibatch reactor **would never** be used for this reaction at this temperature; instead, we would most likely use a CSTR or PFR. See Problem P13-1_B (d) to reflect on this example.



A real-life LEP example of the **Synthron Runaway Reaction** in a semibatch reactor is given in the Additional Material on the CRE Web site

(<http://www.umich.edu/~elements/6e/13chap/obj.html#/additional-materials/>) and also on the Safety Web site ([http://umich.edu/~safeche/assets/pdf/courses/Problems/CRE/344ReactionEngrModule\(2\)PS-Monsanto.pdf](http://umich.edu/~safeche/assets/pdf/courses/Problems/CRE/344ReactionEngrModule(2)PS-Monsanto.pdf)).

13.4 NONISOTHERMAL MULTIPLE REACTIONS

For q multiple reactions with m species occurring in either a semibatch or batch reactor, Equation (13-9) can be generalized in the same manner as the steady-state energy balance to give

$$\frac{dT}{dt} = \frac{\dot{m}_c C_{Pc} (T_{a1} - T) \left[1 - \exp(-UA / \dot{m}_c C_{Pc}) \right] + \sum_{i=1}^q r_{ij} V \Delta H_{Rij(T)} - \sum_{j=1}^m F_{j0} C_{Pj} (T - T_0)}{\sum_{j=1}^m N_{j0} C_{Pj}} \quad (13-24)$$

For large coolant flow rates (i.e., \dot{m}_c), Equation (13-24) becomes

$$\frac{dT}{dt} = \frac{V \sum_{i=1}^q r_{ij} \Delta H_{\text{Rxi}j} - U A (T - T_a) \sum_{j=1}^m F_{j0} C_{\text{P}j} (T - T_0)}{\sum_{j=1}^m N_j C_{\text{P}j}} \quad (13-25)$$

Rearranging Equation (13-25) and letting

$$\dot{Q}_g = V \sum_{i=1}^q r_{ij} \Delta H_{\text{Rxi}j} \quad (13-26)$$

and

$$\dot{Q}_r = U A (T - T_a) + \sum F_{j0} C_{\text{P}j} (T - T_0) \quad (13-27)$$

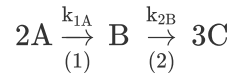
we can write Equation (13-25) in a more compact form

$$\frac{dT}{dt} = \frac{\dot{Q}_g - \dot{Q}_r}{\sum_{j=1}^m N_j C_{\text{P}j}} \quad (13-28)$$

One exothermic reaction and one endothermic reaction! Will the temperature increase or decrease?

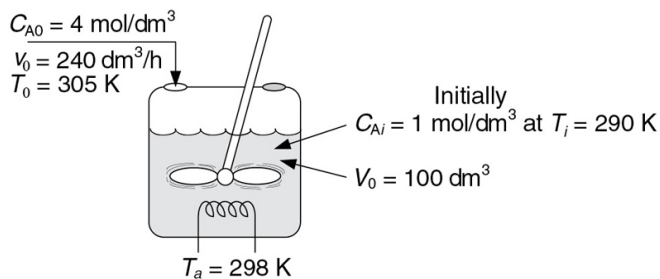
Example 13–5 Multiple Reactions in a Semibatch Reactor

The series reactions



are catalyzed by H_2SO_4 . All reactions are first order in the reactant concentration. However, Reaction (1) is *exothermic* and Reaction (2) is *endothermic*. The reaction is to be carried out in a semibatch reactor that has a heat exchanger inside with $UA = 35000 \text{ cal/h} \cdot \text{K}$ and a constant exchanger temperature, T_a , of 298 K. Pure A enters at a concentration of 4 mol/dm^3 , a volumetric flow rate of $240 \text{ dm}^3/\text{h}$, and a temperature of 305 K. Initially, there is a total of 100 dm^3 of liquid in the reactor, which contains 1.0 mol/dm^3 of A and 1.0 mol/dm^3 of the catalyst H_2SO_4 . The reaction rate is independent of the catalyst concentration. The initial temperature inside the reactor is 290 K.

1. Plot and *analyze* the species concentrations and reactor temperature as a function of time.
2. Analyze the results in (a) and comment on any maximums or minimums in the trajectories.



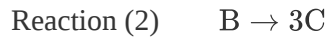
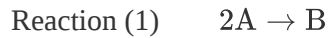
Additional information:

$$k_{1A} = 1.25 \text{ h}^{-1} \text{ at } 320 \text{ K with } E_{1A} = 9500 \text{ cal/mol} \quad C_{P_A} = 30 \text{ cal/mol} \cdot \text{K}$$

$$k_{2B} = 0.08 \text{ h}^{-1} \text{ at } 300 \text{ K with } E_{2B} = 7000 \text{ cal/mol} \quad C_{P_B} = 60 \text{ cal/mol} \cdot \text{K}$$

$$\Delta H_{\text{Rx1A}} = -6500 \text{ cal/mol A} \quad C_{P_C} = 20 \text{ cal/mol} \cdot \text{K}$$

$$\Delta H_{\text{Rx2B}} = +8000 \text{ cal/mol B} \quad C_{P_{\text{H}_2\text{SO}_4}} = 35 \text{ cal/mol} \cdot \text{K}$$

Solution**1. Mole Balances:**

$$\frac{dC_A}{dt} = r_A + \frac{(C_{A0} - C_A)}{V} v_0 \quad (\text{E13-5-1})$$

$$\frac{dC_B}{dt} = r_B - \frac{C_B}{V} v_0 \quad (\text{E13-5.2})$$

$$\frac{dC_C}{dt} = r_C - \frac{C_C}{V} v_0 \quad (\text{E13-5.3})$$

2. Rates:**(a) Rate Laws:**

$$-r_{1A} = k_{1A} C_A \quad (\text{E13-5.4})$$

$$-r_{2B} = k_{2B} C_B \quad (\text{E13-5.5})$$

(b) Relative Rates:

$$r_{1B} = -\frac{1}{2} r_{1A} \quad (\text{E13-5.6})$$

$$r_{2C} = -3 r_{2B} \quad (\text{E13-5.7})$$

(c) Net Rates:

$$r_A = r_{1A} = -k_{1A} C_A \quad (\text{E13-5.8})$$

$$r_B = r_{1B} + r_{2B} = \frac{-r_{1A}}{2} + r_{2B} = \frac{k_{1A} C_A}{2} - k_{2B} C_B \quad (\text{E13-5.9})$$

$$r_C = 3 k_{2B} C_B \quad (\text{E13-5.10})$$

3. Stoichiometry (liquid phase): Use C_A , C_B , C_C

$$N_i = C_i V \quad (\text{E13-5.11})$$

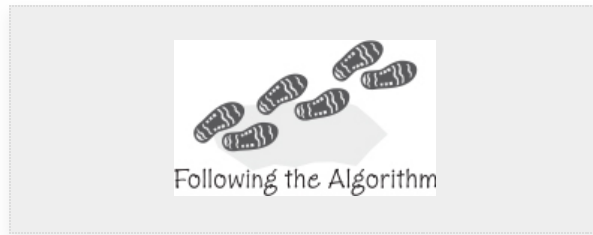
$$V = V_0 + v_0 t \quad (\text{E13-5.12})$$

H₂SO₄ already in the tank

$$N_{\text{H}_2\text{SO}_4} = (C_{\text{H}_2\text{SO}_4,0}) V_0 = \frac{1 \text{ mol}}{\text{dm}^3} \times 100 \text{ dm}^3 = 100 \text{ mol}$$

Only A enters the tank

$$F_{A0} = C_{A0} v_0 = \frac{4 \text{ mol}}{\text{dm}^3} \times 240 \frac{\text{dm}^3}{\text{h}} = 960 \frac{\text{mol}}{\text{h}}$$



4. Energy Balance:

A slight rearrangement of (13-25) for this semibatch reactor gives

$$\frac{dT}{dt} = \frac{UA(T_a - T) - \sum_{j=0} F_{j0} C_{Pj}(T - T_0) + V \sum_{i=1}^q \Delta H_{\text{Rx}ij} r_{ij}}{\sum_{j=1}^m N_j C_{Pj}} \quad (\text{E13-5.13})$$

Expanding

$$\frac{dT}{dt} = \frac{UA(T_a - T) - F_{A0} C_{PA}(T - T_0) + \left[(\Delta H_{\text{Rx}1A})(r_{1A}) + (\Delta H_{\text{Rx}2B})(r_{2B}) \right] V}{\left[C_A C_{PA} + C_B C_{PB} + C_C C_{PC} \right] V + N_{\text{H}_2\text{SO}_4} C_{P_{\text{H}_2\text{SO}_4}}} \quad (13-5.14)$$

Substituting the parameter values into Equation (E13-5.14)

$$\frac{dT}{dt} = \frac{35000(298 - T) - (4)(240)(30)(T - 305) + [(-6500) + (-k_{1A} C_A) + (+8000)(-k_{2B} C_B)] V}{(30 C_A + 60 C_B + 20 C_C)(100 + 240t) + (100)(35)} \quad (\text{E13-5.15})$$

Equations (E13-5.1)–(E13-5.3) and (E13-5.8)–(E13-5.12) can be solved simultaneously with Equation (E13-5.14) using an ODE solver. The Polymath program is shown in Table E13-5.1. The concentration–time and temperature–time trajectories are shown in Figures E13-5.1 and E13-5.2.

TABLE E13-5.1 POLYMATH PROGRAM FOR STARTUP OF
A CSTR

Differential equations

$$1 \quad d(C_a)/d(t) = r_a + (C_{a0} - C_a) \cdot v_0 / V$$

$$2 \quad d(C_b)/d(t) = r_b - C_b \cdot v_0 / V$$

$$3 \quad d(C_c)/d(t) = r_c - C_c \cdot v_0 / V$$

$$4 \quad d(T)/d(t) = (Q_g - Q_r) / ((C_a \cdot 30 + C_b \cdot 60 + C_c \cdot 20) \cdot V + 100 \cdot 35)$$

Explicit equations

$$1 \quad U A = 35000$$

$$2 \quad dH_{rx1} = -6500$$

$$3 \quad dH_{rx2} = 8000$$

$$4 \quad v_0 = 240$$

$$5 \quad V = 100 + v_0 \cdot t$$

$$6 \quad C_{a0} = 4$$

$$7 \quad Q_r = U A \cdot (T - 298) + C_{a0} \cdot v_0 \cdot 30 \cdot (T - 305)$$

$$8 \quad k_{1a} = 1.25 \cdot \exp((9500/1.987) \cdot (1/320 - 1/T))$$

$$9 \quad k_{2b} = 0.08 \cdot \exp((7000/1.987) \cdot (1/300 - 1/T))$$

$$10 \quad r_a = -k_{1a} \cdot C_a$$

$$11 \quad Q_g = (dH_{rx1} \cdot (-k_{1a} \cdot C_a) + dH_{rx2} \cdot (-k_{2b} \cdot C_b)) \cdot V$$

$$12 \quad r_c = 3 \cdot k_{2b} \cdot C_b$$

$$13 \quad r_b = k_{1a} \cdot C_b / 2 - k_{2b} \cdot C_b$$

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	Ca	1.	0.2165095
2	Cao	4.	4.
3	Cb	0	0.8114253
4	Cc	0	2.262699
5	dHrx1	-6500.	-6500.
6	dHrx2	8000.	8000.
7	k1a	0.2664781	9.133834
8	k2b	0.0533618	0.7215678
9	Qg	1.732E+05	3.758E+06
10	Qr	-7.12E+05	4.337E+06
11	ra	-0.2664781	-1.977562
12	rb	0.133239	0.4032827
13	rc	0	1.756495
14	t	0	1.5
15	T	290.	369.1375
16	UA	3.5E+04	3.5E+04
17	V	100.	460.
18	vo	240.	240.

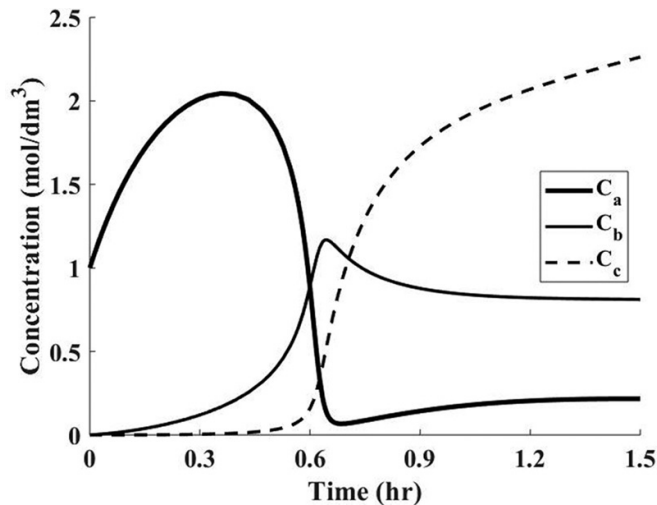


Figure E13-5.1 Concentration–time.

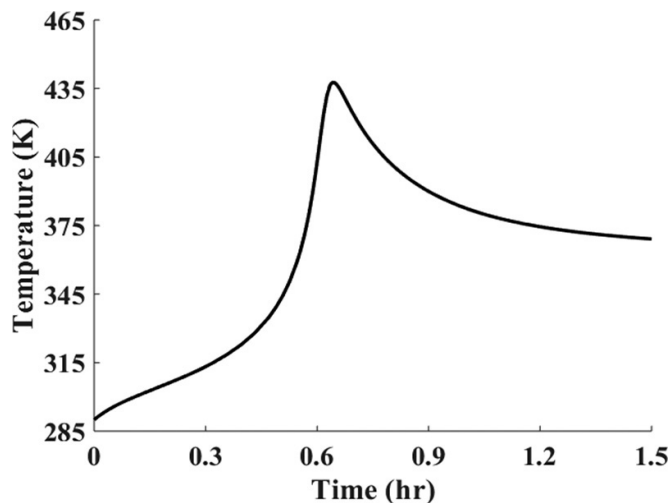
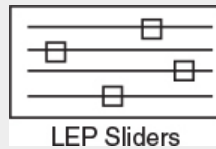


Figure E13-5.2 Temperature (K)–time (h)

Analysis: At the start of the reaction, both C_A and T in the reactor increase because the feed concentrations of C_{A0} (4M) and T_0 (305 K) are greater than the initial settings of C_{Ai} (1 M) and T_i (290 K). This increase continues until the rate of consumption of the reacting species, $(-r_A V)$, is greater than the feed rate to the reactor, F_{A0} . We note that at about $t = 0.2$ hours, the reactor temperature exceeds the feed temperature (i.e., 305 K) as a result of the heat generated by the exothermic reaction (Reaction 1). The temperature continues to rise until about $t = 0.6$ hours, at which point reactant A is virtually all consumed. After this

point the temperature begins to drop for two reasons: (1) the reactor is cooled by the heat exchanger and (2) heat is absorbed by the endothermic reaction rate (Reaction 2). The question is, does the maximum temperature (437 K) exceed a temperature that is too high, resulting in a high vapor pressure that then results in evaporation losses or causes a highly exothermic secondary reaction to set in?



Example 13–6 T2 Laboratories Explosion⁴

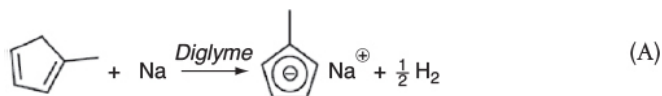
⁴ This example was coauthored by Professors Ronald J. Willey, Northeastern University, Michael B. Cutlip, University of Connecticut, and H. Scott Fogler, University of Michigan, and published in *Process Safety Progress*, 30, 1 (2011).



Figure E13-6.1 Aerial photograph of T2 taken December 20, 2007. (Courtesy of Chemical Safety Board.)

The aftermath of a deadly explosion at T2 Laboratories is shown in [Figure E13-6.1](#). T2 Laboratories manufactured a fuel additive, methylcyclopentadienyl manganese tricarbonyl (MCMT), in a 2450-gal, high-pressure batch reactor utilizing a three-step batch process. (See [http://umich.edu/~safeche/assets/pdf/courses/CRE/344/ReactionEngrModule\(1\)PS-T2.pdf](http://umich.edu/~safeche/assets/pdf/courses/CRE/344/ReactionEngrModule(1)PS-T2.pdf).)

Step 1a. The liquid-phase metalation reaction between methylcyclopentadiene (MCP) and sodium in a solvent of diethylene glycol dimethyl ether (diglyme) to produce sodium methylcyclopentadiene and hydrogen gas is

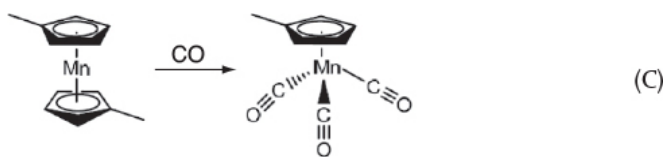


Hydrogen immediately comes out of the solution and is vented at the top into the gas head space and then out of the system.

Step 1b. At the end of Step 1a, MnCl_2 is added. The substitution reaction between sodium methylcyclopentadiene and manganese chloride that produced manganese dimethylcyclopentadiene and sodium chloride is



Step 1c. At the end of Step 1b, CO is added. The carbonylation reaction between manganese dimethylcyclopentadiene and carbon monoxide produces the final product, methylcyclopentadienyl manganese tricarbonyl (MCMT):



We will only consider *Step 1a* as this step is the one in which the explosion occurred.

Procedure

First, solid sodium is mixed in the batch reactor with methylcyclopentadiene dimer and a solvent diethylene glycol dimethyl ether (diglyme). The batch reactor is then heated to about 422 K (300°F) with only slight reaction occurring during this heating process. On reaching 422 K, the heating is turned off, as the exothermic reaction is now proceeding, and the temperature continues to increase without further heating. When the temperature reaches 455.4 K (360°F), the operator initiates cooling using the evaporation of boiling water in the reactor jacket as the heat sink ($T_a = 373.15 \text{ K}$; 212°F).

Before reading further it might be helpful to view the Chemical Safety Board (CSB) video of the accident

(<http://umich.edu/~safeche/courses/ChemicalReactionEngineering.html>).

It's a *really* good video.

What Happened

On December 19, 2007, when the reactor reached a temperature of 455.4 K (360°F), the process operator could not initiate the flow of cooling water to the cooling jacket shown in Figure E13-6.2. Thus, the expected cooling of the reactor was not available and the temperature in the reactor continued to rise. The pressure also increased as hydrogen continued to be produced at an increased rate, to the point that the reactor's pressure control valve system on the 1-in. diameter hydrogen venting stream could no longer vent the gas and maintain the operating pressure at 50 psig (4.4 atm). As the temperature continued to increase further, a previously unknown exothermic secondary reaction of the decomposition of diglyme solvent, also catalyzed by sodium, accelerated rapidly.

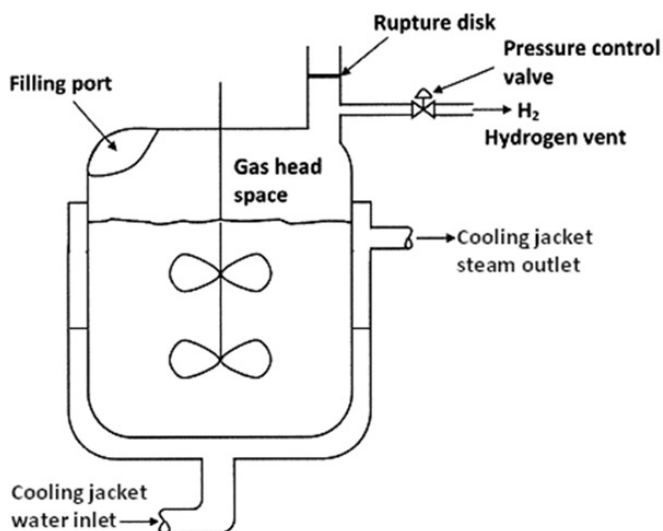
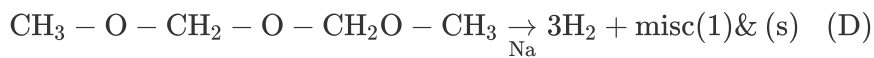


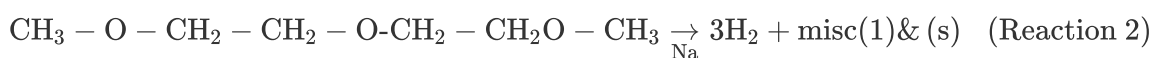
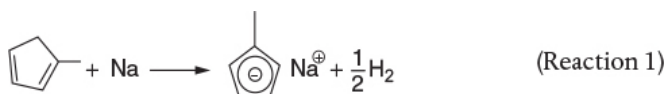
Figure E13-6.2 Reactor.

This reaction produced even more hydrogen, causing the pressure to rise even faster, eventually causing the rupture disk which was set at 28.2 atm absolute (400 psig), to break, in the 4-in. diameter relief line for H₂. Even with the relief line open, the rate of production of H₂ was now far greater than the rate of venting, causing the pressure to continue to increase to the point that it ruptured the reactor vessel initiating a horrific explosion. The T2 plant was completely leveled and four personnel lives were lost. Surrounding businesses were heavily damaged and additional injuries were sustained.

I would like to emphasize again, before continuing with this example, it might be helpful to view the 9-minute Chemical Safety Board (CSB) video, which you can access directly from the CRE Web site (under YouTube videos), or you can read the supporting reports (<http://www.csb.gov/videos/runaway-explosion-at-t2-laboratories/>). Also review the T2 Laboratories Safety Modules ([http://umich.edu/~safeche/assets/pdf/courses/Problems/344ReactionEngineeringModule\(2\)PS050818.pdf](http://umich.edu/~safeche/assets/pdf/courses/Problems/344ReactionEngineeringModule(2)PS050818.pdf)).

Simplified Model

Summarizing the important reactions for Step 1



Let **A = methylcyclopentadiene**, **B = sodium**, **S = solvent (diglyme)**, and **D = H₂**.

This runaway reaction can be approximately modeled with two reactions. These reactions are



(Reaction 1)



(Reaction 2)

Rate laws

In Reaction (1), **A** and **B** react to form products. Reaction (2) represents the decomposition of the liquid-phase solvent diglyme, **S**, catalyzed by the presence of **B**, but this reaction only begins to proceed once a temperature of approximately 470 K is reached. The fact that the solvent diglyme would decompose and also explode was unknown to the plant personnel. If they had researched this reaction system using an ARSST (see Chapter 13 Professional Reference Shelf), they might have seen the potential danger.

The rate laws, along with the specific reaction-rate constants at the initial temperature of 422 K, are

$$-r_{1A} = k_{1A} C_A C_B$$

$$A_{1A} = 5.73 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ hr}^{-1} \text{ with } E_{1A} = 128000 \text{ J/mol K}$$

$$-r_{2S} = k_{2S} C_S$$

$$A_{2S} = 9.41 \times 10^{16} \text{ hr}^{-1} \text{ with } E_{2S} = 800000 \text{ J/mol K}$$

The heats of reaction are constant.

$$\Delta H_{R_{x1A}} = -45400 \text{ J/mol}$$

$$\Delta H_{R_{x2S}} = -320000 \text{ J/mol}$$

The sum of products of the moles of each species and their corresponding heat capacities in the denominator of Equation (13-12) is essentially constant at

$$\sum N_j C_{P_j} = 1.26 \times 10^7 \text{ J/K}$$

Assumptions

Assume that the liquid volume, V_0 , in the reactor remains constant at 4000 dm^3 and that the vapor space, V_H , above the reactor occupies 5000 dm^3 . Any gas, H_2 (i.e., D), that is formed by Reactions (1) and (2) immediately appears as an input stream F_D to the head-space volume. The dissolved H_2 and the vapor pressures for the liquid components in the reactor will be neglected. The initial absolute pressure within the reactor is 4.4 atm (50 psig). During normal operation, the H_2 generated obeys the ideal gas law. The pressure control system on the H_2 vent stream maintains the pressure, P , at 4.40 atm up to a flow of 11400 mol/hr. The reactor vessel will fail when the pressure exceeds 45 atm or the temperature exceeds 600 K.

Additional information:

$UA = 2.77 \times 10^6 \text{ J hr}^{-1} \text{ K}^{-1}$. The concentrations in the reactor at the end of the reactor heating at 422 K are $C_{A0} = 4.3 \text{ mol/dm}^3$, $C_{B0} = 5.1 \text{ mol/dm}^3$, $C_{I0} = 0.088 \text{ mol/dm}^3$, and $C_{S0} = 3 \text{ mol/dm}^3$. The sensible heat of the two gas venting streams may be neglected.

Problem Statement

1. Plot the reactor temperature, the reactant concentrations, and the head-space pressure as a function of time for the case when the reactor cooling fails to work (i.e., $UA = 0$).
2. In Problem P13-1B (f), you will be asked to redo the problem when the cooling water comes as expected whenever the reactor temperature exceeds 455 K.
3. Analyze your results and explain why the trajectories look the way they do, for example, sudden increases in temperature and pressure.

Solution Procedure Overview

We will carry out a two-step procedure of our CRE algorithm by adding a mole balance on the reactor head space in order to determine the pressure in the reactor as a function of time. **(1)** In step 1, we will use the usual mole balance step, coupled with rate laws, stoichiometry, and energy balances to determine the rate of H_2 generation. Because there is no accumulation of H_2 in the reactor, H_2 flows out of the reactor into the head space. **(2)** In step 2, we perform a mole balance on the head space to determine the pressure in the head space and reactor. The remaining steps are part of our CRE algorithm that will allow us to determine temperature, concentration, and pressure as a function of time.

Step (1) Reactor Mole Balances:

Reactor (Assume Constant-Volume Batch)

Liquid

$$\frac{dC_A}{dt} = r_{1A} \quad (\text{E13-6.1})$$

$$\frac{dC_B}{dt} = r_{1A} \quad (\text{E13-6.2})$$

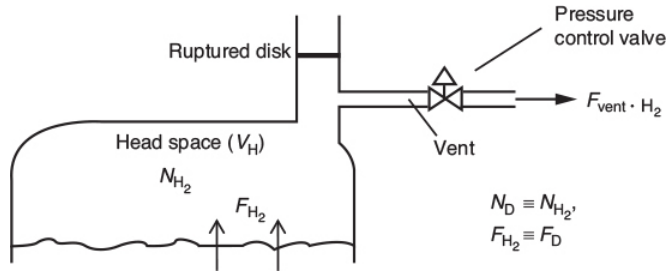
$$\frac{dC_s}{dt} = r_{2S} \quad (\text{E13-6.3})$$

Step (2) Head-Space Mole Balance:

Let N_D = moles of gas D (i.e., H_2) in the reactor vapor space V_V . The flows in and out of the head space are shown in the figure below.

A balance on species D (H_2) in the head-space volume V_H yields

$$\text{Accum} = \text{In} - \text{Out}$$



$$\frac{dN_D}{dt} = F_D - F_{vent} \quad (\text{E13-6.4})$$

where F_{vent} is the molar flow rate of gas out of the head space through one or both outlet lines, and F_D (i.e., F_2) is the molar rate of gas leaving the liquid and entering the head space and is equal to the hydrogen generated in the liquid (see relative rates and net rates in the algorithm where V_0 is the liquid reactor volume).

$$F_D = [(-0.5r_{1A}) + (-3r_{2S})]V_0 \quad (\text{E13-6.5})$$

The assumptions of a perfect gas in the head-space volume and modest changes in T allow Equation (E13-6.4) to be written in terms of total gas pressure in the reactor head space

$$N_D = N_H = \frac{PV_H}{RT_H} \quad (\text{E13-6.6})$$

Substituting for N_D in Equation (E13-6.3) and rearranging

$$\boxed{\frac{dP}{dt} = (F_D - F_{vent}) \frac{RT_H}{V_H}} \quad (\text{E13-6.7})$$

(3) How the Venting Works:

Gas exits the reactor through the pressure control valve line. At low gas production rates, the pressure control valve maintains set-point pressure at the initial pressure by venting all produced gas until the rate of gas production reaches 11400 mol/hr.

$$F_{vent} = F_D \text{ when } F_D < 11,400 \quad (\text{E13-6.8})$$

Just a little help in calculating the flow rate of H₂ out the vent.

We now need to know a little more about the venting system for H₂ and the condition for flow out of the vent. As the pressure increases, but is still below the rupture disk setting, the pressure control line vents to the atmosphere (1 atm) according to the equation

$$F_{\text{vent}} = \Delta PC_{v1} = (P - 1)C_{v1} \quad \text{when } P < 28.2 \text{ atm} \quad (\text{E13-6.9})$$

where P is the absolute pressure in the reactor (atm), 1 atm is the downstream pressure (atmospheric), and the pressure control correlation constant is 3360 mol/hr · atm. If the pressure P within the reactor exceeds 28.2 atm (400 psig), the relief line activated by the rupture disk breaks and vents gas in the reactor at the rate given $F_{\text{vent}} = (P-1)C_{v2}$ where $C_{v2} = 53600 \text{ mol/atm} \cdot \text{h}$.

After the rupture disk blowout at $P = 28.2 \text{ atm}$, both the pressure control line and the rupture disk lines vent the reactor according to the equation

$$F_{\text{vent}} = (P - 1)(C_{v1} + C_{v2}) \quad (\text{E13-6.10})$$

Equations (E13-6.7)–(E13-6.10) can then be used to describe the F_{vent} flow rate with time for the appropriate logic for the values of F_D and P .

(4) Rates:

Laws:

$$(1) -r_{1A} = k_{1A} C_A C_B \quad (\text{E13-6.11})$$

$$k_{1A} = A_{1A} e^{-E_{1A}/RT} \quad (\text{E13-6.12})$$

$$(2) -r_{2S} = k_{2S} C_S \quad (\text{E13-6.13})$$

$$k_{2S} = A_{2S} e^{-E_{2S}/RT} \quad (\text{E13-6.14})$$

Relative Rates:

$$(1) \frac{r_{1A}}{-1} = \frac{r_{1B}}{-1} = \frac{r_{1C}}{1} = \frac{r_{1D}}{1/2} \quad (13-6.15)$$

$$(2) \frac{r_{2S}}{-1} = \frac{r_{2D}}{3} \quad (E13-6.16)$$

Net Rates:

$$r_A = r_B = r_{1A} \quad (E13-6.17)$$

$$r_s = r_{2S} \quad (13-6.18)$$

$$r_D = -\frac{1}{2} r_{1A} + -3r_{2S} \quad (\text{gas generated}) \quad (E13-6.19)$$

(5) Stoichiometry:

Neglect reactor-liquid volume change form loss of product gases.

$$C_A = \frac{N_A}{V_0} \quad (13-6.20)$$

$$C_B = \frac{N_B}{V_0} \quad (13-6.21)$$

$$C_s = \frac{N_s}{V_0} \quad (E13-6.22)$$

$$C_D = \frac{P}{RT} \quad (E13-6.23)$$

(6) Energy Balance:

The batch reactor energy balance is

$$\frac{dT}{dt} = \frac{\dot{Q}_{gb} - \dot{Q}_{rb}}{\Sigma N_j C_{p_j}} \quad (E13-6.24)$$

The heat generated, \dot{Q}_{gb} , and the heated removed, \dot{Q}_{rb} , terms are

$$\dot{Q}_{gb} = V_0 [r_{1A} \Delta H_{Rx1A} + r_{2S} \Delta H_{Rx2S}] \quad (E13-6.25)$$

and

$$\dot{Q}_{rb} = UA(T - T_a) \quad (\text{E13-6.26})$$

Combining the above three equations one obtains

$$\frac{dT}{dt} = \frac{V_0[r_{1A}\Delta H_{R1A} + r_{2S}\Delta H_{R2S}] - UA(T - T_a)}{\sum N_j C_{Pj}} \quad (\text{E13-6.27})$$

Substituting for the rate laws and $\sum N_j C_{Pj}$

$$\frac{dT}{dt} = \frac{V_0[-k_{1A}C_A C_B \Delta H_{R1A} - k_{2S}C_S \Delta H_{R2S}] - UA(T - T_a)}{1.26 \times 10^7 (J/K)} \quad (\text{E13-6.28})$$

(7) Numerical Solutions: “Tricks of the Trade”

A rapid change of temperature and pressure is expected as **Reaction (2)** starts to runaway. This typically results in a “stiff” system of ordinary differential equations, which can become numerically unstable and generate incorrect results. This instability can be prevented by using a software switch (SW) that will set all derivatives to zero when the reactor reaches the explosion temperature or pressure. This switch can have the form of Equation (E13-6.29) in Polymath, as shown in Table E13-6.1, and can be multiplied by the right-hand side of all the differential equations in this problem. This operation will halt (or freeze) the dynamics when the temperature T becomes higher than 600 K or the pressure exceeds 45 atm.

$$\text{SW1} = \text{if } (T > 600 \text{ or } P > 45) \text{ then } (0) \text{ else } (1) \quad (\text{E13-6.29})$$

See http://www.umich.edu/~elements/6e/tutorials/Polymath_Tutorial_to_solve_numerically_unstable_systems.pdf at

Steps to take to prevent your computer from crashing.

TABLE E13-6.1 POLYMATH PROGRAM

Differential equations

$$1 \quad d(CA)/d(t) = SW1 * r1A \text{ mol/dm}^3/\text{hr}$$

$$2 \quad d(CB)/d(t) = SW1 * r1A \text{ change in concentration of cyclomethylpentadiene}$$

$$3 \quad d(CS)/d(t) = SW1 * r2S \text{ change in concentration of diglyme}$$

$$4 \quad d(P)/d(t) = SW1 * ((FD - Fvent) * 0.082 * T / VH)$$

$$5 \quad d(T)/d(t) = SW1 * (Qg - Qr) / \text{SumNCp}$$

Explicit equations

$$1 \quad V0 = 4000 \text{ dm}^3$$

$$2 \quad VH = 5000 \text{ dm}^3$$

$$3 \quad DHR_{x1A} = -45400 \text{ J/mol Na}$$

$$4 \quad DHR_{x2S} = -3.2E5 \text{ J/mol of Diglyme}$$

$$5 \quad \text{SumNCp} = 1.26E7 \text{ J/K}$$

$$6 \quad A1A = 4E14 \text{ per hour}$$

$$7 \quad E1A = 128000 \text{ J/kmol/K}$$

$$8 \quad k1A = A1A * \exp(-E1A / (8.31 * T)) \text{ rate constant reaction 1}$$

$$9 \quad A2S = 1E84 \text{ per hour}$$

$$10 \quad E2S = 800000 \text{ J/kmol/K}$$

$$11 \quad k2S = A2S * \exp(-E2S / (8.31 * T)) \text{ rate constant reaction 2}$$

$$12 \quad SW1 = \text{if } (T > 600 \text{ or } P > 45) \text{ then } (0) \text{ else } (1)$$

$$13 \quad r1A = -k1A * CA * CB \text{ mol/dm}^3/\text{hour (first order in sodium and cyclomethylpentadiene)}$$

14 $r_{2S} = -k_{2S} \cdot C_S$ mol/dm³/hour (first order in diglyme)

15 $FD = (-0.5 \cdot r_{1A} - 3 \cdot r_{2S}) \cdot V_0$

16 $C_{v2} = 53600$

17 $C_{v1} = 3360$

18 $F_{vent} = \text{if } (FD < 11400) \text{ then } (FD) \text{ else if } (P < 28.2) \text{ then } ((P-1) \cdot C_{v1}) \text{ else } ((P-1) \cdot (C_{v1} + C_{v2}))$

19 $UA = 0$ no cooling

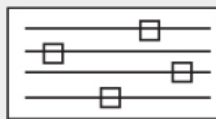
20 $Q_r = UA \cdot (T - 373.15)$

21 $Q_g = V_0 \cdot (r_{1A} \cdot DHR_{x1A} + r_{2S} \cdot DHR_{x2S})$

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	A1A	4.0E+14	4.0E+14
2	A2S	1.0E+84	1.0E+84
3	CA	4.3	9.919E-07
4	CB	5.1	0.800001
5	CS	3.	2.460265
6	Cv1	3360.	3360.
7	Cv2	5.36E+04	5.36E+04
8	DHRx1A	-4.54E+04	-4.54E+04
9	DHRx2S	-3.2E+05	-3.2E+05
10	E1A	1.28E+05	1.28E+05
11	E2S	8.0E+05	8.0E+05
12	FD	2467.445	7.477E+10
13	Fvent	2467.445	2.507E+06
14	k1A	0.0562573	153.6843

15	k2S	8.428E-16	2.533E+06
16	P	4.4	45.01004
17	Qg	2.24E+08	7.975E+15
18	Qr	0	0
19	r1A	-1.233723	-0.000122
20	r2S	-2.529E-15	-6.231E+06
21	SumNCp	1.26E+07	1.26E+07
22	SW1	1.	0
23	t	0	4.
24	T	422.	538.8048
25	UA	0	0
26	V0	4000.	4000.
27	VH	5000.	5000.



LEP Sliders

Note: The second reaction took off about 3.6 hours after starting the reactor.

Also see this example on the Web site **Process Safety Across the Chemical Engineering Curriculum** (<http://umich.edu/~safeche>) and click on Chemical Reaction Engineering Course.

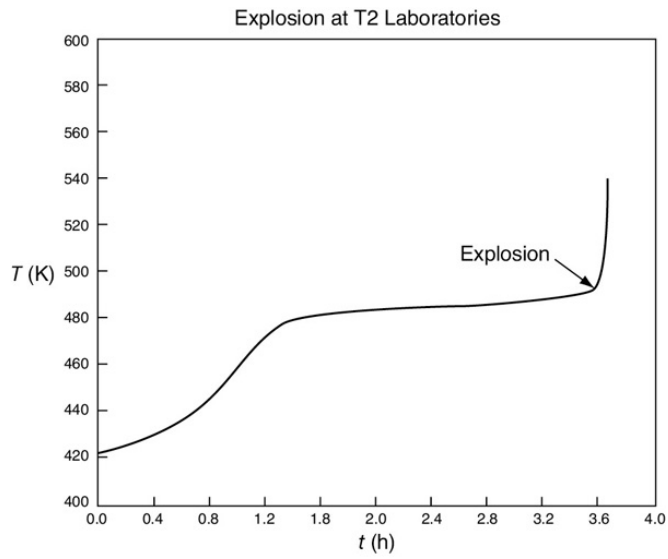


Figure E13-6.3(a) Temperature (K) versus time (h) trajectory.

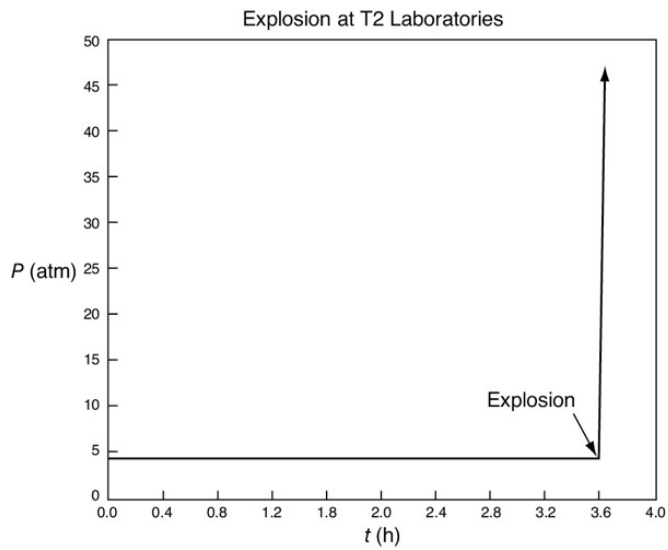


Figure E13-6.3(b) Pressure (atm) versus time (h) trajectory.

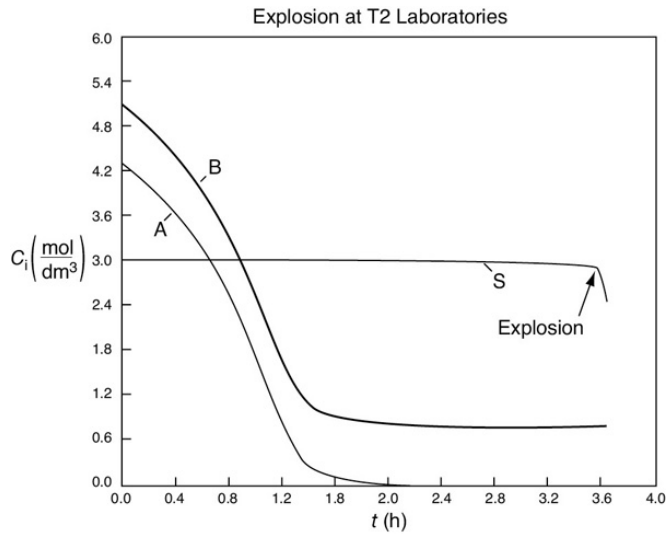


Figure E13-6.3(c) Concentration (mol/dm^3) versus time (h) trajectory.

We now will solve the essential equations from (E13-6.1) through (E13-6.29) for the scenario where there is no cooling and thus $UA = 0$. Also the switch SW1 must be implemented in all the differential equations as discussed above.

We note from Figures E13-6.3(a)–(b) that the explosion occurred at approximately 3.6 hours after startup and the concentration of diglyme begins to drop sharply before that point, as seen in Figure E13-6.3(c). We also note that numerical instabilities occur at about the point of the arrows in these figures because of the rapid increase in temperature.

Analysis: Runaway would not have occurred if (1) the cooling system had not failed, causing the reactor temperature to rise and initiate a second reaction, and (2) the solvent diglyme had not decomposed at the higher temperature to produce hydrogen gas (D). The rate of production of H_2 gas was greater than the removal of H_2 from the head space, causing the pressure to build up to the point that it ruptured the reactor vessel. Also, had the Advanced Reactor System Screening Tool (ARSST) been used to study this

reaction, additional preventative actions could have been implemented. The details with an example for the ARSST are given in the Chapter 13 Professional Reference Shelf on the Web site (http://www.umich.edu/~elements/6e/13chap/pdf/CD_ARSST_ProfRef.pdf).

Use of an ARSST may have provided information on diglyme that could have prevented this accident.

13.5 AND NOW... A WORD FROM OUR SPONSOR—SAFETY 13 (AWFOS—S13 SAFETY ANALYSIS OF THE T2 LABORATORIES INCIDENT)

In this AWFOS—S, we are going to draw from Safety Module 1 “*T2 Laboratories Explosion*” from the Chemical Reaction Engineering modules (<http://umich.edu/~safeche/courses/ChemicalReactionEngineering.html>) on the *Process Safety Across the Chemical Engineering Curriculum* (<http://umich.edu/~safeche/index.html>). In going through this module, first view the CSB Video and then analyze the relevance of the Safety Analysis to the video.

Safety Analysis of the Incident

Activity: Production of methylcyclopentadienyl manganese tricarbonyl (MCMT), which involves an exothermic reaction.

Hazard: Dangerous reaction chemistry involving toxic and flammable chemicals, with a high potential for a *runaway reaction*. Toxicity, flammability, or reactivity hazards were involved in all the production steps of MCMT. Hazardous chemicals used or generated during production steps included sodium metal, carbon monoxide, hydrogen, and organometallic compounds.

Incident: A *runaway reaction* during production of MCMT resulted in a powerful explosion and fire. Failure of the cooling system caused the explosion. The blast killed 4

employees, and injured 32 other people. It demolished the entire plant and caused extensive damage to local businesses. Decomposition of the diglyme solvent became significant at elevated temperatures that caused a significant increase in temperature and pressure leading to the runaway reaction. The 2500-gal reactor's pressure relief valve ruptured when it exceeded the set pressure. The reactor pressure continued to increase and eventually led to the explosion and fire.

Initiating Event: Failure of cooling water system led a to a runaway reaction in the metalation step of the process. This runaway resulted in uncontrolled rise in temperature and pressure inside the reactor leading to its rupture.

Preventative Actions and Safeguards: Sole reliance on city water for cooling should have been avoided and additional cooling systems should have been ready to use as a backup. A thorough understanding of reaction chemistry could have prevented the accident. This understanding could have been achieved by carrying out ARSST experiments to learn the ignition temperature of diglyme and the cooling requirement of the system. A complete description of the ARSST is given in the expanded material for Chapter 13 (http://www.umich.edu/~elements/6e/13chap/pdf/CD_ARST_ProfRef.pdf). Firefighting procedures and explosion barriers should have been in place to reduce the damage. Different levels of alarms, pressure relief systems, and safety inter-locks should have been installed to give different layers of protection from a potential disaster.

Contingency Plan/Mitigating Actions: Alarm system should be initiated as temperature and pressure increases. Emergency quenching system should be made available. Barrier walls should surround the reactor. Appropriate emergency pressure relief systems and other design safeguards should have been installed. Plan for possible accidents, including evacuation drill and emergency response exercises should have been in place.

Lessons Learned: Improved industry practices and a thorough and complete understanding of the chemistry and

hazards of the reaction being carried out can help prevent these kinds of accidents. A Kepner–Tregoe potential problem analysis[†] of the system should have been carried out. All incidents must be thoroughly investigated to find the root cause, and corrective actions must be taken immediately. Effective operating procedures and training programs should be developed, and any changes to existing processes should be carefully managed. Management of change and careful analysis of any change in operation should be done before they are implemented.

[†] H. S. Fogler, S. E. LeBlanc and B. Rizzo, *Strategies for Creative Problem Solving*, 3rd ed., p. 208.

The preventative and mitigating actions described above can be put into a BowTie diagram as shown in Figures 13-2 and 13-3.

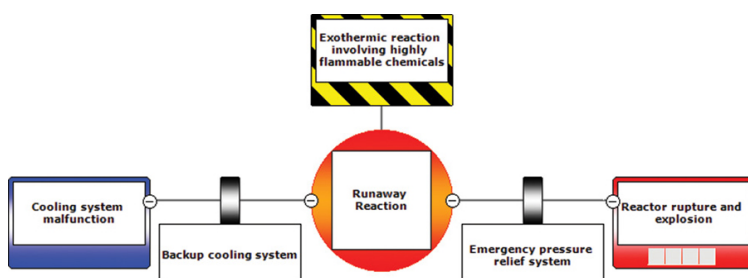
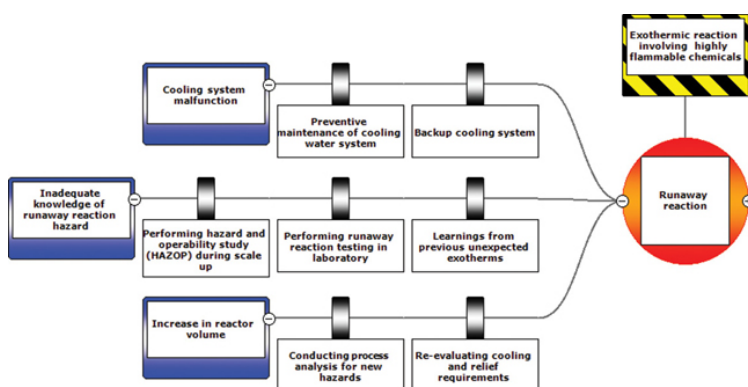


Figure 13-2 Abbreviated BowTie diagram for T2 Laboratories incident.



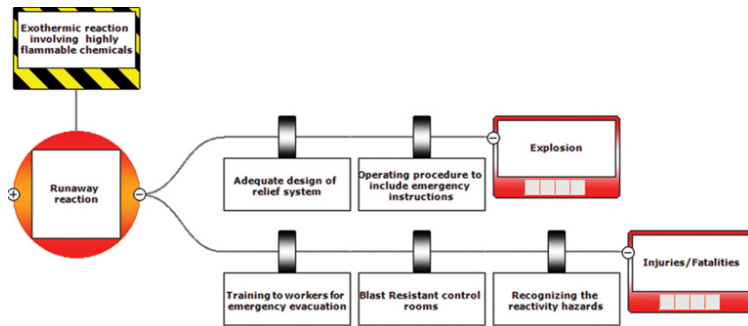


Figure 13-3 Full BowTie Diagram for T2 Laboratories Incident.

Closure. After completing this chapter, the reader should be able to apply the unsteady-state energy balance to CSTRs, semibatch, and batch reactors. The reader should also be able to discuss reactor safety using the ONCB and the T2 Laboratories case studies of explosions to help prevent future accidents. Included in the reader's discussion should be how to start up a reactor so as not to exceed the practical stability limit. After studying these examples, the reader should be able to describe how to operate reactors in a safe manner for both single and multiple reactions.

SUMMARY

1. The energy balance on unsteady operation of a CSTR and semibatch reactors

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s - \sum F_{i0} C_{P_i} (T - T_{i0}) + [-\Delta H_{Rx}(T)](-r_A V)}{\sum N_i C_{P_i}} \quad (\text{S13-1})$$

Using the heat exchange Equation (13-12) and neglecting shaft work

$$\frac{dT}{dt} = \frac{\dot{Q}_{gs} - \dot{Q}_{rs}}{\sum N_i C_{P_i}} \quad (\text{S13-2})$$

$$\dot{Q}_{rs} = (r_A V) (\Delta H_{Rx}) \quad (\text{S13-3})$$

$$\dot{Q}_{rs} = \sum F_{i0} C_{P_i} (T - T_{i0}) + \dot{m}_c C_{P_c} [T - T_{a1}] \left[1 - \exp\left(\frac{-UA}{\dot{m}_c C_{P_c}}\right) \right] \quad (\text{S13-4})$$

For large coolant flow rates, $\dot{m}_c C_{P_c}$, Equation (13-22) reduces to

$$\frac{dT}{dt} = \frac{\overbrace{(r_A V)(\Delta H_{Rx})}^{\dot{Q}_g} - \overbrace{[\Sigma F_{i0} C_{P_i}(T - T_{i0}) + U A(T - T_a)]}^{\dot{Q}_{rs}}}{\Sigma N_i C_{P_i}} \quad (\text{S13-5})$$

2. Batch reactors

a. Non-adiabatic

$$\frac{dT}{dt} = \frac{\dot{Q}_{gb} - \dot{Q}_{rb}}{\Sigma N_i C_{P_i}} = \frac{\dot{Q}_{gb} - \dot{Q}_{rb}}{N_{A0}(\Sigma \Theta_i C_{P_i} + \Delta C_P X)} \quad (\text{S13-6})$$

where

$$\dot{Q}_{gb} = (r_A V)(\Delta H_{Rx}) \quad (\text{S13-7})$$

$$\dot{Q}_{rb} = \dot{m}_c C_{P_c}(T - T_{a1}) \left[1 - \exp\left(\frac{-UA}{\dot{m}_c C_{P_c}}\right) \right] \quad (\text{S13-8})$$

b. Adiabatic

$$X = \frac{C_{P_s}(T - T_0)}{-\Delta H_{Rx}(T)} = \frac{\Sigma \Theta_i C_{P_i}(T - T_0)}{-\Delta H_{Rx}(T)} \quad (\text{S13-9})$$

$$T = T_0 + \frac{[-\Delta H_{Rx}(T_0)]X}{C_{P_s} + X\Delta C_P} = T_o + \frac{[-\Delta H_{Rx}(T_0)]X}{\sum_{i=1}^m \Theta_i C_{P_i} + X\Delta C_P} \quad (\text{S13-10})$$

3. Semibatch reactors and startup of CSTR

$$\frac{dT}{dt} = \frac{\dot{Q}_{gs} - \dot{Q}_{rs}}{\Sigma N_i C_{P_i}} \quad (\text{S13-11})$$

Where \dot{Q}_{gs} is the same as Equation (S13-7) and \dot{Q}_{rs} (sub **rs**, i.e., “**heat removed**” from semibatch) is

$$\dot{Q}_{rs} = \sum F_{i0} C_{P_{i0}}(T - T_{i0}) + \dot{m}_c C_{P_c}[T - T_{a1}] \left[1 - \exp\left(\frac{-UA}{\dot{m}_c C_{P_c}}\right) \right] \quad (\text{S13-12})$$

4. Multiple reactions (q reactions and m species)

$$\frac{dT}{dt} = \frac{\overbrace{\sum_{j=1}^q r_{ij} V \Delta H_{Rxi j}(T)}^{\dot{Q}_g} - \overbrace{\sum_{j=1}^m F_{j0} C_{P_i} (T - T_0) + \dot{m}_c C_{p_c} (T - T_{a1})}^{\dot{Q}_{rs}} \left[1 - \exp\left(\frac{-UA}{\dot{m}_c C_{p_c}}\right) \right]}{\sum_{j=1}^m N_i C_{P_i}} \quad (\text{S13-13})$$

where i = reaction number and j = species.

CRE WEB SITE MATERIALS

([HTTP://WWW.UMICH.EDU/~ELEMENTS/6E/13CHAP/OBJ.HTML#/](http://www.umich.edu/~elements/6e/13chap/obj.html#/))

Useful Links



Evaluation



Professional Reference Shelf

(<http://umich.edu/~elements/6e/13chap/prof.html>)

R13.1 The Complete ARSST

(http://umich.edu/~elements/6e/13chap/pdf/CD_ARSST_ProfRef.pdf)

In this section, further details are given to size safety valves to prevent runaway reactions.

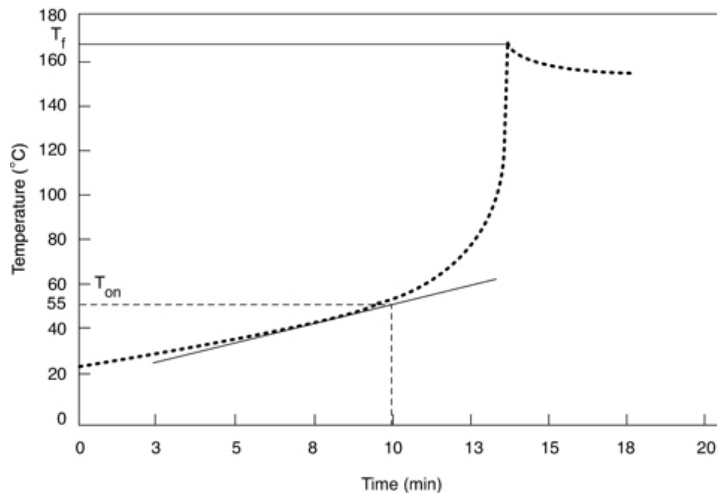


Figure R13.1 Temperature–time trajectory for hydrolysis of acetic anhydride in an ARSST.

If an ARSST experiment had been carried out with MCP and diglyme, then precautions may have been taken such that the explosion would most likely not have occurred.

R13.2 Falling Off the Upper Steady State

(<http://umich.edu/~elements/6e/13chap/prof-uppersteadystate.html>)

R13.3 Control of a CSTR

(<http://umich.edu/~elements/6e/13chap/pdf/controlCSTR.pdf>)

In this section, we discuss the use of proportional (P) and integral (I) control of a CSTR. Examples include I and PI control of an exothermic reaction.

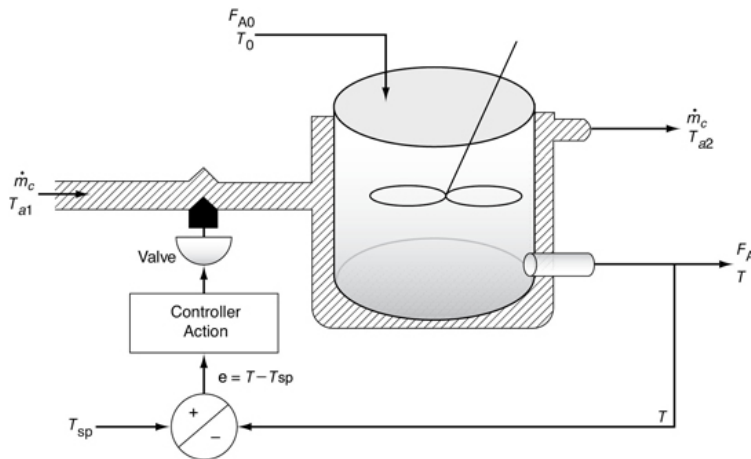


Figure R13.3 Reactor with coolant flow-rate control system.

Proportional integral action

$$z = z_0 + k_c (T - T_{SP}) + \frac{k_c}{\tau} \int_0^t (T - T_{SP}) dt$$

R13.4 Linearized Stability Theory

(http://umich.edu/~elements/6e/13chap/pdf/CD_CH09_Linearized_ProfRef3.pdf)

R13.5 Approach to Steady-State Phase-Plane Plots and Trajectories of Concentration versus Temperature
(<http://umich.edu/~elements/6e/13chap/prof-steadystate.html>)

Startup of a CSTR (Figure R13.5) and the approach to the steady state (CRE Web site). By mapping out regions of the concentration–temperature phase plane, one can view the approach to steady state and learn whether the practical stability limit is exceeded. The steady-state trajectories are shown for the mole balance (MB = 0) and energy balance (EB = 0). Use Wolfram to explore these trajectories shown below.

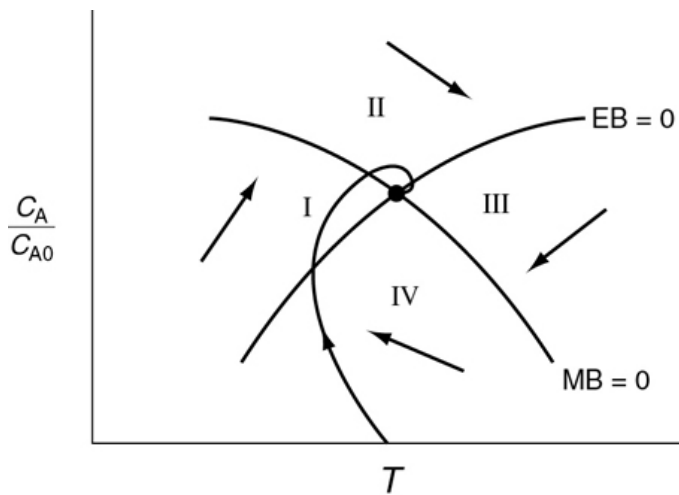


Figure R13.5 Startup of a CSTR.

R13.6 Adiabatic Operation of a Batch Reactor
(<http://umich.edu/~elements/6e/13chap/prof-adiabaticbatch.html>)

R13.7 Unsteady Operation of Plug-Flow Reactor
(<http://umich.edu/~elements/6e/13chap/prof-unsteadyplug.html>)

QUESTIONS, SIMULATIONS, AND PROBLEMS

Questions

Q13-1_A QBR (*Question Before Reading*). What conditions cause reactions to *runaway* and *explode* and what

could be done to insure runaway does not occur?

Q13-2_A **i>clicker.** Go to the Web site

(http://www.umich.edu/~elements/6e/13chap/iclicker_ch13_q1.html) and view five i>clicker questions.

Choose one that could be used as is, or a variation thereof, to be included on the next exam. You also could consider the opposite case and explain why the question should **not** be on the next exam. In either case, explain your reasoning.

Q13-3 Discuss with a classmate what are the most important safety considerations to address for exothermic reactions. To help answer this question, prepare a list of safety considerations for designing and operating chemical reactors. See the August 1985 issue of *Chemical Engineering Progress*, vol. 81, no. 7, p. 29.

Q13-4 Go to the LearnChemE screencast link for Chapter 13 (<http://www.umich.edu/~elements/6e/13chap/learn-cheme-videos.html>).

(a) View one of the screencast 5- to 6-minute video tutorials and list two of the most important points.

(b) What are the two mole balances for species B?

Q13-5 AWFOS–S13 Make a list of at least four things you learned from this section.

(a) Were any or all of the things discussed in the *Safety Analysis of the Incident* and *BowTie Diagram* in place when the reactor exploded?


(b) Were there any safety issues T2 did address?

Computer Simulations and Experiments

P13-1_B Review the example problems in this chapter and use a software package such as Polymath, Wolfram, or MATLAB to carry out a parameter sensitivity analysis to answer the following “What if...” questions.

What if...

1. **Example 13-1: Batch Reactor with an Exothermic Reaction**
Wolfram

1. *Adiabatic Case:* Use Wolfram to see whether you can find a trajectory that is ready “to ignite” and whose trajectory looks like a “cobra” ready to strike, . *Hint:* Vary T_0 to learn the point at which the reaction runs away at 2500 s.
2. *Heat Exchange Case:* (1) Vary UA and T_{a1} and suggest conditions at which runaway might occur. (2) Use the plot of Q_r and Q_g as a function of time to describe and explain what you see as you vary T_{a1} and N_{A0} from their maximum to minimum values.
3. Write three conclusions on what you found in experiments (i) and (ii).

Polymath

4. How much time would it take to achieve 90% conversion for adiabatic operation if the reaction were started on a very cold day where the initial temperature was 20°F? (Methanol won’t freeze at this temperature.)
5. Now, consider that a heat exchanger is added to the reactor for the propylene oxide reaction; the parameters are: $C_{A0} = 1 \text{ lb-mol/ft}^3$, $V = 1.2 \text{ ft}^3$, $(\sum N_i C_{p_i} = 403 \text{ Btu}^\circ\text{R})$, neglect ΔC_p , $UA = 0.22 \text{ Btu/}^\circ\text{R/s}$, and $T_a = 498 \text{ K}$. Plot and analyze the trajectories X , T , Q_g , and Q_r as a function of time.

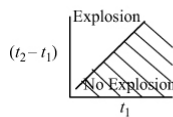


2. Example 13-2: Safety in Chemical Plants with Exothermic Runaway Reactions.

This is another **Stop and Smell the Roses Simulation**.

Wolfram

1. View the temperature trajectory for the base case and then describe how it changes when the charge (i.e., the amount initially in the reactor) is varied above and below the base case value.
2. Show the explosion would not have occurred for the triple production case if the heat exchanger had not failed. *Hint:* Set the sliders for t_1 and $t_2 = 45$ minutes in the Wolfram LEP.
3. Does it make any sense to plot the down time, $(t_2 - t_1)$, versus time since the start of the reaction that the reactor fails, (t_1) to identify regions where the explosion will and will not occur? Explain.



t_1 = start of down time
 t_2 = end of down time





If it does make sense, please prepare such a plot; if not, explain why.

Hint: Choose t_1 and then find the largest t_2 for which the reaction will not runaway. Choose another larger value of t_1 and repeat.

Continue in this manner to construct your plot.

4. Use Wolfram to find a value of N_{A0} below which no explosion would occur when all other variables remain as in the base case. Repeat for N_{B0} .
5. Use Wolfram to find the value of NC_p and also of UA , above which no explosion would occur.
6. Develop a set of guidelines as to how the reaction should be quenched should the cooling fail. Perhaps safe operation could be discussed using a plot of the length of the cooling failure, $t_2 - t_1$, as a function of the time at which the cooling failed, t_1 , for the different charges of ONCB.
7. Write a set of conclusions related to safety from your experiments in (i) and (v).

Polymath

8. Modify the Polymath code to show that no explosion would have occurred if the cooling was not shut off for the 9.04-kmol charge of ONCB, or if the cooling was shut off for 10 minutes after 45 minutes of operation for the 3.17-kmol ONCB charge.
9. Find a set of parameter values that would cause the explosion to occur at exactly 12:18 A.M. For example, include the mass and heat capacities of the metal reactor and/or make a new estimate of UA .



10. Finally, what if a 1/2-in. rupture disk rated at 800 psi had been installed and did indeed rupture at 800 psi (270°C)? Would the explosion still have occurred? *Note:* The mass flow rate varies with the cross-sectional area of the disk. Consequently, for the conditions of the reaction, the maximum mass flow rate out of the 1/2-in. disk can be found by comparing it with the mass flow rate of 830 kg/min of the 2-in. disk. Go to the *Living Example Problems on the Web site* and explore on your own the ONCB explosion described in [Example 13-2](#). Explain what you would do to prevent an explosion of this type from ever occurring again while still operating at the triple production specified by management.

This problem was written in honor of Ann Arbor, Michigan's own Grammy Award-winning artist, Bob Seger (https://www.youtube.com/channel/UComKJVf5rNLI_RfC_rbt7qg/videos).

3. **Example 13-3: Startup of a CSTR**

Wolfram

1. What is the minimum coolant flow such that there is no upturn in temperature–concentration profile for Case 2 ($T_i = 339\text{ K}$, $C_{Ai} = 0$)?
2. Is it possible to prevent crossing of practical stability limit for Case 3 ($T_i = 344\text{ K}$, $C_{Ai} = 2.26$) by varying coolant temperature, coolant flow, or overall heat transfer coefficient? If so, which is the parameter and which should be varied to achieve that?
3. Use Wolfram to find initial temperatures and concentrations that will cause the temperature trajectory to exceed the practical stability limit, and then write a conclusion.

Polymath

4. Consider the case when $C_{Ai} = 0.1\text{ lb mol/ft}^3$ and $T_i = 150^\circ\text{F}$. What is the minimum coolant temperature such that the practical stability limit is not exceeded?
5. Describe what happens to the trajectories for an entering temperature of 70°F , an initial reactor temperature of 160°F , and an initial concentration of propylene oxide of 0.1 M .
6. Try various combinations of T_0 , T_i , and C_{Ai} , and report your results in terms of temperature–time trajectories and temperature–concentration phase planes.
7. Find a set of conditions above which the practical stability limit will be reached or exceeded, and those conditions below which it will not.
8. Vary the coolant flow rate and compare with the base case given in Figures E13-3.1 to E13-3.4. Describe what you find and then write a conclusion.

COMSOL CSTR Startup

Go to the COMSOL hot button on the LEP Web site for Chapter 13 (http://www.umich.edu/~elements/6e/13chap/comsol_lep_tutorial.html) to access this LEP in COMSOL.

9. Vary the tank volume between 1 and 5 m^3 and describe the differences in the trajectories and the time to reach steady state and exceeding a practical stability limit of 360 K .
10. Use the base case parameters for the trajectory $T_i = 340\text{ K}$ and $C_i = 1400\text{ mol/m}^3$ to find the maximum feed temperature you can have that will not exceed the practical stability limit of 360 K ?
11. Pick two operating parameters from v_0 , V_{tank} , T_0 , T_a , m_c , and UA to vary from minimum to maximum values, and describe what you find.
12. Vary the activation energy, E_A , and discuss the effect of E_A on the number of oscillations to reach steady state.
13. Write three conclusions from your COMSOL experiments (ix) through (xii).

4. **Example 13-4: LEP Semibatch**

Wolfram

1. Use Wolfram to vary C_{B0} and describe how the maximum in C_C varies.
2. List the slider variables that have virtually no effect on the temperature trajectory. Repeat for the concentration trajectory.
3. Which parameter, when varied, causes the graphs of T and T_{a2} to overlap each other?
4. What is the minimum inlet temperature such that 100% conversion of A is still achieved?
5. Write three conclusions on what you found from your experiments (i) through (iv).

Polymath

6. At what times will the number of moles of C ($N_C = C_C V$) and the concentration of species C reach a maximum?
7. Are the times in part (i) that these maximums occur different, and if so, why? What would the X versus t and T versus t trajectories look like if the coolant rate were increased by a factor of 10? Why is the reaction time (252 seconds) so short?
8. *Problem.* Assume the surface area contacting the reacting fluid changes with time. The initial fluid volume in the reactor is 0.2 m^3 and the inlet volumetric flow rate is $0.004 \text{ m}^3/\text{s}$. Calculate the heat exchanger area as a function of time if the half-pipe jacket on page 684 is 0.5 m in diameter. Repeat for diameters of 1.0 and 0.25 m.

5. Example 13-5: LEP Multiple Reactions in a Semibatch Reactor

Wolfram

1. Assume a secondary reaction ignites when the reactor temperature reaches 450 K. Find the value (or combination thereof) of C_{A0} and v_0 above which the secondary reaction will ignite.
2. Vary C_{A0} and v_0 between their maximum and minimum values and describe how the concentration trajectories change and why they change the way they do.
3. Which parameter, when varied, results in equal concentration of A, B, and C at some point in time? What is the parameter value? Write two conclusions.

Polymath

4. Vary the volumetric flow rate (between $24 < v_0 < 1000$) and compare with the base case. Describe any trends you find.
5. Plot and analyze the trajectories of $N_A = C_A V$ and $N_B = C_B V$ for long times (e.g., $t = 15$ hours). What do you observe?
6. Can you show for long times that $N_A \cong C_{A0} v_0 / k_{1A}$ and $N_B \cong C_{A0} v_0 / 2k_{2B}$?
7. If species B is the desired product, how would you maximize N_B ?

6. Example 13-6: LEP T2 Laboratories Explosion

Wolfram

This problem is a **Stop and Smell the Roses Simulation**. We need to spend more time than usual exploring this problem. First view the video described on the Web site

([http://umich.edu/~safeche/assets/pdf/courses/Problems/CRE/344ReactionEngrModule\(1\)PS-T2.pdf](http://umich.edu/~safeche/assets/pdf/courses/Problems/CRE/344ReactionEngrModule(1)PS-T2.pdf)).



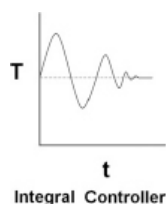
1. Vary the liquid volume, V_0 , and learn its effect on pressure profile. What is the critical value of V_0 at which pressure shoots up?
2. Which parameter will you vary such that concentration of B is always higher than concentration of C?
3. Vary different parameters and check whether it is possible that the temperature limitation is reached before the pressure limitation.
4. Find a value of the heat of reaction for the secondary reaction of diglyme, below which no explosion would have occurred.
5. Write a set of conclusions and of the lessons learned.

Polymath

6. Review the safety module
([http://umich.edu/~safeche/assets/pdf/courses/Problems/344ReactionEngineeringModule\(2\)PS050818.pdf](http://umich.edu/~safeche/assets/pdf/courses/Problems/344ReactionEngineeringModule(2)PS050818.pdf)) and fill out the safety algorithm. Write a set of conclusions and the lessons learned.
 7. (a) What did you learn from watching the video? (b) Suggest how this reactor system should be modified and/or operated in order to eliminate any possibility of an explosion. (c) Would you use backup cooling and, if so, how? (d) How could you learn whether a second reaction could be set in at a higher temperature? *Hint: See PRS R13.1 The Complete ARSST.*
 8. Download the *Living Example Polymath E13-6*. Plot C_A , C_B , C_C , P , and T as a function of time. Vary UA between 0.0 and 2.77×10^6 J/h/K to find the lowest value of UA that you observe a runaway to find the value of UA below which you would observe *runaway*. Describe the trends as you approach runaway. Did it occur over a very narrow range of UA values? *Hint: The problem becomes very stiff near the explosion condition when $T > 600$ K or $P > 45$ atm, so you will need to set all derivatives equal to zero so that the numerical solution will complete the analysis and hold all variables at the explosion point of the reactor.*
 9. Now let's consider the actual operation in more detail. The reactor contents are heated from 300 K to 422 K at a rate of $\dot{T} = 4$ K/minute. At 422 K, the reaction rate is sufficient such that heating is turned off. The reactor temperature continues to rise because the reaction is exothermic, and, when the temperature reaches 455 K, the cooling water turns on and cooling is initiated. Model this situation for the case when $UA = 2.77 \times 10^6$ J/h/K and when $UA = 0$.
 10. What is the maximum time in minutes that the cooling can be lost ($UA = 0$) starting at the time when the reactor temperature reaches 455 K so that the reactor will not reach the explosion point? The conditions are those of part (1) of this problem.
 11. Vary the parameters and operating conditions and describe what you find.
7. **LEP PRS R13.2 Example CD13-5.** Download the *Living Example Problem for Falling Off the Upper Steady State*. Try varying the entering temperature, T_0 , between 80°F and 68°F, and plot the steady-state conversion as a function of T_0 . Vary the coolant rate between 10,000 and

400 mol/h. Plot conversion and reactor temperature as a function of coolant rate.

8. **LEP PRS R13.3 Example CD13-2.** Download the *Living Example Problem*. Vary the gain, k_C , between 0.1 and 500 for the integral controller of the CSTR. Is there a lower value of k_C that will cause the reactor to fall to the lower steady state or an upper value to cause it to become unstable? What would happen if T_0 were to fall to 65°F or 60°F?
9. **LEP PRS R13.3 Example CD13-3.** Download the *Living Example Problem*. Learn the effects of the parameters k_C and τ_1 . Which combination of parameter values generates the least and greatest oscillations in temperature? Which values of k_C and τ_1 return the reaction to steady state the quickest?

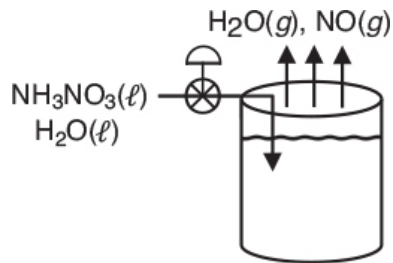
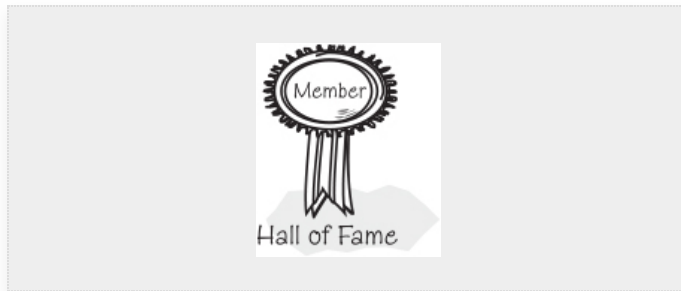


10. **SACHE.** Go to the SACHE Web site (www.sache.org). On the left-hand menu, select “SaChe Products.” Select the “All” tab and go to the module titled: “Safety, Health and the Environment (S, H & E).” The problems are for KINETICS (i.e., CRE). There are some example problems marked K and explanations in each of the above S, H & E selections. Solutions to the problems are in a different section of the site. Specifically look at: *Loss of Cooling Water* (K-1), *Runaway Reactions* (HT-1), *Design of Relief Values* (D-2), *Temperature Control and Runaway* (K-4) and (K-5), and *Runaway and the Critical Temperature Region* (K-7). Go through the K problems and write a paragraph on what you have learned. Your instructor or department chair should have the username and password to enter the SACHE Web site in order to obtain the module with the problems.

Problems

P13-2_B OEQ (Old Exam Question). The following is an excerpt from *The Morning News*, Wilmington, Delaware (August 3, 1977): “Investigators sift through the debris from blast in quest for the cause [that destroyed the new nitrous oxide plant]. A company spokesman said it appears more likely that the [fatal] blast was caused by another gas—ammonium nitrate—used to produce nitrous oxide.” An 83% (wt) ammonium nitrate and 17% water solution is fed at 200°F to the CSTR operated at a temperature of about 510°F. Molten ammonium nitrate decomposes directly to produce gaseous nitrous oxide and steam. It is

believed that pressure fluctuations were observed in the system and, as a result, the molten ammonium nitrate feed to the reactor may have been shut off approximately 4 minutes prior to the explosion. A starving artist's conception of the system is shown below



1. Can you explain the cause of the blast?
2. If the feed rate to the reactor just before shutoff was 310 lb_m of solution per hour, what was the exact temperature in the reactor just prior to shutdown? Use the data to calculate the exact time it took for the reactor to explode after the feed was shut off to the reactor.

Assume that at the time the feed to the CSTR stopped, there was 500 lb_m of ammonium nitrate in the reactor at a temperature of 520°F. The conversion in the reactor is virtually complete at about 99.99%. Additional data for this problem are given in Problem 12-5C. How would your answer change if 100 lb_m of solution were in the reactor? 310 lb_m? 800 lb_m? What if $T_0 = 100^\circ\text{F}$? 500°F ? How would you start up or shut down and control such a reaction?

Safety—Shut Down: An Open-Ended Problem.

Rather than shut off the total feed to the reactor, it should be diluted with pure water at a volumetric rate v_w while reducing the ammonium nitrate reactant feed

rate. Keep the same total volumetric feed v_0 rate and entering temperature. Choose a v_w and plot the reactor temperature and composition as a function of time. At what time could you shut off the water feed safely?

P13-3B The liquid-phase reaction in Problems P11-4_A and P12-7_A is to be carried out in a semibatch reactor. There are 500 mol of A initially in the reactor at 25°C. Species B is fed to the reactor at 50°C and a rate of 10 mol/min. The feed to the reactor is stopped after 500 mol of B has been fed.

1. Plot and analyze the temperature Q_r , Q_g and conversion as a function of time when the reaction is carried out adiabatically. Calculate to $t = 2$ hours.
2. Plot and analyze the conversion as a function of time when a heat exchanger ($UA = 100 \text{ cal/min}\cdot\text{K}$) is placed in the reactor and the ambient temperature is constant at 50°C. Calculate to $t = 3$ hours.
3. Repeat part (b) for the case where the reverse reaction cannot be neglected.

New parameter values:

$k = 0.01 \text{ (dm}^3/\text{mol} \cdot \text{min)}$ at 300 K with $E = 10 \text{ kcal/mol}$

$V_0 = 50 \text{ dm}^3$, $v_0 = 1 \text{ dm}^3/\text{min}$, $C_{A0} = C_{B0} = 10 \text{ mol/dm}^3$

For the reverse reaction: $k_r = 0.1 \text{ min}^{-1}$ at 300 K with $E_r = 16 \text{ kcal/mol}$

P13-4B OEQ (Old Exam Question). Sophia and Nic are operating a batch reactor at their grandfather's plant in Kärlläs, Jofostan. The reaction is first-order, irreversible, liquid-phase, and exothermic. An inert coolant is added to the reaction mixture to control the temperature. The temperature is kept constant by varying the flow rate of the coolant (see Figure P13-4B).

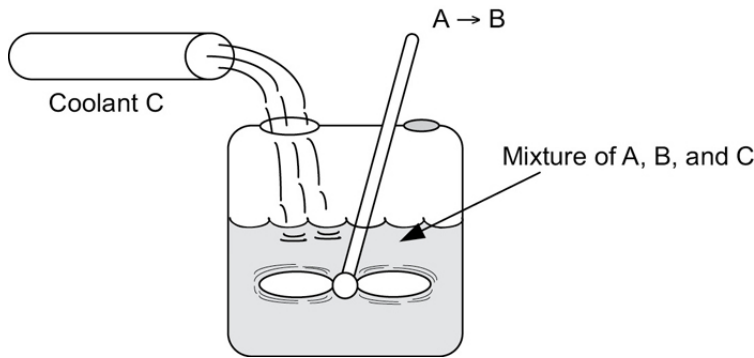


Figure P13-4B Semibatch reactor with inert coolant stream.

1. Help them calculate the flow rate of the coolant 2 hours after the start of the reaction. (**Ans:** $F_C = 3.157 \text{ lb/s}$)
2. It is proposed that rather than feeding a coolant to the reactor, a solvent be added that can be easily boiled off, even at moderate temperatures. The solvent has a heat of vaporization of 1000 Btu/lb and initially there are 25 lb-mol of A placed in the tank. The initial volume of solvent and reactant is 300 ft^3 . Determine the solvent evaporation rate as a function of time. What is the rate at the end of 2 hours?

Additional information:

Temperature of reaction: 100°F

Value of k at 100°F : $1.2 \times 10^{-4} \text{ s}^{-1}$

Temperature of coolant: 80°F

Heat capacity of all components: $0.5 \text{ Btu/lb}^\circ\text{F}$

Density of all components: 50 lb/ft^3

$\Delta H_{\text{Rx}}^\circ$: $-25000 \text{ Btu/lb-mol}$

Initially:

Vessel contains only A (no B or C present)

C_{A0} : 0.5 lb-mol/ft^3

Initial volume: 50 ft^3

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P13-5_B The reaction

is carried out adiabatically in a constant-volume batch reactor. The rate law is

$$-r_A = k_1 C_A^{1/2} C_B^{1/2} - k_2 C_C$$

Plot and analyze the conversion, temperature, and concentrations of the reacting species as a function of time.

Additional information:

Initial Temperature = 100°C

$$k_1 (373 \text{ K}) = 2 \times 10^{-3} \text{ s}^{-1} \quad E_1 = 100 \text{ kJ/mol}$$

$$k_2 (373 \text{ K}) = 3 \times 10^{-5} \text{ s}^{-1} \quad E_2 = 150 \text{ kJ/mol}$$

$$C_{A0} = 0.1 \text{ mol/dm}^3 \quad C_{pA} = 25 \text{ J/mol} \cdot \text{K}$$

$$C_{B0} = 0.125 \text{ mol/dm}^3 \quad C_{pB} = 25 \text{ J/mol} \cdot \text{K}$$

$$\Delta H_{R_x}^\circ (298 \text{ K}) = -40000 \text{ J/mol A} \quad C_{pC} = 40 \text{ J/mol} \cdot \text{K}$$

P13-6_B The elementary irreversible liquid-phase reaction

is to be carried out in a semibatch reactor in which B is fed to A. The volume of A in the reactor is 10 dm³, the initial concentration of A in the reactor is 5 mol/dm³, and the initial temperature in the reactor is 27°C. Species B is fed at a temperature of 52°C and a concentration of 4 M. It is desired to obtain at least 80% conversion of A in as short a time as possible, but at the same time the temperature of the reactor must not rise above 130°C. You should try to make approximately 120 mol of C in a 24-hour day, allowing for 30 minutes to empty and fill the reactor between each batch. The coolant flow rate through the reactor is 2000 mol/min. There is a heat exchanger in the reactor.

1. What volumetric feed rate (dm³/min) do you recommend?
2. How would your answer or strategy change if the maximum coolant rate dropped to 200 mol/min? To 20 mol/min?

Additional information:

$$\Delta H_{\text{Rx}}^{\circ} = -55,000 \text{ cal/mol A}$$

$$C_{\text{P}_A} = 35 \text{ cal/mol} \cdot \text{K}, \quad C_{\text{P}_B} = 20 \text{ cal/mol} \cdot \text{K}, \quad C_{\text{P}_C} = 75 \text{ cal/mol} \cdot \text{K}$$

$$k = 0.0005 \frac{\text{dm}^6}{\text{mol}^2 \cdot \text{min}} \text{ at } 27^{\circ}\text{C with } E = 8000 \text{ cal/mol}$$

$$UA = 2500 \frac{\text{cal}}{\text{min} \cdot \text{K}} \text{ with } T_a = 17^{\circ}\text{C}$$

$$C_{\text{P}} (\text{coolant}) = 18 \text{ cal/mol} \cdot \text{K}$$

P13-7B The irreversible reaction liquid phase in Problems P11-4A and P12-7A



is to be carried out in a 10 dm^3 batch reactor.

Plot and analyze the temperature and the concentrations of A, B, and C as a function of time for the following cases:

(a) Adiabatic operation.

(b) Values of UA of 10000, 40000, and 100000 $\text{J/min} \cdot \text{K}$.

(c) Use $UA = 40000 \text{ J/min} \cdot \text{K}$ and different initial reactor temperatures.

An equal molar feed in A and B enters at 27°C , and the volumetric flow rate is $2 \text{ dm}^3/\text{s}$ and $C_{A0} = 0.1 \text{ kmol/m}^3$.

Additional information:

$$\Delta H_A^{\circ} (273 \text{ K}) = -20 \text{ kcal/mol}, \quad \Delta H_B^{\circ} (273 \text{ K}) = -15 \text{ kcal/mol},$$

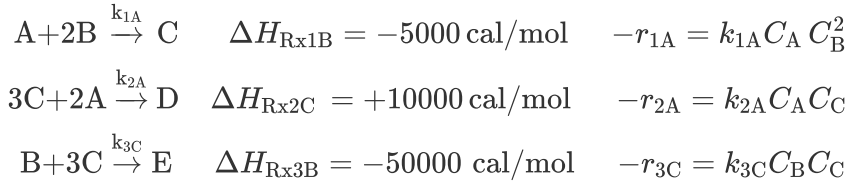
$$\Delta H_C^{\circ} (273 \text{ K}) = -41 \text{ kcal/mol}$$

$$C_{\text{P}_A} = C_{\text{P}_B} = 15 \text{ cal/mol} \cdot \text{K} \quad C_{\text{P}_C} = 30 \text{ cal/mol} \cdot \text{K}$$

$$k = 0.01 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \text{ at } 300 \text{ K} \quad E = 10000 \text{ cal/mol} \quad K_C = 10 \text{ m}^3/\text{mol} \text{ at } 450$$

P13-8B Use the reaction and corresponding parameter values in Problem P12-16B to describe the startup of a CSTR with $T_i = 25^{\circ}\text{C}$ and $C_{Ai} = 0.0$. *Hint:* Plot the concentration and temperature trajectories as well as the phase-plane plots of C_A versus T for various values of T_i and C_{Ai} .

P13-9B **OEQ** (Old Exam Question). The following reactions are taking place in a 2000-dm^3 liquid-phase batch reactor under a pressure of 400 psig:



The initial temperature is 450 K and the initial concentrations of A, B, and C are 1.0, 0.5, and 0.2 mol/dm³, respectively. The coolant flow rate was at its maximum value so that $T_{a1} = T_{a2} = T_a = 400$ K, so that the product, the exchange area, and the overall heat transfer coefficient, UA , is $UA = 100 \text{ cal/s} \cdot \text{K}$.

- (a) If $Q_r > Q_g$ at time $t = 0$, and there is no failure of the heat exchange system, is there any possibility that the reactor will run away? Explain.
- (b) What is Q_r at $t = 0$?
- (c) What is Q_g at $t = 0$?
- (d) What is the initial rate of increase in temperature, (i.e., dT/dt) at $t = 0$?

$$\frac{dT}{dt} = \text{-----} [\text{Numerical Answer}]$$

- (e) Suppose that the ambient temperature T_a is lowered from 400 K to 350 K; what is the initial rate of reactor temperature change?

$$\frac{dT}{dt} = \text{-----} [\text{Numerical Answer}]$$

Plot the temperatures and all the concentrations as a function of time up to $t = 1000$ seconds.

- (f) A suggestion was made to add 50 moles of inerts at a temperature of 450 K. Will the addition of the inerts make runaway more likely or less likely? How? Show quantitatively.

Additional information:

As a first approximation, assume all heats of reaction are constant (i.e., $\Delta C_{p,ij} \cong 0$). Specific reaction rates at 450 K are

$$\begin{aligned}
 k_{1A} &= 1 \times 10^{-3} \left(\text{dm}^3/\text{mol} \right)^2/\text{s} & C_{pA} &= 10 \text{ cal/mol/K} & C_{pD} &= 80 \text{ cal/mol/K} \\
 k_{2B} &= \frac{1}{3} \times 10^{-3} \left(\text{dm}^3/\text{mol} \right)^2/\text{s} & C_{pB} &= 10 \text{ cal/mol/K} & C_{pE} &= 80 \text{ cal/mol/K} \\
 k_{3C} &= 0.6 \times 10^{-3} \left(\text{dm}^3/\text{mol} \right)^2/\text{s} & C_{pC} &= 50 \text{ cal/mol/K}
 \end{aligned}$$

P13-10_B Synthron Explosion LEP. Read the Synthron example in Chapter 13 Additional Materials on the CRE Web Site

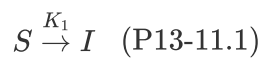
(<http://www.umich.edu/~elements/6e/13chap/obj.html#/additional-materials/>)

Wolfram and Python

1. Describe and discuss the base case temperature-time trajectory.
2. What is the critical initial volume of reactants (V_0) above which the reactor will explode? For the sake of simplicity, assume the reactor will explode if the contents of the reactor remain above 350 K at 500 s after the start of the reaction, as the lack of cooling will result in an unsafe pressure increase.
3. Vary two parameters of your choice that you think will have the most effect on the explosion and describe what you find.
4. Write a set of conclusions.

Zachary Gdowski, Ayush Agrawal and Mayur Tikmani
participated in developing this problem.

P13-11_B STOP THE PRESSES – COVID-19 Analysis. As the final edits to the Sixth Edition were being made, the coronavirus pandemic struck and it was decided to expand Problem P9-7 and apply it to the pandemic. (Mayur Tikmani, Devosmita Sen, Manjeet Singh, and Jagana Janan Sai participated in developing this problem.) We will start the modeling after 770 people have been infected. Let H = Healthy, S = Susceptible, I = Infected, D = Died, and R = Recovered. Treat each of the following interactions as an elementary reaction. The first reaction could result from a healthy person contacting the virus on a surface.



$$I + S \xrightarrow{K_2} 2I \quad (\text{P13-11.2})$$

$$I \xrightarrow{K_3} r \quad (\text{P13-11.3})$$

$$I \xrightarrow{K_4} D \quad (\text{P13-11.4})$$

$$H = r + S \quad (\text{P13-11.5})$$

Wolfram and Python

- (i) Derive equations for the populations of S, I, R, and D as a function of time.
- (ii) Use Wolfram to see if the resulting equations can be matched to Figures P13-11_B (a) and P13-11_B (b).
- (iii) If we could vary k_1 , k_2 , k_3 , and k_4 , at what concentration of infected people does the death rate become critical?
- (iv) Compare your model with the data from China for two extreme cases: (1) $k_1 = 0$ with $I(0) = 770$, and (2) $k_1 = 2 \times 10^{-7} \text{ day}^{-1}$ and $I(0) = 0$.
- (v) Vary the parameters k_1 , k_2 , k_3 , and k_4 along with $I(t = 0)$ and $S(t = 0)$ and write a set of conclusions.
- (vi) Apply the PSSH to the concentration of ill people and comment on your results.
- (vii) Critique the COVID-19 model and initial concentrations and discuss the changes you would make.

Additional Information:

$$k_1 = 6 \times 10^{-7} \text{ day}^{-1} \text{ (initial infection rate)}$$

$$k_2 = 10.58 \times 10^{-9} \text{ (people*day)}^{-1} \text{ (rate of spread of infection)}$$

$$k_3 = 14.5645 \text{ day}^{-1} \text{ (recovery rate)}$$

$$k_4 = 2 \times 10^{-3} \text{ day}^{-1} \text{ (death rate)}$$

Initial values:

$$S(0) = 1.3864 \times 10^9 \text{ people (population that is not social distancing)}$$

$$I(0) = 770 \text{ people infected at the start of the modeling}$$

$$R(0) = 0$$

$$D(0) = 0$$

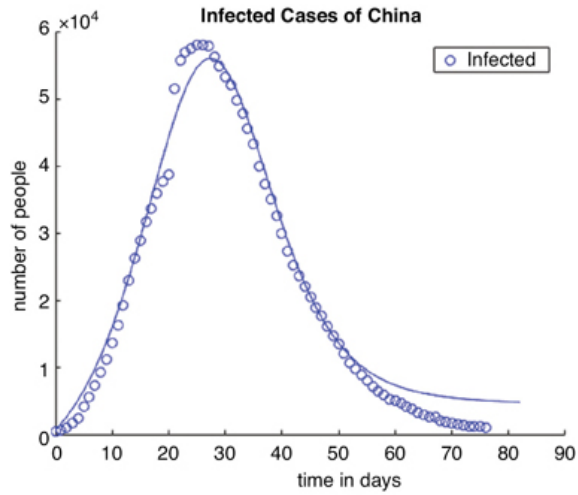


Figure P13-11_B (a) Infected People as a Function of Time

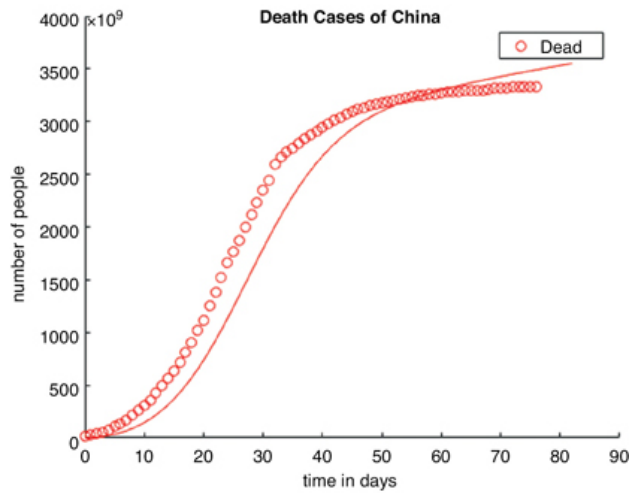


Figure P13-11_B (b) Dead People as a Function of Time

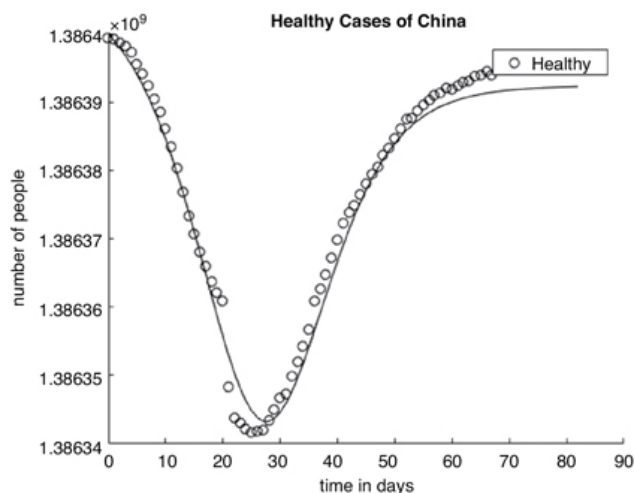


Figure P13-11_B (c) Healthy People as a Function of Time

• Additional Homework Problems

A number of homework problems that can be used for exams or supplementary problems or examples are found on the CRE Web site,
www.umich.edu/~elements/6e/index.html.

SUPPLEMENTARY READING

1. A number of solved problems for batch and semibatch reactors can be found in
 S. M. WALAS, *Chemical Reaction Engineering Handbook*. Amsterdam: Gordon and Breach, 1995, pp. 386–392, 402, 460–462, and 469.

Safety

- DANIEL A. CROWL and JOSEPH F. LOUVAR, *Chemical Process Safety: Fundamentals with Applications*, 3rd ed. Upper Saddle River, NJ: Prentice Hall, 2001.
- T. F. EDGAR, “From the Classical to the Postmodern Era,” *Chem. Eng. Educ.*, 31, 12 (1997).
- TREVOR A. KLETZ, “Bhopal Leaves a Lasting Legacy: The Disaster Taught Some Hard Lessons That the Chemical Industry Still Sometimes

Forgets,” *Chemical Processing*, p. 15 (Dec. 2009).

Links

1. Be sure to review the author’s Web site *Process Safety Across the Chemical Engineering Curriculum* (<http://umich.edu/~safeche/index.html>). In particular, review the tutorials (e.g., the BowTie Diagram).
2. The SChE Web site has a great discussion on reactor safety with examples (www.sache.org). You will need a username and password; both can be obtained from your department chair. Hit the 2003 Tab. Go to K Problems.
3. The reactor lab developed by Professor Herz and discussed in Chapters 4 and 5 could also be used here: www.reactorlab.net.
4. See the Center for Chemical Process Safety (CCPS) Web site, www.aiiche.org/ccps/.



14. Mass Transfer Limitations in Reacting Systems

Giving up is the ultimate tragedy.

—Robert J. Donovan

or

It ain't over 'til it's over.

—Yogi Berra NY Yankees

Overview. Many industrial reactions are carried out at high temperatures where the overall rate of reaction is limited by the rate of mass transfer of reactants between the bulk fluid and the catalytic surface. By mass transfer, we mean any process in which diffusion plays a role. Under these circumstances our generation term becomes a little more complicated as we cannot directly use the rate laws discussed in [Chapter 3](#). Now we have to consider the fluid velocity and the fluid properties when writing the mole balance. In the rate laws and catalytic reaction steps described in [Chapter 10](#) (diffusion, adsorption, surface reaction, desorption, and diffusion), we neglected the diffusion steps.

In this chapter we discuss how to determine the rate of reaction and how to size reactors when the reactions are limited by mass transfer. To do this we

- Present the fundamentals of diffusion and molar flux, and then write the mole balance in terms of the mole fluxes for rectangular and for cylindrical coordinates ([Section 14.1](#)).
- Incorporate Fick's first law into our mole balance in order to describe flow, diffusion, and reaction ([Section 14.2](#)).
- Model diffusion through a stagnant film to a reacting surface ([Section 14.3](#)).
- Introduce the mass transfer coefficient, k_c , and describe how it is used to design mass transfer-limited reactions ([Section 14.4](#)).
- Focus on one of the engineer's most important skills, that is, to answer "What if..." questions, as *Robert the Worrier* does ([Section 14.5](#)).

The Algorithm

1. Mole balance
2. Rate law
3. Stoichiometry
4. Combine
5. Evaluate

14A MASS TRANSFER FUNDAMENTALS

14.1 DIFFUSION FUNDAMENTALS

The first step in our CRE algorithm is the mole balance, which we now need to extend to include the molar flux, W_{Az} , and diffusional effects. The molar flow rate of A in a given direction, such as the z direction down the length of a tubular reactor, is just the product of the flux, W_{Az} ($\text{mol/m}^2 \cdot \text{s}$), and the cross-sectional area, A_c (m^2); that is,

$$F_{Az} = A_c W_{Az}$$

In the previous chapters, we have only considered plug flow with no diffusion superimposed, in which case

$$W_{Az} = \frac{C_A v}{A_c}$$

We now drop the plug-flow assumption and extend our discussion of mass transfer in catalytic and other mass transfer-limited reactions. In [Chapter 10](#), we focused on the middle three steps (3, 4, and 5) in a catalytic reaction shown in [Figure 14-1](#) and neglected steps (1), (2), (6), and (7) by assuming the reaction was surface-reaction limited. In this chapter, we describe the first and last steps (1) and (7), as well as showing other applications in which mass transfer plays a role.

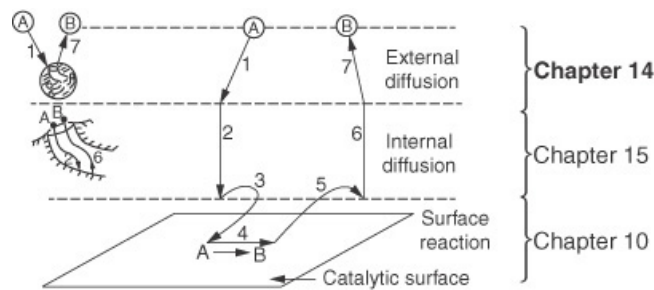


Figure 14-1 Steps in a heterogeneous catalytic reaction.

Where are we going??[†]

[†] “If you don’t know where you are going, you’ll probably wind up some place else.” Yogi Berra, NY Yankees

We want to arrive at the mole balance that incorporates both diffusion and reaction effects, such as Equation (14-17) on page 746, that is,

$$D_{AB} \frac{d^2 C_A}{dz^2} - U_z \frac{dC_A}{dz} + r_A = 0$$

We begin with [Section 14.1.1](#) where we write the mole balance on Species A in three dimensions in terms of the molar flux, \mathbf{W}_A . In [Section 14.1.2](#) we write \mathbf{W}_A in terms of the bulk flow of A in the fluid, \mathbf{B}_A and the diffusion flux \mathbf{J}_A of A that is superimposed on bulk flow. In [Section 14.1.3](#) we use the previous two subsections as a basis to finally write the molar flux, \mathbf{W}_A , in terms of concentration using Fick’s first law, \mathbf{J}_A , and the bulk flow, \mathbf{B}_A . Next, in [Section 14.2](#) we combine diffusion convective transport and reaction in our mole balance.

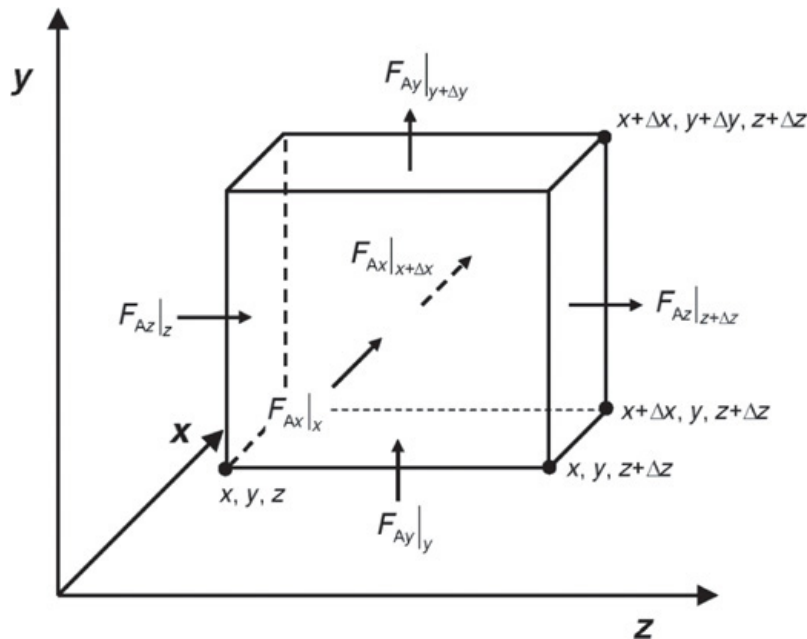
14.1.1 Definitions

Diffusion is the spontaneous intermingling or mixing of atoms or molecules by random thermal motion. It gives rise to motion of the species *relative* to motion of the mixture. In the absence of other gradients (such as temperature, electric potential, or gravitational potential), molecules of a given

species within a single phase will always diffuse from regions of higher concentrations to regions of lower concentrations. This gradient results in a molar flux of the species (e.g., A), \mathbf{W}_A (moles/area=time), in the direction of the concentration gradient. The flux of A, \mathbf{W}_A , is relative to a fixed coordinate (e.g., the lab bench) and is a vector quantity with typical units of $\text{mol/m}^2 \cdot \text{s}$. In rectangular coordinates

$$\mathbf{W}_A = iW_{Ax} + jW_{Ay} + kW_{Az}$$

We now apply the mole balance to species A, which flows and reacts in an element of volume $\Delta V = \Delta x \Delta y \Delta z$ to obtain the variation of the molar fluxes in three dimensions.



$$F_{Az} = W_{Az} \Delta x \Delta y$$

$$F_{Ay} = W_{Ay} \Delta x \Delta z$$

$$F_{Ax} = W_{Ax} \Delta z \Delta y$$

$$\begin{aligned}
& \left[\begin{array}{c} \text{Molar} \\ \text{flow rate} \\ \text{in} \end{array} \right]_z - \left[\begin{array}{c} \text{Molar} \\ \text{flow rate} \\ \text{out} \end{array} \right]_{z+\Delta z} + \left[\begin{array}{c} \text{Molar} \\ \text{flow rate} \\ \text{in} \end{array} \right]_{y+\Delta y} - \left[\begin{array}{c} \text{Molar} \\ \text{flow rate} \\ \text{out} \end{array} \right]_{y+\Delta y} + \\
& \Delta x \Delta y W_{Az|z} - \Delta x \Delta y W_{Az|z+\Delta z} + \Delta x \Delta z W_{Ay|y} - \Delta x \Delta z W_{Ay|y+\Delta y} + \\
& \left[\begin{array}{c} \text{Molar} \\ \text{flow rate} \\ \text{in} \end{array} \right]_x - \left[\begin{array}{c} \text{Molar} \\ \text{flow rate} \\ \text{out} \end{array} \right]_{x+\Delta x} + \left[\begin{array}{c} \text{Rate of} \\ \text{generation} \end{array} \right] = \left[\begin{array}{c} \text{Rate of} \\ \text{accumulation} \end{array} \right] \\
& \Delta z \Delta y W_{Ax|x} - \Delta z \Delta y W_{Ax|x+\Delta x} + r_A \Delta x \Delta y \Delta z = \Delta x \Delta y \Delta z \frac{\partial C_A}{\partial t}
\end{aligned}$$

Mole balance

where r_A is the rate of generation of A by reaction per unit volume (e.g., mol/m³/h).

Dividing by $\Delta x \Delta y \Delta z$ and taking the limit as they go to zero, we obtain the molar flux balance in rectangular coordinates

$$-\frac{\partial W_{Ax}}{\partial x} - \frac{\partial W_{Ay}}{\partial y} - \frac{\partial W_{Az}}{\partial z} + r_A = \frac{\partial C_A}{\partial t} \quad (14-1)$$

The corresponding balance in cylindrical coordinates with no variation in the rotation about the **z**-axis is

COMSOL

$$-\frac{1}{r} \frac{\partial}{\partial r} (r W_{Ar}) - \frac{\partial W_{Az}}{\partial z} + r_A = \frac{\partial C_A}{\partial t} \quad (14-2)$$

We will now evaluate the flux terms \mathbf{W}_A . We have taken the time to derive the molar flux equations in this form because they are now in a form that is consistent with the partial differential equation (PDE) solver COMSOL, which is accessible from the CRE Web site.

14.1.2 Molar Flux: W_A

The molar flux of A, \mathbf{W}_A , is the result of two contributions: \mathbf{J}_A , the molecular diffusion flux relative to the bulk motion of the fluid produced by a concentration gradient, and \mathbf{B}_A , the flux resulting from the bulk motion of the fluid:

Total flux = diffusion + bulk motion

$$\mathbf{W}_A = \mathbf{J}_A + \mathbf{B}_A \quad (14-3)$$

The bulk-flow term for species A is the total flux of all molecules relative to a fixed coordinate times the mole fraction of A, y_A ; that is, $\mathbf{B}_A = y_A \sum \mathbf{W}_i$.

For a two-component system of A diffusing in B, the flux of A is

$$\mathbf{W}_A = \mathbf{J}_A + y_A (\mathbf{W}_A + \mathbf{W}_B) \quad (14-4)$$

The diffusional flux, \mathbf{J}_A , is the flux of A molecules that is superimposed on the bulk flow. It tells how fast A is moving ahead of the bulk flow velocity, that is, the molar average velocity.

The flux of species A, \mathbf{W}_A , is wrt a *fixed coordinate system* (e.g., the lab bench) and is just the concentration of A, C_A , times the particle velocity of species A, \mathbf{U}_A , at that point

$$\mathbf{W}_A = \mathbf{U}_A C_A$$

$$\frac{\text{mol}}{\text{m}^2 \text{S}} = \left(\frac{\text{m}}{\text{s}} \right) \left(\frac{\text{mol}}{\text{m}^3} \right)$$

By particle velocities, we mean the vector average of millions of molecules of A at a given point. Similarly for species B:

$\mathbf{W}_B = \mathbf{U}_B C_B$; substituting into the bulk-flow term

$$\mathbf{B}_A = y_A \sum \mathbf{W}_i = y_A (\mathbf{W}_A + \mathbf{W}_B) = y_A (C_A \mathbf{U}_A + C_B \mathbf{U}_B)$$

Writing the concentration of A and B in the generic form in terms of the mole fraction, y_i , and the total concentration, c , that is, $C_i = y_i c$, and then factoring out the total concentration, c , the bulk flow, \mathbf{B}_A , is

$$\mathbf{B}_A = (c y_A)(y_A \mathbf{U}_A + y_B \mathbf{U}_B) = C_A \mathbf{U}$$

Molar average velocity \mathbf{U}

where \mathbf{U} is the molar average velocity: $\mathbf{U} = \sum \mathbf{y}_i \mathbf{U}_i$. The molar flux of A can now be written as

$$\mathbf{W}_A = \mathbf{J}_A + C_A \mathbf{U} \quad (14-5)$$

We now need to determine the equation for the molar flux of A, \mathbf{J}_A , that is superimposed on the molar average velocity.

14.1.3 Fick's First Law

Experimentation with frog legs led to Fick's first law.

Our discussion on diffusion will be restricted primarily to binary systems containing only species A and B. We now wish to determine *how* the molar diffusive flux of a species (i.e., \mathbf{J}_A) is related to its concentration gradient. As an aid in the discussion of the transport law that is ordinarily used to describe diffusion, recall similar laws from other transport processes. For example, in conductive heat transfer the constitutive equation relating the heat flux \mathbf{q} and the temperature gradient is Fourier's law, $\mathbf{q} = -k_t \nabla T$, where k_t is the thermal conductivity.

Constitutive equations in heat, momentum, and mass transfer

In rectangular coordinates, the gradient is in the form

$$\nabla = i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z}$$

The mass transfer law for the diffusional flux of A resulting from a concentration gradient is analogous to Fourier's law for heat transfer and is given by **Fick's first law**[†]

[†] Adolf Fick was an interesting character as evidenced by his use of frogs to study diffusion.

$$J_A = -D_{AB} \nabla C_A \quad (14-6)$$

D_{AB} is the diffusivity of A in B $\left(\frac{\text{m}^2}{\text{s}}\right)$. Combining Equations (14-5) and (14-6), we obtain an expression for the molar flux of A in terms of concentration for constant total concentration

Molar flux equation

$$W_A = -D_{AB} \nabla C_A + C_A U \quad (14-7)$$

In one dimension, that is, z , the molar flux term is

$$W_{Az} = -D_{AB} \frac{dC_A}{dz} + C_A U_z \quad (14-8a)$$

Where U_z is the axial velocity, in radial coordinates with no variations in the angular (θ) direction

$$W_{Ar} = -D_{AB} \frac{dC_A}{dz} + C_A U_r \quad (14-8b)$$

Where U_r is the fluid's radial velocity

14.2 BINARY DIFFUSION

Although many systems involve more than two components, the diffusion of each species can be treated as if it were diffusing through another single species rather than through a mixture by defining an effective diffusivity.

14.2.1 Evaluating the Molar Flux

Now the task is to evaluate the bulk-flow term.

We now consider A diffusing in B. Substituting Equation (14-6) into Equation (14-4) we obtain

$$W_A = -D_{AB} \nabla C_A + y_A (W_A + W_B) \quad (14-9)$$

Before going to Section 14.2.2 it would be helpful to evaluate the bulk flow term ($y_A (W_A + W_B)$) for five limiting situations. These situations are given by Equations 14-10 through 14-13 in Table 14-1 on page 745.

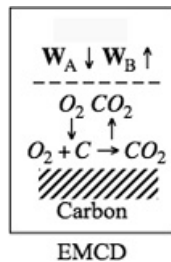
TABLE 14-1 EVALUATING W_A FOR SPECIES A DIFFUSING IN SPECIES B

1. Equal molar counter diffusion (EMCD) of species A and B. For every molecule of A that diffuses in the forward direction, one molecule of B diffuses in the reverse direction

$$W_A = -W_B$$

$$W_A = J_A = -D_{AB} \nabla C_A \quad (14-10)$$

An example of EMCD is the oxidation of solid carbon; for every mole of oxygen that diffuses



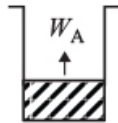
to the surface to react with the carbon surface, one mole of carbon dioxide diffuses away from the surface. $W_{O_2} = -W_{CO_2}$

2. Species A diffusing through stagnant species B ($W_B = 0$). This situation usually occurs when a solid boundary is involved and there is a stagnant fluid layer next to the boundary through which A is diffusing.

$$W_A = J_A + y_A W_A$$

$$W_A = \frac{J_A}{1-y_A} = -\frac{D_{AB}\nabla C_A}{1-y_A} = +cD_{AB}\nabla \ln(1-y_A) \quad (14-11)$$

An example is the evaporation of a liquid in a test tube into air



3. Bulk flow of A is much greater than molecular diffusion of A, that is, $B_A \gg J_A$

$$W_A = B_A = y_A (W_A + W_B) = C_A U \quad (14-12)$$

This case is the plug-flow model we have been using in the previous chapters in this book

$$F_A = W_A A_c = C_A \overbrace{U A_c}^v = v C_A$$

4. For small bulk flow $J_A \gg B_A$, we get the same result as EMCD, that is, Equation (14-10)

$$W_A = J_A = -D_{AB} \nabla C_A \quad (14-10)$$

5. Knudsen Diffusion: Occurs in porous catalysts where the diffusing molecules collide more often with the pore walls than with each other

$$W_A = J_A = -D_K \nabla C_A \quad (14-13)$$

and D_K is the Knudsen diffusion.¹

¹ C. N. Satterfield, *Mass Transfer in Heterogeneous Catalysis*, Cambridge: MIT Press, 1970, pp. 41–42, discusses Knudsen flow in catalysis and gives the expression for calculating D_K .

14.2.2 Diffusion and Convective Transport

When accounting for diffusional effects, the molar flow rate of species A, F_A , in a specific direction \mathbf{z} , is the product of molar flux in that direction, W_{Az} , and the cross-sectional area normal to the direction of flow, A_c

$$F_{Az} = A_c W_{Az}$$

In terms of concentration, the flux is

$$W_{Az} = -D_{AB} \frac{dC_A}{dz} + C_A U_z$$

The molar flow rate is

$$F_{Az} = W_{Az} A_C = \left[-D_{AB} \frac{dC_A}{dz} + C_A U_z \right] A_C \quad (14-14)$$

Similar expressions follow for W_{Ax} and W_{Ay} . Substituting for the flux W_{Ax} , W_{Ay} , and W_{Az} into Equation (14-1), we obtain

Flow, diffusion, and reaction
This form is used in COMSOL Multiphysics.

$$D_{AB} \left[\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right] - U_x \frac{\partial C_A}{\partial x} - U_y \frac{\partial C_A}{\partial y} - U_z \frac{\partial C_A}{\partial z} + r_A = \frac{\partial C_A}{\partial t} \quad (14-15)$$

In terms of axial and radial coordinates with no angular variation and no radial velocity U_r we have

$$D_{AB} \left[\frac{\partial}{\partial r} \left(\frac{r dC_A}{dr} \right) + \frac{\partial^2 C_A}{\partial z^2} \right] - U_z \frac{\partial C_A}{\partial z} + r_A = \frac{\partial C_A}{\partial t} \quad (14-16)$$

Equation (14-15) and (14-16) are in a user-friendly form to apply to the PDE solver, COMSOL. For one dimension at steady state, Equation (14-15) reduces to

$$D_{AB} \frac{d^2 C_A}{dz^2} - U_z \frac{dC_A}{dz} + r_A = 0 \quad (14-17)$$

In order to solve Equation (14-17) we need to specify the boundary conditions. In this chapter we will consider some of the simple boundary conditions, and in Chapter 18 we will consider the more complicated boundary conditions, such as the Danckwerts' boundary conditions.

We will now use this form of the molar flow rate in our mole balance in the z direction of a tubular flow reactor

$$\frac{dF_A}{dV} = \frac{d(A_c W_{Az})}{d(A_c z)} = \frac{dW_{Az}}{dz} = r_A$$

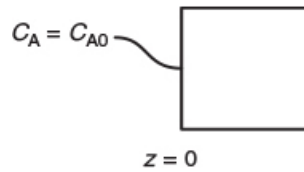
However, we first have to discuss the boundary conditions in solving this equation.

14.2.3 Boundary Conditions

The most common boundary conditions are presented in Table 14-2.

TABLE 14-2 TYPES OF BOUNDARY CONDITIONS

1. Specify a concentration at a boundary (e.g., $z = 0$, $C_A = C_{A0}$).

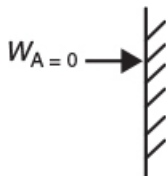


For an instantaneous reaction at a boundary, the concentration of the reactants at the boundary is taken to be zero (e.g., $C_{As} = 0$). See Chapter 18 for the more exact and complicated Danckwerts' boundary conditions at $z = 0$ and $z = L$.

2. Specify a flux at a boundary.

1. No mass transfer to a boundary

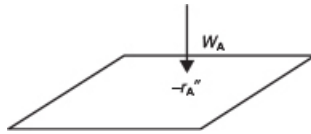
$$W_A = 0 \quad (14-18)$$



for example, at the wall of a nonreacting pipe. Species A cannot diffuse into the solid pipe wall so $W_A = 0$ and then

$$\frac{dC_A}{dr} = 0 \quad \text{at } r = R \quad (14-19)$$

That is, because the diffusivity is finite, the only way the flux can be zero is if the concentration gradient is zero.



2. Set the molar flux to the surface equal to the rate of reaction on the surface

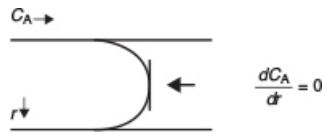
$$W_A (\text{surface}) = -r_A'' (\text{surface}) \quad (14-20)$$

The rate of reaction proceeds only as fast as the reactants diffuse to, and arrive at the surface where they react.

3. Set the molar flux to the boundary equal to convective transport across a boundary layer

$$W_A (\text{boundary}) = k_c (C_{Ab} - C_{As}) \quad (14-21)$$

where k_c is the mass transfer coefficient and C_{As} and C_{Ab} are the surface and bulk concentrations, respectively.



3. Planes of symmetry. When the concentration profile is symmetrical about a plane, the concentration gradient is zero in that plane of symmetry. For example, in the case of radial diffusion in a pipe, at the center of the pipe

$$\frac{dC_A}{dr} = 0 \quad \text{at } r = 0 \quad (14-22)$$

14.2.4 Temperature and Pressure Dependence of D_{AB}

Before closing this brief discussion on mass-transfer fundamentals, further mention should be made of the diffusion coefficient. Equations for predicting gas diffusivities are given by Fuller and are also given in Perry's *Handbook*.^{2,3} The orders of magnitude of the diffusivities for gases, liquids, and solids and the manner in which they vary with temperature and pressure are given in Table 14-3.⁴ We note that the Knudsen, liquid, and solid diffusivities are independent of total pressure.

² E. N. Fuller, P. D. Schettler, and J. C. Giddings, *Ind. Eng. Chem.*, 58(5), 19 (1966).

³ R. H. Perry and D. W. Green, *Chemical Engineer's Handbook*, 7th ed. New York: McGraw-Hill, 1999.

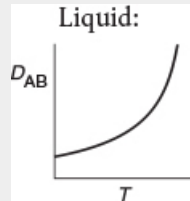
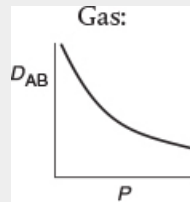
⁴ To estimate liquid diffusivities for binary systems, see K. A. Reddy and L. K. Doraiswamy, *Ind. Eng. Chem. Fund.*, 6, 77 (1967).

TABLE 14-3 DIFFUSIVITY RELATIONSHIPS FOR GASES, LIQUIDS, AND SOLIDS

Phase	Order of Magnitude		Temperature and Pressure Dependences ^a
	cm ² /s	m ² /s	
Gas			
Bulk	10 ⁻¹	10 ⁻⁵	$D_{AB} (T_2, P_2) = D_{AB} (T_1, P_1) \frac{P_1}{P_2} \left(\frac{T_2}{T_1} \right)^{1.75}$
Knudsen	10 ⁻²	10 ⁻⁶	$D_A (T_2) = D_A (T_1) \left(\frac{T_2}{T_1} \right)^{1/2}$
Liquid	10 ⁻⁵	10 ⁻⁹	$D_{AB} (T_2) = D_{AB} (T_1) \frac{\mu_1}{\mu_2} \left(\frac{T_2}{T_1} \right)$
Solid	10 ⁻⁹	10 ⁻¹³	$D_{AB} (T_2) = D_{AB} (T_1) \exp \left[\frac{E_D}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \right]$

^a μ_1, μ_2 , liquid viscosities at temperatures T_1 and T_2 , respectively; E_D , diffusion activation energy.

It is important to know the magnitude and the T and P dependence of the diffusivity.



14.3 MODELING DIFFUSION WITH CHEMICAL REACTION

We now consider the situation where species A does not react as it diffuses through a hypothetical stagnant film to a surface where it does react. In Chapter 15 we consider the case when species A does react as it diffuses through a stagnant film.

Table 14-4 provides an algorithm for both of these situations.

TABLE 14-4 STEPS IN MODELING CHEMICAL SYSTEMS WITH DIFFUSION AND REACTION

1. Define the problem and state the assumptions.
2. Define the system on which the balances are to be made.
3. Perform a differential mole balance on a particular species.
4. Obtain a differential equation in W_A by rearranging your balance equation properly and taking the limit as the volume of the

element goes to zero.

5. Substitute the appropriate expression involving the concentration gradient for W_A from [Section 14.2](#) to obtain a second-order differential equation for the concentration of A.^a
6. Express the reaction rate r_A (if any) in terms of concentration and substitute into the differential equation.
7. State the appropriate boundary and initial conditions.
8. Put the differential equations and boundary conditions in dimensionless form.
9. Solve the resulting differential equation for the concentration profile.
10. Differentiate this concentration profile to obtain an expression for the molar flux of A.
11. Substitute numerical values for symbols.

^aIn some instances it may be easier to integrate the resulting differential equation in Step 4 before substituting for W_A .

The purpose of presenting algorithms (e.g., [Table 14-4](#)) to solve reaction engineering problems is to give the readers a starting point or framework with which to work if they were to get stuck. It is expected that once readers are familiar and comfortable using the algorithm/framework, they will be able to move in and out of the framework as they develop creative solutions to nonstandard chemical reaction engineering problems.

Use Table 14-4 to Move In \rightleftharpoons Out of the algorithm (Steps 1 \rightarrow 10) to generate creative solutions.

14.3.1 Diffusion through a Stagnant Film to a Particle

We will first discuss the diffusion of reactants from the bulk fluid to the external surface of a particle that is either solid or liquid. Here our attention will focus on the flow past a single particle as shown in Figure 14-2(a) and its corresponding boundary layer shown in Figure 14-2(b). The particle can be either a liquid droplet, a catalyst pellet or a combustible solid grain. The reaction takes place only on the external surface and not in the fluid surrounding it. The fluid velocity in the vicinity of the spherical pellet will vary with position around the sphere. The hydrodynamic boundary layer is usually defined as the distance from a solid object to where the fluid velocity is 99% of the bulk velocity, U_0 . Similarly, the mass transfer boundary-layer thickness, δ , is defined as the distance from a solid object to where the concentration of the diffusing species reaches 99% of the bulk concentration.

A reasonable representation of the concentration profile for a reactant A diffusing to the external surface is shown in Figure 14-2. As illustrated, the change in concentration of A from C_{Ab} to C_{As} takes place in a very narrow fluid layer next to the surface of the sphere. Nearly all of the resistance to mass transfer is found in this layer.

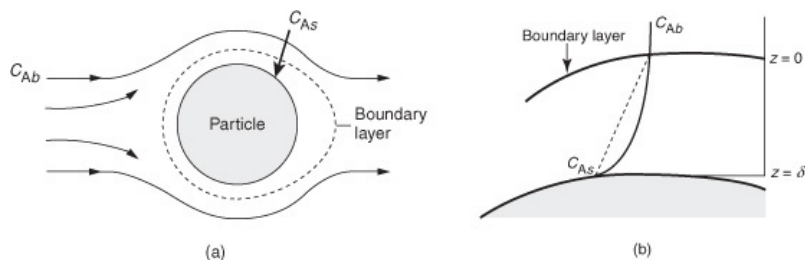


Figure 14-2 Boundary layer around the surface of spherical particle.

The concept of a hypothetical stagnant film within which all the resistance to external mass transfer exists

A useful way of modeling diffusive transport is to treat the fluid layer next to a solid boundary as a hypothetical stagnant film of thickness δ , which we cannot measure. We say that *all* the resistance to mass transfer is found (i.e., lumped) within this hypothetical stagnant film of thickness δ , and the properties (i.e., concentration, temperature) of the fluid at the outer edge of the film are identical to those of the bulk fluid. This model can readily be used to solve the differential equation for diffusion through a stagnant film. The dashed line in Figure 14-2(b) represents the concentration profile predicted by the hypothetical stagnant film model, while the solid line gives the actual profile. If the film thickness is much smaller than the radius of the pellet (which is usually the case), curvature effects can be neglected. As a result, only the one-dimensional diffusion equation must be solved, as shown in Figure 14-3.

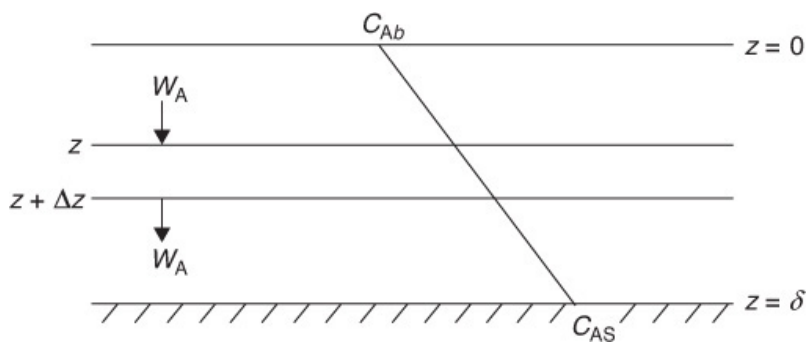


Figure 14-3 Concentration profile for dilute concentration in stagnant film mode.

We are going to carry out a mole balance on species A diffusing through the fluid between $z = z$ and $z = z + \Delta z$ at steady state for the unit cross-sectional area, A_c

$$\begin{array}{ccccccc}
 \text{In} & - & \text{Out} & + & \text{Generation} & = & \text{Accumulation} \\
 W_{Az}|_z & - & W_{Az}|_{z+\Delta z} & + & 0 & = & 0
 \end{array}$$

dividing by Δz and taking the limit as $\Delta z \rightarrow 0$

$$\frac{dW_{Az}}{dz} = 0$$

For diffusion through a stagnant film at *dilute* concentrations

$$J_A \gg y_A (W_A + W_B) \quad (14-23)$$

or for EMCD, we have using Fick's first law

$$W_{Az} = -D_{AB} \frac{dC_A}{dz} \quad (14-24)$$

Substituting for W_{Az} and dividing by D_{AB} we have

$$\frac{d^2 C_A}{dz^2} = 0$$

Integrating twice to get $C_A = K_1 z + K_2$, using the boundary conditions at

$$\begin{aligned} z = 0 \quad C_A &= C_{Ab} \\ z = \delta \quad C_A &= C_{As} \end{aligned}$$

we obtain the concentration profile

$$C_A = C_{Ab} + (C_{As} - C_{Ab}) \frac{z}{\delta} \quad (14-25)$$

To find the flux to the surface we substitute Equation (14-25) into Equation (14-24) to obtain

$$W_{Az} = \frac{D_{AB}}{\delta} [C_{Ab} - C_{As}] \quad (14-26)$$

At steady state the flux of A to the surface will be equal to the rate of reaction of A on the surface. We also note that another example of diffusion through a stagnant film as applied to transdermal drug delivery is given in the [Chapter 14 Expanded Material](#) on the CRE Web site.

14.4 THE MASS TRANSFER COEFFICIENT

We now interpret the ratio (D_{AB}/δ) in Equation (14-26).

While the boundary-layer thickness will vary around the sphere, we will take it to have a mean film thickness δ . The ratio of the diffusivity D_{AB} to the film thickness δ is the mass transfer coefficient, k_c , that is,

$$k_c = \frac{D_{AB}}{\delta} \quad (14-27)$$

Combining Equations (14-26) and (14-27), we obtain the average molar flux from the bulk fluid to the surface

$$W_{Az} = k_c (C_{Ab} - C_{As}) \quad (14-28)$$

The mass transfer coefficient

In this stagnant film model, we consider all the resistance to mass transfer to be lumped into the thickness δ . The reciprocal of the mass transfer coefficient can be thought of as this resistance

$$W_{Az} = \text{Flux} = \frac{\text{Driving force}}{\text{Resistance}} = \frac{C_{Ab} - C_{As}}{(1/k_c)} \quad (14-29)$$

Molar flux of A to the surface

How Do I find the Mass Transfer Coefficient? The mass transfer coefficient is found either by experimentation or from correlations analogous to what one finds for a heat transfer coefficient. These correlations are usually in the form of the Sherwood number, Sh , as a function of the Reynolds number, Re , and the Schmidt number, Sc , that is,

$$Sh = f(Re, Sc) \quad (14-30)$$

where

Sherwood

$$\text{Sh} = \frac{k_c'' L''}{D_{AB}} \quad (14-31)$$

Schmidt

$$\text{Sc} = \frac{\nu}{D_{AB}} = \frac{\mu/\rho}{D_{AB}} \quad (14-32)$$

Reynolds

$$\text{Re} = \frac{U'' L''}{\nu} = \frac{U'' L'' \rho}{\mu} \quad (14-33)$$

where

" L " is the characteristic length (m) (e.g., d_p , diameter of the particle)

ν = Kinematic viscosity (m^2/s) = μ/ρ

μ = viscosity ($\text{kg}/\text{m} \cdot \text{s}$)

ρ = density (kg/m^3)

U = free stream velocity (m/s)

D_{AB} = diffusivity (m^2/s)

As an example, the mass transfer coefficient for flow around a single spherical particle can be found from the *Frössling correlation*.[†]

[†]N. Frössling, *Gerlands Beitr. Geophys.*, 52, 170 (1938).

$$\text{Sh} = 2 + 0.6 \text{Re}^{1/2} \text{Sc}^{1/3} \quad (14-34)$$

For turbulent flow, the number 2 in this equation can be neglected with respect to the second term and the resulting

correlation is shown in Table 14-5.[‡]

[‡] **Just out...** An article in August 2019 issue of the *AIChE Journal* expands this correlation. Y. Wang and J G. Brasseur, “Enhancement of mass transfer from particles by local shear-rate and correlations with application to drug dissolution,” *AIChE J.*, 65 (8), (August 2019). Equation (14-34) is derived for dissolution in an infinite fluid while Professor Wang’s article *AIChE J.* discusses dissolution in a confined domain. The corrections are particularly important at low Reynolds number and this article guides you through these corrections. However, the nomenclature is different. For example, the Sherwood number is given as $Sh = R/\delta$, so it might help if you referred to Professor Wang’s earlier article 2012 Y. Yang, et.al., *Mol. Pharm.*, 9, 1052 (2012).

The correlation given for low Re is reported as

$$Sh = Sh_0 + 0.0177 Re^{0.46} Sc^{0.68}$$

where Sh_0 is a function of the Schmidt number Sc . For example, when

$$5 < Sc < 100$$

then

$$Sh_0 = 1.2 + Sc^{0.82}$$

Other values of Sh_0 are given in Professor Wang’s article.

After calculating the numerical value of Sh , given the parameters to calculate Re and Sc , the mass transfer coefficient can be calculated

$$k_c = \frac{Sh D_{AB}}{d_p} \quad (\text{m/s}) \quad (14-35)$$

Correlation for geometries other than a single spherical particle are given in Table 14-5.

TABLE 14-5 MASS TRANSFER CORRELATIONS

Turbulent flow, mass transfer to pipe wall	
$Sh = .332 (Re)^{1/2} (Sc)^{1/3}$	

Mass transfer to a single sphere	$Sh = 2 = 0.6 Re^{1/2} Sc^{1/3}$
Mass transfer in fluidized beds	$\phi J_D = \frac{0.765}{Re^{.82}} + \frac{0.365}{Re^{0.386}}$
Mass transfer to packed beds	$\phi J_D = 0.453 Re^{0.453}$
$J_D = \frac{Sh}{ReSc^{1/3}}$	

What if I cannot find the mass transfer correlation for my situation or geometry? In this case, see whether a correlation for the heat transfer coefficient exists and then go to (<http://www.umich.edu/~elements/6e/14chap/obj.html#/additio-nal-materials/>) to learn how to turn that heat transfer correlation into a mass transfer correlation.

The Sherwood, Reynolds, and Schmidt numbers are used in forced convection mass transfer correlations.

14B APPLICATIONS

14.5 MASS TRANSFER TO A SINGLE PARTICLE

Mass transfer to single particles is important in catalytic reactions and in dust explosions. In this section we consider two limiting cases of diffusion and reaction on a catalyst particle.⁵ In the first case, the reaction is so rapid that the rate of diffusion of the reactant to the surface limits the reaction rate. In the second case, the reaction is so slow that virtually no concentration gradient exists in the gas phase (i.e., rapid diffusion with respect to surface reaction).

⁵ A comprehensive list of correlations for mass transfer to particles is given by G. A. Hughmark, *Ind. Eng. Chem. Fund.*, 19(2), 198 (1980).

14.5.1 First-Order Rate Laws

To easily show the limitations of mass transfer and reaction rate we will consider first order kinetics. For the case of either the burning of a combustible dust particle or for reaction on a catalyst surface at high temperatures, the rate law is taken as apparent first order.

Figure 14-4 shows the mass transfer flux of A to the surface, W_A , the reaction on the surface r''_{As} , and the mass transfer flux of B away from the surface. In the examples discussed here species A can be thought of as oxygen and B as the combustion products, for example, CO_2 . The reaction on the surface is taken as apparent first order.

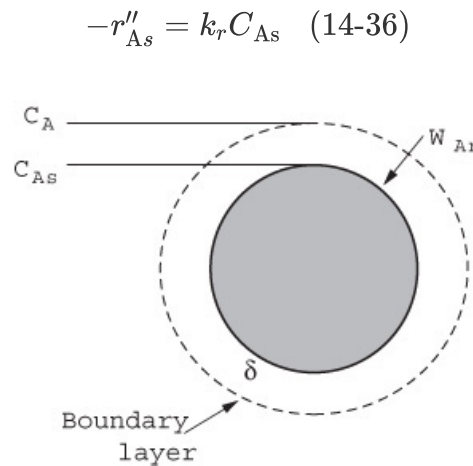


Figure 14-4 Diffusion to, and reaction on, external surface of pellet.

Using boundary conditions 2b. and 2c. in Table 14-2, we obtain

$$W_{A|\text{surface}} = -r''_{As} \quad (14-37)$$

$$W_A = k_c(C_A - C_{As}) = k_r C_{As} \quad (14-38)$$

The concentration at the surface, C_{As} , is not as easily measured as is the bulk concentration, C_A . Consequently, we need to eliminate C_{As} from the equation for the flux and rate of reaction. Solving Equation (14-38) for C_{As} yields

$$C_{As} = \frac{k_c C_A}{k_r + k_c} \quad (14-39)$$

and the rate of reaction on the surface becomes

Molar flux of A to the surface is equal to the rate of consumption of A on the surface.

$$W_A = -r''_{As} = \frac{k_c k_r C_A}{k_r + k_c} \quad (14-40)$$

One will often find the flux to or from the surface written in terms of an *effective* transport coefficient k_{eff}

$$W_A = -r''_{As} = k_{\text{eff}} C_A \quad (14-41)$$

where

$$k_{\text{eff}} = \frac{k_c k_r}{k_c + k_r} \quad (14-42)$$

We will now consider the extremes of rapid and slow reaction at the particle surface.

14.5.2 Limiting Regimes

Rapid Reaction. We first consider how the overall rate of reaction may be increased when the rate of mass transfer to the surface limits the overall rate of reaction. Under these circumstances, the specific reaction-rate constant is much greater than the mass transfer coefficient

$$k_r \gg k_c$$

and

$$k_{\text{eff}} = k_c$$

$$W_A = -r''_{As} = \frac{k_c C_A}{1 + k_c/k_r} \approx k_c C_A \quad (14-43)$$

To increase the rate of reaction per unit surface area of a solid sphere, one must increase C_A and/or k_c . In this gas-phase catalytic reaction example, and for most liquids, the Schmidt

number is sufficiently large that the number 2 in Equation (14-34) is negligible with respect to the second term when the Reynolds number is greater than 25. As a result, Equation (14-34) gives

It is important to know how the mass transfer coefficient varies with fluid velocity, particle size, and physical properties.

$$\begin{aligned} k_c &= 0.6 \left(\frac{D_{AB}}{d_p} \right) \text{Re}^{1/2} \text{Sc}^{1/3} \\ &= 0.6 \left(\frac{D_{AB}}{d_p} \right) \left(\frac{U d_p}{\nu} \right)^{1/2} \left(\frac{\nu}{D_{AB}} \right)^{1/3} \end{aligned} \quad (14-44)$$

$$\begin{aligned} k_c &= 0.6 \times \frac{D_{AB}^{2/3}}{\nu^{1/6}} \times \frac{U^{1/2}}{d_p^{1/2}} \\ k_c &= 0.6 \times (\text{Term 1}) \times (\text{Term 2}) \end{aligned} \quad (14-45)$$



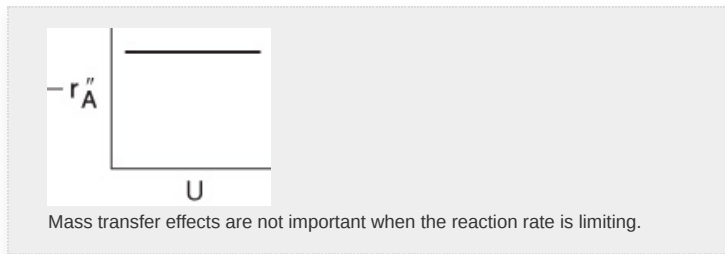
Term 1 is a function of the physical properties D_{AB} and ν , which depend on temperature and pressure only. The diffusivity always increases with increasing temperature for both gas and liquid systems. However, the kinematic viscosity ν increases with temperature ($\nu \propto T^{3/2}$) for gases and decreases exponentially with temperature for liquids. Term 2 is a function of flow conditions and particle size. Consequently, to increase k_c and thus the overall rate of reaction per unit surface area, one may either decrease the particle size or increase the velocity of the fluid flowing past the particle. For this particular case of flow past a single sphere, we see that if the velocity is doubled, the mass transfer coefficient and consequently the rate of reaction is increased by a factor of

$$(U_2/U_1)^{0.5} = 2^{0.5} = 1.41 \text{ or } 41\%$$

Reaction Rate Limited

Slow Reaction. Here, the specific reaction-rate constant is small with respect to the mass transfer coefficient

$$W_A = -r''_{AS} = \frac{k_r C_A}{1 + k_r/k_c} \approx k_r C_A \quad (14-46)$$



The specific reaction rate is independent of the velocity of fluid and for the solid sphere considered here, independent of particle size. *However*, for porous catalyst pellets, k_r may depend on particle size for certain situations, as shown in Chapter 15.

Figure 14-5 shows the variation in reaction rate with Term 2 in Equation (14-45), the ratio of velocity to particle size. At low velocities, the mass transfer boundary-layer thickness is large and diffusion limits the reaction. As the velocity past the sphere is increased, the boundary-layer thickness decreases, and the mass transfer across the boundary layer no longer limits the rate of reaction. One also notes that for a given (i.e., fixed) velocity, reaction-limiting conditions can be achieved by using very small particles. However, the smaller the particle size, the greater the pressure drop in a packed bed. When one is obtaining reaction-rate data in the laboratory, one must operate at sufficiently high velocities or sufficiently small particle sizes to ensure that the reaction is not mass transfer-limited when collecting data.

When collecting rate-law data, operate in the reaction-limited region.

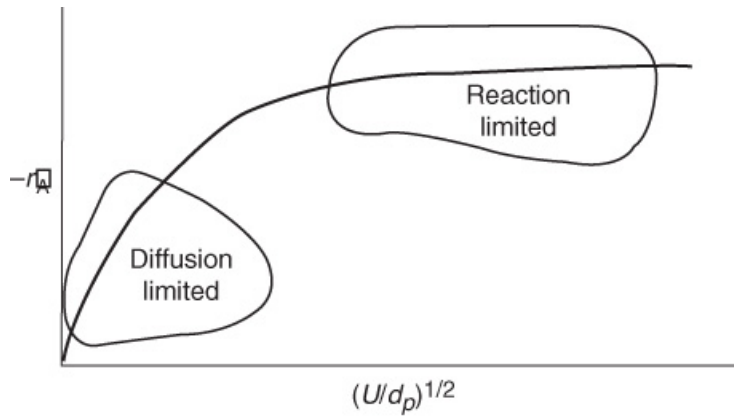


Figure 14-5 Regions of mass transfer-limited and reaction-limited reactions.

Before we analyze Equation (14-40) in more detail, we will describe examples involving a dust particle fire of granular carbon in air and a catalyst particle in a liquid slurry. In both cases we will use $k_r \gg k_s$ so that $-r''_{As} = W_A = k_c C_A$.

Example 14–1 Mass Transfer of Oxygen to a Burning Carbon Particle

A schematic of the transfer of oxygen to the particle is shown in [Figure 14-4](#). The gas-phase diffusivity in the flame (1000 K) surrounding the particle is taken as $10^{-4} \text{ m}^2/\text{s}$ and the particle diameter is $50 \text{ }\mu\text{m}$ ($5 \times 10^{-5} \text{ m}$). The concentration of oxygen in the bulk air (21% at 1 atm and 298 K) is 8.58 mol/m^3 . The reaction is virtually instantaneous so that the concentration of oxygen on the surface of the particle is zero, that is, $C_{As} = 0$. The heat of reaction is $\Delta H_{Rx} = -93.5 \text{ kJ/mol}$ carbon.

Calculate molar flux, W_A ($\text{mol/m}^2/\text{s}$) and molar flow \dot{m}_A (mol/s) to the particle. For a dust cloud density of 200 g/m^3 , calculate the heat generated per particle \dot{q}_p , and the heat generated per volume of cloud.

Solution

The flux to the surface is

$$W_A = k_c [C_{A\infty} - C_{As}] \cong k_c C_{A\infty} \quad (\text{E14-1.1})$$

For particles that are sufficiently small such that they are in Stoke's flow, (i.e., it follows the fluid) the fluid velocity relative to the particle is zero, (i.e., $U \cong 0$). For a single particle in Stoke's flow, the Sherwood number for a spherical particle

$$\text{Sh} = 2 + 0.61 (\text{Re}^{1/2} \text{Sc}^{1/3}) \cong 2$$

reduces to

$$\text{Sh} = \frac{k_c d_p}{D_{AB}} = 2 \quad (\text{E14-1.2})$$

The corresponding molar flux of oxygen to the surface where it reacts virtually instantaneously ($C_{As} = 0$) at

the surface

$$k_c = \frac{Sh}{d_p/D_{AB}} = \frac{2D_{AB}}{d_p} = \frac{2(10^{-4} \text{ m}^2/\text{s})}{5 \times 10^{-5} \text{ m}} = 4 \text{ m/s}$$

$$W_A = k_c (C_{A\infty}) = 2 \frac{D_{AB}}{d_p} C_{A\infty} \quad (\text{E14-1.3})$$

$$W_A = \frac{2(10^{-4} \text{ m}^2/\text{s})}{50 \times 10^{-6} \text{ m}} \left(8.58 \frac{\text{mol}}{\text{m}^3} \right) = 34.3 \text{ mol/m}^2 \cdot \text{s}$$

The molar flux (mol/m²/s) of oxygen to *one* particle is

$$W_A = -r_A'' = 34.3 \text{ mol/m}^2 \cdot \text{s}$$

The molar flow (mol/s) of oxygen, \dot{m}_A , to *one* particle with surface area A_P is

$$\dot{m}_A = A_P W_A = \pi d_p^2 W_A = \pi (50 \times 10^{-6} \text{ m})^2 34.3 \text{ mol/m}^2 \cdot \text{s}$$

$$\dot{m}_A = 2.7 \times 10^{-7} \text{ mol/s}$$

Heat Effects

Now let's estimate the heat generated for this burning particle and then for the dust cloud with n_p , the number of particles per unit volume. Figure 8.40 of Ogle[†] gives the minimum dust explosion concentration, in air, C_{cloud} , as approximately 200 g/m³. The mass of one 50 μm carbon dust particle is

[†] Ibid, page 480.

$$\begin{aligned} m_P &= \rho_c V = \rho_c \frac{\pi d_p^3}{6} = \left(2.226 \times 10^6 \text{ g/m}^3 \right) \frac{\pi}{6} (5 \times 10^{-5})^3 \text{ m}^3 \\ &= 14.5 \times 10^{-8} \text{ g/particle} \end{aligned}$$

The corresponding particle concentration is

$$n_P = \frac{C_{\text{cloud}}}{m_p} = \frac{200 \text{ g/m}^3}{14.5 \times 10^{-8} \text{ g/particle}}$$

$$n_p = 1.38 \times 10^9 \text{ particles/m}^3$$

The heat generated by a single particle \dot{q}_P (kJ/particle) is just the molar flux of O_2 (i.e., $-r''_{As} = W_A$) times the surface area of particle times the heat of reaction, that is,

$$\dot{q}_P = (-r''_{As} A_P) (-\Delta H_{Rx})$$

The heat generated per unit volume of dust cloud, \dot{Q}_{gd} , with a concentration of dust particles, n_p , is

$$\dot{Q}_{gd} = n_p \dot{q}_P = (-r''_{As} n_p A_P) (-\Delta H_{Rx})$$

The rate of heat generated per particle, \dot{q}_P , times the particle concentration, n_p , gives the heat generated per unit volume of dust as

$$\dot{Q}_{gd} = n_p \dot{q}_P = n_p \dot{q}_P = n_p \dot{m}_A (-\Delta H_{Rx}) = \frac{1.38 \times 10^9}{\text{m}^3} \times 2.7 \times 10^{-7} \frac{\text{mol}}{\text{s}} \times \left(93.5 \frac{\text{kJ}}{\text{mol}} \right)$$

$$\dot{Q}_{gd} = 34586 \text{ kJ/s} \cdot \text{m}^3$$

Analysis: We calculated the molar flux as well as the mass flow of oxygen to the surface of a burning particle. The molar flux of O_2 to the surface is equal to the rate of reaction per unit surface area. Knowing the reaction rate, the dust density, and the heat of reaction we calculated the heat generated per particle and per unit volume of dust cloud.

We will continue our discussion on single dust particles when we discuss the shrinking core model. However, let's first make a comparison with a larger particle, 0.1 cm, suspended in a body of flowing liquid.

Example 14–2 Rapid Liquid-Phase Reaction on the Surface of a Catalyst

Calculate the molar flux, W_{Ar} , of reactant A to a single catalyst pellet 1 cm in diameter suspended in a large body of liquid B. The reactant is present in dilute concentrations, and the reaction is considered to take place instantaneously at the external pellet surface (i.e., $C_{As} \approx 0$). The bulk concentration of the reactant A is 1.0 M, and the free-stream liquid velocity past the sphere is 0.1 m/s. The kinematic viscosity (i.e., $\frac{\mu}{\rho}$) is 0.5 centistoke (cS; 1 centistoke = 10^{-6} m²/s), and the liquid diffusivity of A in B is $D_{AB} = 10^{-10}$ m²/s at 300 K.

If the surface reaction is rapid, then diffusion limits the overall rate.

Solution

For dilute concentrations of the solute, the radial flux is

$$W_{Ar} = k_c (C_{Ab} - C_{As}) \quad (\text{E14-2.1})$$

Because reaction is assumed to occur instantaneously on the external surface of the pellet, $C_{As} = 0$. Also, C_{Ab} is given as 1 mol/dm³.

$$W_{Ar} = k_c C_{Ab} \quad (\text{E14-2.2})$$

The mass transfer coefficient for single spheres is calculated from the Frössling correlation

$$\begin{aligned} \text{Sh} &= \frac{k_c d_p}{D_{AB}} = 2 + 0.6 \text{Re}^{1/2} \text{Sc}^{1/3} \\ \text{Re} &= \frac{\rho d_p U}{\mu} = \frac{d_p U}{\nu} = \frac{(0.01 \text{ m})(0.1 \text{ m/s})}{0.5 \times 10^{-6} \text{ m}^2/\text{s}} = 2000 \end{aligned} \quad (14-34)$$

Liquid Phase

$$Re = 2000$$

$$Sc = 5000$$

$$Sh = 460$$

$$k_c = 4.6 \times 10^{-6} \text{ m/s}$$

$$Sc = \frac{v}{D_{AB}} = \frac{5 \times 10^{-7} \text{ m}^2/\text{s}}{10^{-10} \text{ m}^2/\text{s}} = 5000$$

Substituting these values into Equation (14-34) gives us

$$Sh = 2 + 0.6 (2000)^{0.5} (5000)^{1/3} = 460.7 \quad (\text{E14-2.3})$$

$$k_c = \frac{D_{AB}}{d_p} Sh = \frac{10^{-10} \text{ m}^2/\text{s}}{0.01 \text{ m}} \times 460.7 = 4.61 \times 10^{-6} \text{ m/s} \quad (\text{E14-2.4})$$

$$C_{Ab} = 1.0 \text{ mol/dm}^3 = 10^3 \text{ mol/m}^3$$

Substituting for k_c and C_{Ab} in Equation (E14-2.2), the molar flux to the surface is

$$W_{Ar} = (4.61 \times 10^{-6} \text{ m/s}) (10^3 - 0) \text{ mol/m}^3 = 4.61 \times 10^{-3} \text{ mol/m}^2 \cdot \text{s}$$

Because $W_{Ar} = r''_{AS}$, this rate is also the rate of reaction per unit surface area of catalyst.

$$-r''_{AS} = 0.0046 \text{ mol/m}^2 \cdot \text{s} = 4.6 \times 10^{-5} \text{ mol/dm}^2 \cdot \text{s}$$

The mass transfer flow to the particle is

$$\begin{aligned} \dot{n}_A &= \pi d_p^2 (-r''_A) = \pi (0.01 \text{ m})^2 (0.0046 \text{ mol/m}^2 \cdot \text{s}) \\ \dot{n}_A &= 1.45 \times 10^{-6} \text{ mol/s} \end{aligned}$$

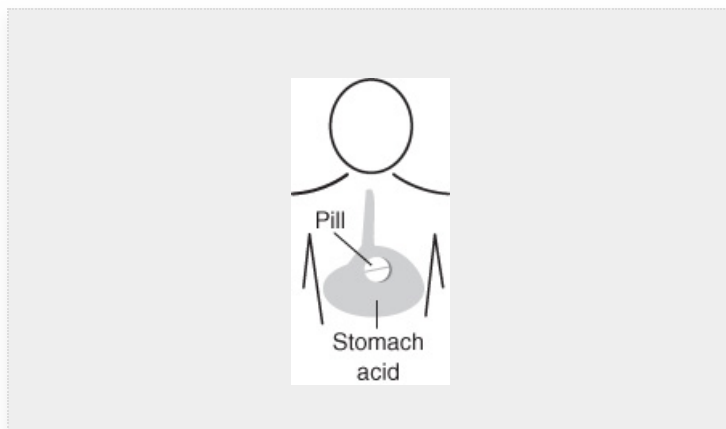
Analysis: In this example we calculated the rate of reaction on the external surface of a catalyst pellet in a

liquid reactant when external mass transfer was limiting the reaction rate. To determine the rate of reaction, we used correlations to calculate the mass transfer coefficient and then used k_c to calculate the flux to the surface, which in turn was equal to the rate of surface reaction.

14.6 THE SHRINKING CORE MODEL

14.6.1 Dust Explosions, Particle Dissolution, and Catalyst Regeneration

Many situations arise in heterogeneous reactions where a gas-phase species reacts with a species contained in an inert solid matrix or solid combustible dust particles. The burning of a combustible dust is shown in [Figure 14-6\(a\)](#). The removal of carbon from catalyst particles that have been deactivated by fouling is shown in [Figure 14-6\(b\)](#) (see [Section 10.7.1](#)). The catalyst regeneration process to reactivate the catalyst by burning off the carbon is discussed in the expanded material on the CRE Web site.



The shrinking core model is used to describe situations in which solid particles are being consumed either by dissolution or reaction and, as a result, the amount of the material being consumed is “shrinking.” For example, to design the time release of drugs into the body’s system, one must focus on the rate of dissolution of capsules and solid pills in the stomach.

We now apply the shrinking core model to dust explosions where solid organic particles such as sugar are burned, to the formation of an ash layer around a burning coal particle, to catalyst regeneration. In this section we focus primarily on dust explosions and catalyst regeneration, and leave other applications such as drug delivery as exercises at the end of the chapter.

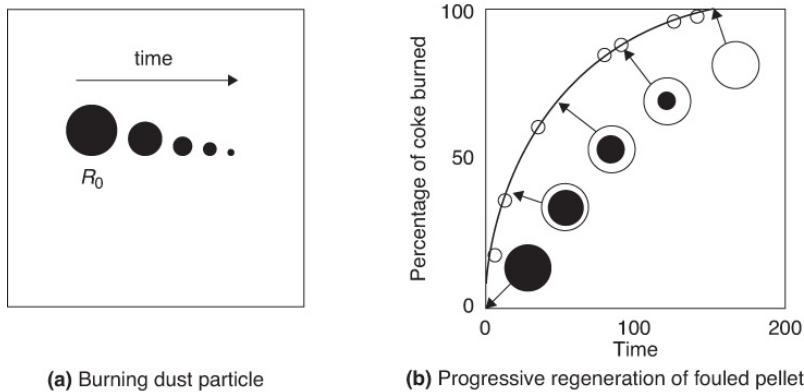
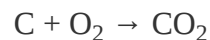


Figure 14-6 Shell progressive regeneration of fouled pellet.

To illustrate the principles of the shrinking core model, we shall consider the burning of carbon dust particle. As the carbon continues to burn the radius of dust particles shrink from R_0 initially to R at time t as shown in Figure 14-6(a).

As shown in Figure 14-7, oxygen diffuses from the bulk gas at R_∞ to the radius R , where it reacts with carbon to form carbon dioxide, which then diffuses out from the particle. The reaction



at the solid surface is very rapid, so the rate of oxygen diffusion to the surface controls the rate of carbon removal from the core. Although the core of

Oxygen must diffuse through the porous pellet matrix until it reaches the unreacted carbon core.

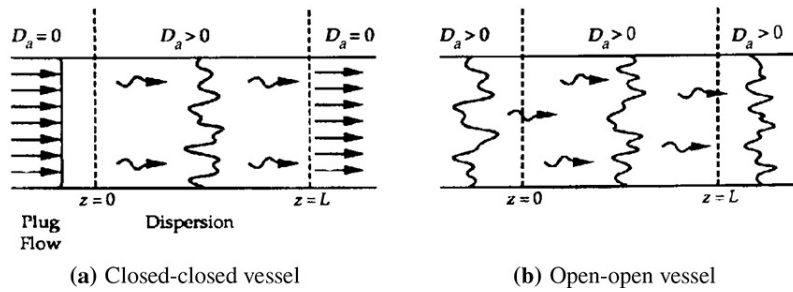


Figure 14-7 Sphere of radius R .

carbon is shrinking with time (an unsteady-state process), we assume the concentration profiles at any instant in time to be the steady-state profiles over the distance $(R_\infty - R)$ when R_∞ is some larger distance from the surface of the particle, for example, $R_\infty \approx \infty$. This assumption is known as the *quasi-steady state assumption* (QSSA).

QSSA Use steady-state profiles

To study how the radius of unreacted carbon changes with time, we must first find the rate of diffusion of oxygen to the carbon surface. Next, we perform a mole balance on the elemental carbon and equate the rate of consumption of the carbon particle to the rate of diffusion of oxygen to the gas-carbon interface.

In applying a differential oxygen mole balance over the increment Δr located somewhere between R_∞ and R , we recognize that O_2 does not react in this region and reacts only when it reaches the solid carbon interface located at $r = R$. We shall let species A represent O_2 .

Step 1: The mole balance on O_2 (i.e., A) between r and $r + \Delta r$ is

$$\left[\begin{array}{c} \text{Rate} \\ \text{in} \end{array} \right] - \left[\begin{array}{c} \text{Rate} \\ \text{out} \end{array} \right] + \left[\begin{array}{c} \text{Rate of} \\ \text{generation} \end{array} \right] = \left[\begin{array}{c} \text{Rate of} \\ \text{accumulation} \end{array} \right]$$

$$W_{Ar}4\pi r^2 \Big|_r - W_{Ar}4\pi r^2 \Big|_{r+\Delta r} + 0 = 0$$

Dividing through by $-4\pi\Delta r$ and taking the limit gives

Mole balance on oxygen

$$\lim_{\Delta r \rightarrow 0} \frac{W_{Ar}r^2|_{r+\Delta r} - W_{Ar}r^2|_r}{\Delta r} = \frac{d(W_{Ar}r^2)}{dr} = 0 \quad (14-47)$$

Step 2: The constitutive equation for constant total molar concentration becomes

$$W_{Ar} = -D_{AB} \frac{dC_A}{dr} \quad (14-48)$$



Combining Equations (14-17) and (14-48) and dividing by $(-D_{AB})$ gives

$$\boxed{\frac{d}{dr} \left(r^2 \frac{dC_A}{dr} \right) = 0} \quad (14-49)$$

Step 3: Boundary conditions for burning of a dust particle

At a large distance from the dust particle $r \sim \infty$ then

$C_A = C_{A\infty}$ At the dust particle's surface, $r = R$ then

$C_A = 0$

Step 4: Integrating twice yields

$$r^2 \frac{dC_A}{dr} = K_1$$

$$C_A = \frac{-K_1}{r} + K_2$$

Using the boundary conditions for a spherical dust particle to eliminate K_1 and K_2 , the concentration profiles is

$$C_A = C_{A\infty} \left(1 - \frac{R}{r}\right) \quad (14-50)$$

A schematic representation of the profile of O_2 is shown in Figure 14-8 at a time when the inner core has receded to a radius R . The zero on the r axis corresponds to the center of the sphere

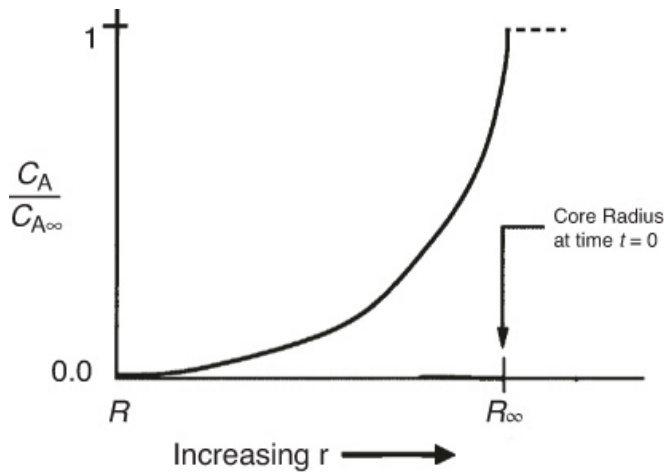


Figure 14-8 Oxygen concentration profile shown from the external radius of the pellet (R) to a large distance R_∞ from the center of the burning particle. The gas–carbon interface is located at R .

Step 5: The molar flux of O_2 to the gas–carbon interface for a dust particle is

$$W_{Ar} = -D_{AB} \frac{dC_A}{dr} = -\frac{D_{AB}C_{A\infty}}{R} \quad (14-51)$$

Step 6: We now carry out an overall balance on elemental carbon. Elemental carbon does not enter or leave the particle.

$$\begin{aligned} \left[\begin{array}{c} \text{Rate} \\ \text{in} \end{array} \right] - \left[\begin{array}{c} \text{Rate} \\ \text{out} \end{array} \right] + \left[\begin{array}{c} \text{Rate of} \\ \text{generation} \end{array} \right] &= \left[\begin{array}{c} \text{Rate of} \\ \text{accumulation} \end{array} \right] \\ 0 - 0 + r''_A \cdot 4\pi R^2 &= \frac{d\left(\frac{4}{3}\pi R^3 \rho_c \phi_c\right)}{dt} \end{aligned} \quad (14-52)$$

Where ρ_c is the molar density of the solid carbon, simplifying gives

$$\frac{dR}{dt} = \frac{r''_A}{\rho_c \phi_c} \quad (14-53)$$

In terms of particle diameter, d_p ,

$$\frac{dd_p}{dt} = \frac{2r''_A}{\rho_c \phi_c} \quad (14-54)$$

Step 7: The rate of disappearance of carbon is equal to the flux of O_2 to the gas–carbon interface:

A. Surface reaction limiting

$$-r''_A = k_r C_{A,S} \quad (14-55)$$

$$\frac{dd_p}{dt} = \frac{2r''_A}{\rho_c \phi_c} = \frac{2k_r C_{A,\infty}}{\rho_c \phi_c} \quad (14-56)$$

The initial conditions are

$$\left. \begin{array}{ll} t = 0 & d_p = d_{p0} \\ t = t & d_p = d_p \end{array} \right\} \quad (14-57)$$

$$\boxed{d_{p0}^2 - d_p^2 = \frac{2k_r}{\rho_c \phi_c} C_{A,S} t} \quad (14-58)$$

B. Diffusion Limiting

$$\begin{aligned} -r''_A &= W_A = k_c C_{A,\infty} \\ \frac{dd_p}{dt} &= \frac{2r''_A}{\rho_c \phi_c} = -2 \left(\frac{2D_{AB}}{d_p} \right) \frac{C_{A,\infty}}{\rho_c \phi_c} = -\frac{4D_{AB}C_{A,\infty}}{\rho_c \phi_c} \frac{1}{d_p} \end{aligned}$$

Again using the boundary conditions in Equation (14-57), we obtain

$$\boxed{d_{p0}^2 - d_p^2 = \frac{8D_{AB}C_{A,\infty}}{\rho_c \phi_c} t = K_S t} \quad (14-59)$$

$$K_S = \frac{8D_{AB}C_{A\infty}}{\rho_c\phi_c}$$

where K_S is the burning rate constant, s^{-1} .[†]

[†]R. A. Ogle *Dust Explosion Dynamics*, Amsterdam: Elsevier, 2017.

The time for complete combustion ($d_P = 0$) of a particle of diameter d_{p0} is

$$t_c = \frac{d_{p0}^2}{K_S} = \frac{d_{p0}^2 \rho_c \phi_c}{8D_{AB}C_{A\infty}} \quad (14-60)$$

Example 14–3 Combustion Time for a Single Particle

There is a 100 micron carbon dust particle in air at 1 atm. Calculate K_S and the time for the particle to burn completely ($d_p = 0$). The average value of the diffusivity near the burning particle is $10^{-4} \text{ m}^2/\text{s}$ and the density of the carbon particle is $2.26 \times 10^6 \text{ g/m}^3$.

Solution

The concentration of gas at 1 atm and 273 K is 0.046 mol/dm^3 . The corresponding concentration of O_2 at the outside the boundary layer correcting for the temperature at 298 K, that is, $C_{A\infty}$ is

$$C_{\text{O}_2} = 0.21 \quad C_t = (0.21) \left(0.0446 \frac{\text{mol}}{\text{dm}^3} \right) \frac{273}{298} \left(\frac{10 \text{ dm}}{\text{m}} \right)^3 = 8.58 \frac{\text{mol}}{\text{m}^3}$$

The molar density of the solid carbon particle is

$$\begin{aligned} \rho_c &= \frac{2.26 \times 10^6 \text{ g/m}^3}{12 \text{ g/mol}} = 188333 \frac{\text{mol}}{\text{m}^3} \\ \phi_c &= 1 \\ K_S &= \frac{8D_{AB}C_{A\infty}}{\rho_c} = \frac{8(10^{-4} \text{ m}^2/\text{s}) \left(\frac{8.58 \text{ mol}}{\text{m}^3} \right)}{0.1883 \cdot 10^6 \text{ mol/m}^3} = 365 \times 10^{-10} \text{ m}^2/\text{s} \end{aligned}$$

The units used by R. A. Ogle in his book *Dust Explosion Dynamic*, Elsevier 2017, are μm and ms , in which case K_S becomes

$$K_S = 365 \times 10^{-10} \text{ m}^2/\text{s} \left(\frac{10^6 \mu\text{m}}{1 \text{ m}} \right)^2 \left(\frac{1 \text{ s}}{10^3 \text{ ms}} \right) = 36.5 \mu\text{m}^2/\text{ms}$$

This value of K_S is about an order of magnitude smaller than a burning liquid droplet. Calculate, t_c , the time for the dust particle to completely burn

$$t_c = \frac{d_{p0}^2}{K_S} = \frac{(100 \mu\text{m})^2}{36.5 \mu\text{m}^2/\text{ms}} = 274 \text{ ms}$$



The time for a blink of an eye is approximately 400 ms.

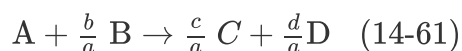
Analysis: This analysis shows how to calculate time to consume a 100 micron carbon particle. The time is quite short, leading to a dust explosion. Be sure to view the Chemical Safety Board (CSB) video on the CRE Web site (<http://www.csb.gov/imperial-sugar-company-dust-explosion-and-fire/>).

14C PACKED-BED APPLICATIONS

14.7 MASS TRANSFER-LIMITED REACTIONS IN PACKED BEDS

A number of industrial reactions are potentially mass transfer-limited because they may be carried out at high temperatures without the occurrence of undesirable side reactions. In mass transfer-dominated reactions, the surface reaction is so rapid that the rate of transfer of reactant from the bulk gas or liquid phase to the surface limits the overall rate of reaction.

Consequently, mass transfer-limited reactions respond quite differently to changes in temperature and flow conditions than do the rate-limited reactions discussed in previous chapters. In this section the basic equations describing the variation of conversion with the various **PBR** design parameters (catalyst weight, flow conditions) will be developed. To achieve this goal, we begin by carrying out a mole balance on the following generic mass transfer-limited reaction



carried out in a packed-bed reactor (Figure 14-9). A steady-state mole balance on reactant A in the reactor segment between z and $z + \Delta z$ is

$$\left[\begin{array}{c} \text{Molar} \\ \text{rate in} \end{array} \right] - \left[\begin{array}{c} \text{Molar} \\ \text{rate out} \end{array} \right] + \left[\begin{array}{c} \text{Molar rate of} \\ \text{generation} \end{array} \right] = \left[\begin{array}{c} \text{Molar rate of} \\ \text{accumulation} \end{array} \right] \quad (14-62)$$

$$F_{Az|z} - F_{Az|z+\Delta z} + r_A'' a_c (A_c \Delta z) = 0$$

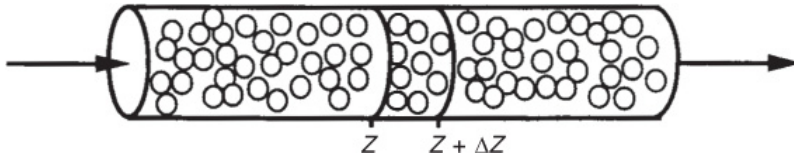


Figure 14-9 Packed-bed reactor.

where r_A'' = rate of generation of A per unit of catalytic surface area, $\text{mol/s} \cdot \text{m}^2$

a_c = external surface area of catalyst per volume of catalytic bed, m^2/m^3

$$A_c = \frac{\text{Volume of solid}}{\text{Volume of bed}} \times \frac{\text{Surface area}}{\text{Volume of solid}} = (1 - \phi) \left[\frac{\pi d_p^2}{\left(\pi d_p^3 / 6 \right)} \right]$$

$$= 6(1 - \phi)/d_p \text{ for packed beds, } \text{m}^2/\text{m}^3$$

ϕ = porosity of the bed (i.e., void fraction)⁶

⁶ In the nomenclature for Chapter 4, for the Ergun equation for pressure drop.

d_p = particle diameter, m

A_c = cross-sectional area of tube containing the catalyst, m^2

Dividing Equation (14-62) by $A_c \Delta z$ and taking the limit as $\Delta z \rightarrow 0$, we have

$$-\frac{1}{A_c} \left(\frac{dF_{Az}}{dz} \right) + r_A'' A_c = 0 \quad (14-63)$$

We now need to express F_{Az} and r_A'' in terms of concentration.

The molar flow rate of A in the axial direction is

$$F_{Az} = A_c W_{Az} = (J_{Az} + B_{Az}) A_c \quad (14-64)$$

Axial diffusion is neglected.

In almost all situations involving flow in packed-bed reactors, the amount of material transported by diffusion or dispersion in the axial direction is negligible compared with that transported by convection (i.e., bulk flow)

$$J_{Az} \ll B_{Az}$$

(In Chapter 18 we consider the case when dispersive effects (e.g., diffusion) must be taken into account.) Neglecting dispersion, Equation (14-14) becomes

$$F_{Az} = A_c W_{Az} = A_c B_{Az} = U C_A A_c \quad (14-65)$$

where U is the superficial molar average velocity through the bed (m/s). Substituting for F_{Az} in Equation (14-63) gives us

$$- \frac{d(C_A U)}{dz} + r_A'' a_c = 0 \quad (14-66)$$

For the case of constant superficial velocity U

Differential equation describing flow and reaction in a packed bed

$$\boxed{-U \frac{dC_A}{dz} + r_A'' a_c = 0} \quad (14-67)$$

For reactions at steady state, the molar flux of A to the particle surface, W_{Ar} (mol/m² · s) (see Figure 14-10), is equal to the rate of disappearance of A on the surface $-r_A''$ (mol/m² · s); that is

$$-r_A'' = W_{Ar} \quad (14-68)$$

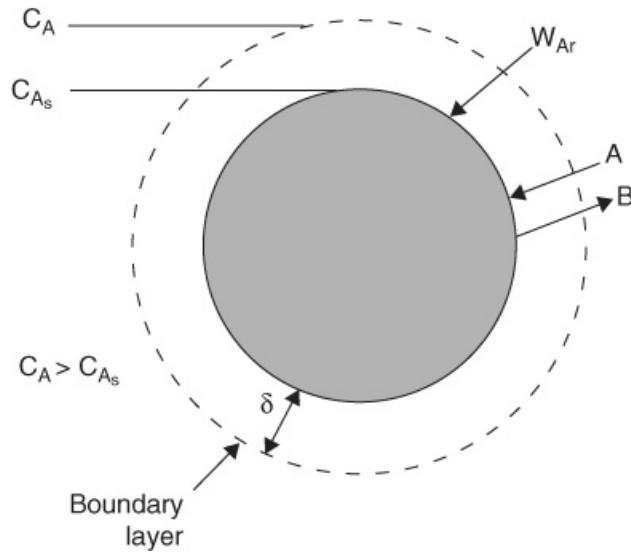
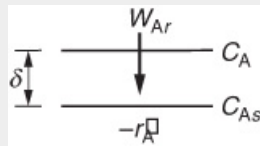


Figure 14-10 Diffusion across stagnant film surrounding catalyst pellet.



From [Section 14.4](#), the boundary condition at the external surface is

$$-r_A'' = W_{Ar} = k_c (C_A - C_{A_s}) \quad (14-69)$$

where k_c = mass transfer coefficient = (D_{AB}/δ) , (m/s)

C_A = bulk concentration of A (mol/m³)

C_{A_s} = concentration of A at the catalytic surface (mol/m³)

Substituting for $-r_A''$ in [Equation \(14-67\)](#), we have

$$-U \frac{dC_A}{dz} - k_c a_c (C_A - C_{A_s}) = 0 \quad (14-70)$$

In reactions that are completely mass transfer-limited, it is not necessary to know the rate law.

In most mass transfer-limited reactions, the surface concentration is negligible with respect to the bulk concentration (i.e., $C_A \gg C_{AS}$)

$$-U \frac{dC_A}{dz} = k_c a_c C_A \quad (14-71)$$

Integrating with the limit, at $z = 0$, $C_A = C_{A0}$

$$\frac{C_A}{C_{A0}} = \exp \left(-\frac{k_c a_c}{U} z \right) \quad (14-72)$$

The corresponding variation of reaction rate along the length of the reactor is

$$-r''_A = k_c C_{A0} \exp \left(-\frac{k_c a_c}{U} z \right) \quad (14-73)$$

The concentration and conversion profiles down a reactor of length L are shown in Figure 14-11.

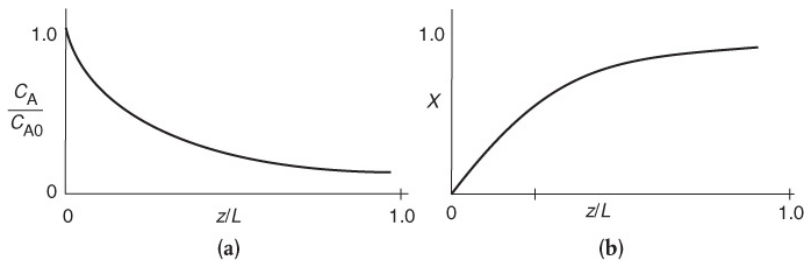


Figure 14-11 Axial concentration (a) and conversion (b) profiles in a packed bed.

To determine the reactor length L necessary to achieve a conversion X , we combine the definition of conversion

$$X = \frac{C_{A0} - C_{AL}}{C_{A0}} \quad (14-74)$$

Reactor concentration profile for a mass transfer-limited reaction

with the evaluation of Equation (14-72) at $z = L$ to obtain

$$\ln \frac{1}{1-X} = \frac{k_c a_c}{U} L \quad (14-75)$$

14.8 ROBERT THE WORRIER

Robert is an engineer who is always worried (which is a Jofostanian trait). He always thinks something bad will happen if we change an operating condition such as flow rate or temperature, or an equipment parameter such as particle size. Robert's motto is "If it ain't broke, don't fix it." We can help Robert be a little more adventuresome by analyzing how the important parameters vary as we change operating conditions in order to predict the outcome of such a change. We first look at Equation (14-75) and see that conversion depends on the parameters k_c , a_c , U , and L . We now examine how each of these parameters will change as we change operating conditions. We first consider the effects of temperature and flow rate on conversion.

To learn the effect of flow rate on conversion, we need to know how flow rate affects the mass transfer coefficient. That is, we must determine the correlation for the mass transfer coefficient for the particular geometry and flow field. For flow through a packed bed, the correlation given by Thoenes and Kramers for $0.25 < \phi < 0.5$, $40 < \text{Re}' < 4000$, and $1 < \text{Sc} < 4000$ is⁷

⁷ D. Thoenes, Jr. and H. Kramers, *Chem. Eng. Sci.*, 8, 271 (1958).



Thoenes–Kramers correlation for flow through packed beds

$$\text{Sh}' = 1.0 (\text{Re}')^{1/2} \text{Sc}^{1/3} \quad (14-76)$$

$$\left[\frac{k_c d_p}{D_{AB}} \left(\frac{\phi}{1-\phi} \right) \frac{1}{\gamma} \right] = \left[\frac{U d_p \rho}{\mu (1-\phi) \gamma} \right]^{1/2} \left(\frac{\mu}{\rho D_{AB}} \right)^{1/3} \quad (14-77)$$

where $\text{Re}' = \frac{\text{Re}}{(1-\phi)\gamma}$

$$\text{Sh}' = \frac{\text{Sh} \phi}{(1-\phi)\gamma}$$

d_p = particle diameter (equivalent diameter of a sphere of the same volume), m

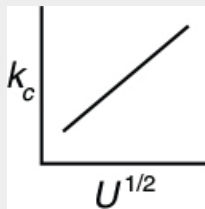
$$= [(6/\pi) (\text{volume of pellet})]^{1/3}, \text{ m}$$

ϕ = void fraction (porosity) of packed bed

γ = shape factor (external surface area divided by πd_p^2)

and

U , ρ , μ , ν , and D_{AB} are as previously defined.



For constant fluid properties and particle diameter

$$k_c \propto U^{1/2} \quad (14-78)$$

We see that the mass transfer coefficient increases with the square root of the superficial velocity through the bed.

Therefore, *for a fixed concentration, C_A* , such as that found in a differential reactor, the rate of reaction should vary with $U^{1/2}$

For diffusion-limited reactions, reaction rate depends on particle size and fluid velocity.

$$-r_A'' \propto k_c C_A \propto U^{1/2}$$

However, if the gas velocity is continually increased, a point is reached where the reaction becomes reaction rate–limited and, consequently, is independent of the superficial gas velocity, as shown in [Figure 14-5](#).

Many mass transfer correlations in the literature are often reported in terms of the Colburn J factor (i.e., J_D), which is a function of the Reynolds number. The relationship between J_D and the numbers we have been discussing is

$$J_D = \frac{Sh}{Sc^{1/3} Re} \quad (14-79)$$

[Figure 14-12](#) shows data from a number of investigations for the J factor as a function of the Reynolds number for a wide range of particle shapes and gas-flow conditions. *Note:* There are serious deviations from the Colburn analogy when the concentration gradient and temperature gradient are coupled, as shown by Venkatesan and Fogler.⁸

⁸ R. Venkatesan and H. S. Fogler, *AIChE J.*, 50, 1623 (July 2004).

Colburn J factor

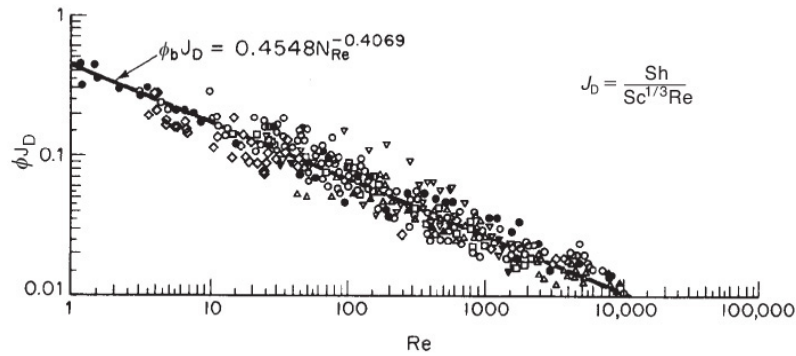


Figure 14-12 Mass transfer correlation for packed beds. $\phi_b \equiv \phi$ [Reprinted by permission. Copyright © 1977, American Chemical Society. Dwivedi, P. N. and S. N. Upadhyay, “Particle-Fluid Mass Transfer in Fixed and Fluidized Beds.” *Industrial & Engineering Chemistry Process Design and Development*, 1977, 16 (2), 157–165.]

A correlation for flow through packed beds in terms of the Colburn J factor

Dwivedi and Upadhyay review a number of mass transfer correlations for both fixed and fluidized beds and arrive at the following correlation, which is valid for both gases ($Re > 10$) and liquids ($Re > 0.01$) in either fixed or fluid-ized beds:⁹

⁹ P. N. Dwivedi and S. N. Upadhyay, *Ind. Eng. Chem. Process Des. Dev.*, 16, 157 (1977).

$$\phi J_D = \frac{0.765}{Re^{0.82}} + \frac{0.365}{Re^{0.386}} \quad (14-80)$$

For nonspherical particles, the equivalent diameter used in the Reynolds and Sherwood numbers is

$d_p = \sqrt{A_p/\pi} = 0.564 \sqrt{A_p}$, where A_p is the external surface area of the pellet.

To obtain correlations for mass transfer coefficients for a variety of systems and geometries, see either D. Kunii and O. Levenspiel, *Fluidization Engineering*, 2nd ed. Butterworth-Heinemann, 1991, Chap. 7, or W. L. McCabe, J. C. Smith, and

P. Harriott, *Unit Operations in Chemical Engineering*, 6th ed.
New York: McGraw-Hill, 2000. For other correlations for
packed beds with different packing arrangements, see I.
Colquhoun-Lee and J. Stepanek, *Chemical Engineer*, 108
(Feb. 1974).

Example 14–4 Mass Transfer Effects in Maneuvering a Space Satellite

Hydrazine has been studied extensively for use in monopropellant thrusters for space flights of long duration. Thrusters are used for altitude control of communication satellites. Here, the decomposition of hydrazine over a packed bed of alumina-supported iridium catalyst is of interest.¹⁰ In a proposed study, a 2% hydrazine in 98% helium mixture is to be passed over a packed bed of cylindrical particles 0.25 cm in diameter and 0.5 cm in length at a gas-phase velocity of 150 m/s and a temperature of 450 K. The kinematic viscosity of helium at this temperature is $4.94 \times 10^{-5} \text{ m}^2/\text{s}$. The hydrazine decomposition reaction is believed to be externally mass transfer-limited under these conditions. If the packed bed is 0.05 m in length, what conversion can be expected? Assume isothermal operation.

¹⁰ O. I. Smith and W. C. Solomon, *Ind. Eng. Chem. Fund.*, 21, 374.

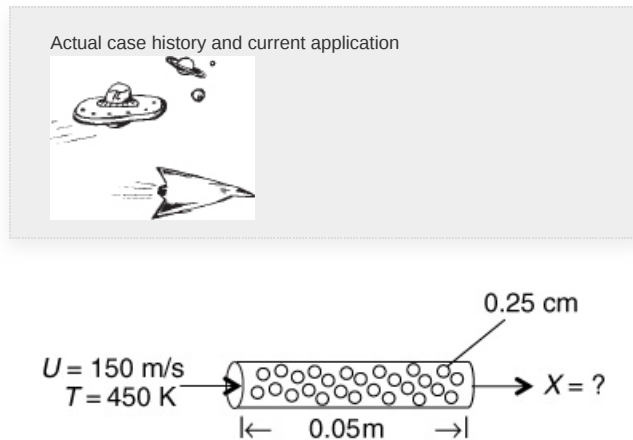


Figure E14-4.1 PBR.

Additional information:

$$D_{AB} = 0.69 \times 10^{-4} \text{ m}^2/\text{s} \text{ at } 298 \text{ K}$$

Bed porosity: 40%

Bed fluidicity: 95.7%

Solution

The following solution is detailed and a bit tedious, but it is important to know the details of how a mass transfer coefficient is calculated.

Rearranging Equation (14-64) gives us

$$X = 1 - e^{-(k_c a_c / U)L} \quad (\text{E14-4.1})$$

(a) Using the Thoenes–Kramers correlation to calculate the mass transfer coefficient, k_c

1. First we find the volume-average particle diameter

$$d_p = \left(\frac{6V}{\pi} \right)^{1/3} = \left(6 \frac{\pi D^2}{4} \frac{L}{\pi} \right)^{1/3} \quad (\text{E14-4.2})$$

2. Surface area per volume of bed

$$a_c = 6 \left(\frac{1-0.4}{d_p} \right) = 6 \left(\frac{1-0.4}{3.61 \times 10^{-3} \text{ m}} \right) = 998 \text{ m}^2/\text{m}^3 \quad (\text{E14-4.3})$$



Tedious reading and calculations, but we gotta know how to do the nitty-gritty.

3. Mass transfer coefficient

$$\text{Re} = \frac{d_p U}{\nu} = \frac{(3.61 \times 10^{-3} \text{ m})(150 \text{ m/s})}{4.94 \times 10^{-5} \text{ m}^2/\text{s}} = 10942$$

For cylindrical pellets

$$\gamma = \frac{2\pi r L_p + 2\pi r^2}{\pi d_p^2} = \frac{(2)(0.005/2)(0.005) + (2)(0.0025/2)^2}{(3.61 \times 10^{-3})^2} = 1.20 \quad (\text{E14-4.4})$$

$$\text{Re}' = \frac{\text{Re}}{(1-\phi)\gamma} = \frac{10942}{(0.6)(1.2)} = 15173$$

Correcting the diffusivity to 450 K using Table 14-3 gives us

$$D_{AB}(450 \text{ K}) = D_{AB}(298 \text{ K}) \times \left(\frac{450}{298}\right)^{1.75} = (0.69 \times 10^{-4} \text{ m}^2/\text{s}) (2.06) \quad (\text{E14-4.5})$$

$$D_{AB}(450 \text{ K}) = 1.42 \times 10^{-5} \text{ m}^2/\text{s}$$

$$\text{Sc} = \frac{v}{D_{AB}} = \frac{4.94 \times 10^{-5} \text{ m}^2/\text{s}}{1.42 \times 10^{-4} \text{ m}^2/\text{s}} = 0.35$$

Representative values

Gas Phase

$$\text{Re}' = 15173$$

$$\text{Sc} = 0.35$$

$$\text{Sh}' = 86.66$$

$$k_c = 6.15 \text{ m/s}$$

Substituting Re' and Sc into Equation (14-65) yields

$$\text{Sh}' = (15173.92)^{1/2} (0.35)^{1/3} = (123.18) (0.70) = 86.6 \quad (\text{E14-4.6})$$

$$k_c = \frac{D_{AB}(1-\phi)}{d_p \phi} \gamma(\text{Sh}') = \left(\frac{1.42 \times 10^{-4} \text{ m}^2/\text{s}}{3.61 \times 10^{-3} \text{ m}} \right) \left(\frac{1-0.4}{0.4} \right) \times (1.2) (86.66)$$

$$\boxed{k_c = 6.15 \text{ m/s}} \quad (\text{E14-4.7})$$

The conversion is

$$X = 1 - \exp \left[- \left(6.15 \text{ m/s} \right) \left(\frac{998 \text{ m}^2/\text{m}^3}{150 \text{ m/s}} \right) (0.05 \text{ m}) \right] \quad (\text{E14-4.8})$$

$$= 1 - 0.13 = 0.87$$

We find 87% conversion.

(b) Colburn J_D factor to calculate k_c . To find k_c , we first calculate the surface-area-average particle diameter.

For cylindrical pellets, the external surface area is

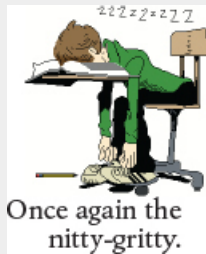
$$A = \pi d L_p + 2\pi \left(\frac{d^2}{4} \right) \quad (\text{E14-4.9})$$

$$d_p = \sqrt{\frac{A}{\pi}} = \sqrt{\frac{\pi d L_p + 2\pi(d^2/4)}{\pi}} \quad (\text{E14-4.10})$$

$$= \sqrt{(0.0025)(0.005) + \frac{(0.0025)^2}{2}} = 3.95 \times 10^{-3} \text{ m}$$

$$a_c = \frac{6(1-\varphi)}{d_p} = 910.74 \text{ m}^2/\text{m}^3$$

$$\begin{aligned} \text{Re} &= \frac{d_p U}{\nu} = \frac{(3.95 \times 10^{-3} \text{ m})(150 \text{ m/s})}{4.94 \times 10^{-5} \text{ m}^2/\text{s}} \\ &= 11996.04 \end{aligned}$$



Typical values

Gas Phase

$$\text{Re} = 11996$$

$$J_D = 0.025$$

$$\text{Sc} = 0.35$$

$$\text{Sh} = 212$$

$$k_c = 7.63 \text{ m/s}$$

$$\phi J_D = \frac{0.765}{\text{Re}^{0.82}} + \frac{0.365}{\text{Re}^{0.386}} \quad (14-79)$$

$$\begin{aligned} &= \frac{0.765}{(11996)^{0.82}} + \frac{0.365}{(11996)^{0.386}} = 3.5 \times 10^{-4} + 9.7 \times 10^{-3} \quad (\text{E14-4.11}) \\ &= 0.010 \end{aligned}$$

$$J_D = \frac{0.010}{0.4} = 0.025 \quad (\text{E14-4.12})$$

$$\text{Sh} = \text{Sc}^{1/3} \text{Re}(\text{J}_D) \quad (\text{E14-4.13})$$

$$= (0.35)^{1/3} (11996)(0.025) = 212$$

$$k_c = \frac{D_{AB}}{d_p} \text{Sh} = \frac{1.42 \times 10^{-4}}{3.95 \times 10^{-3}} (212) = 7.63 \text{ m/s}$$

$$\begin{aligned} \text{Then } X &= 1 - \exp \left[- (7.63 \text{ m/s}) \left(\frac{910 \text{ m}^2/\text{m}^3}{150 \text{ m/s}} \right) (0.05 \text{ m}) \right] \\ &\simeq 0.9 \end{aligned} \quad (\text{E14-4.14})$$

Fluidicity?? Red herring!

If there were such a thing as the **bed fluidicity**, given in the problem statement, it would be a useless piece of information. Make sure that you know what information you need to solve problems, and go after it. Do not let additional data confuse you or lead you astray with useless information or facts that represent someone else's bias, and which are probably not well founded.

14.9 WHAT IF . . . ? (PARAMETER SENSITIVITY)

As we have stressed many times, one of the most important skills of an engineer is to be able to predict the effects of changes of system variables on the operation of a process. The engineer needs to determine these effects quickly through approximate but reasonably close calculations, which are sometimes referred to as “back-of-the-envelope calculations.”¹¹ This type of calculation is used to answer such questions as “**What** will happen **if** I decrease the particle size?” “**What if** I triple the flow rate through the reactor?”

¹¹ Prof. J. D. Goddard, University of Michigan, 1963–1976. Professor Emeritus at the University of California, San Diego.

J. D. Goddard's



Back of the Envelope

To help answer these questions, we recall Equation (14-45) and our discussion on page 754. There, we showed the mass transfer coefficient for a packed bed was related to the product of two terms: Term 1 was dependent on the physical properties and Term 2 was dependent on the system properties. Rewriting Equation (14-45) as

$$k_c \propto \left(\frac{D_{AB}^{2/3}}{v^{1/6}} \right) \left(\frac{U^{1/2}}{d_p^{1/2}} \right) \quad (14-81)$$

one observes from this equation that the mass transfer coefficient increases as the particle size decreases. The use of sufficiently small particles offers another technique to escape from the mass transfer-limited regime into the reaction-rate-limited regime.

Find out how the mass transfer coefficient varies with changes in *physical properties* and *system properties*.

Example 14–5 The Case of Divide and Be Conquered

A mass transfer-limited reaction is being carried out in two reactors of equal volume and packing, connected in series as shown in Figure E14-5.1. Currently, 86.5% conversion is being achieved with this arrangement. It is suggested that the reactors be separated and the flow rate be divided equally among each of the two reactors (Figure E14-5.2) to decrease the pressure drop and hence the pumping requirements. In terms of achieving a higher conversion, Robert is wondering if this is a good idea.

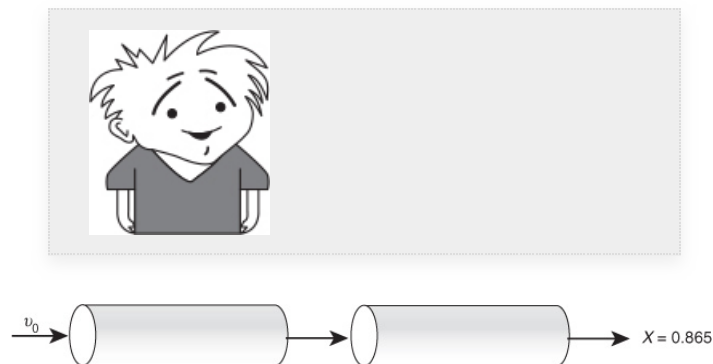


Figure E14-5.1 Series arrangement.

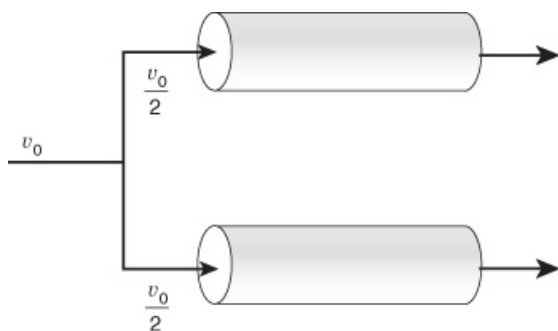


Figure E14-5.2 Parallel arrangement.

Reactors in series versus reactors in parallel

Solution

For the series arrangement we were given, $X_1 = 0.865$, and for the parallel arrangement, the conversion is unknown, that is, $X_2 = ?$ As a first approximation, we neglect the effects of small changes in temperature and pressure on mass transfer.

We recall Equation (14-75), which gives conversion as a function of reactor length. For a mass transfer-limited reaction

$$\ln \frac{1}{1-X} = \frac{k_c a_c}{U} L \quad (14-75)$$

For case 1, the undivided system

$$\begin{aligned} \left(\ln \frac{1}{1-X_1} \right) &= \frac{k_{c1} a_c}{U_1} L_1 \quad (\text{E14-51}) \\ X_1 &= 0.865 \quad \underline{\text{Answer 1}} \end{aligned}$$

For case 2, the divided system

$$\begin{aligned} \left(\ln \frac{1}{1-X_2} \right) &= \frac{k_{c2} a_c}{U_2} L_2 \quad (\text{E14-5.2}) \\ X_2 &=? \end{aligned}$$

We now take the ratio of case 2 (divided system) to case 1 (undivided system)

$$\frac{\ln \frac{1}{1-X_2}}{\ln \frac{1}{1-X_1}} = \frac{k_{c2}}{k_{c1}} \left(\frac{L_2}{L_1} \right) \frac{U_1}{U_2} \quad (\text{E14-5.3})$$

The surface area per unit volume a_c is the same for both systems.

From the conditions of the problem statement we know that

$$\begin{aligned} L_2 &= \frac{1}{2} L_1, U_2 = \frac{1}{2} U_1, \text{ and } X_1 = 0.865 \\ X_2 &= ? \end{aligned}$$

However, we must also consider the effect of the division on the mass transfer coefficient. From Equation (14-81) we know that

$$k_c \propto U^{1/2}$$

$$\frac{k_{c2}}{k_{c1}} = \left(\frac{U_2}{U_1} \right)^{1/2} \quad (\text{E14-5.4})$$

Multiplying by the ratio of superficial velocities yields

$$\frac{U_1}{U_2} \left(\frac{k_{c2}}{k_{c1}} \right) = \left(\frac{U_1}{U_2} \right)^{1/2} \quad (\text{E14-5.5})$$

$$\begin{aligned} \ln \frac{1}{1-X_2} &= \left(\ln \frac{1}{1-X_1} \right) \frac{L_2}{L_1} \left(\frac{U_1}{U_2} \right)^{1/2} \\ &= \left(\ln \frac{1}{1-0.865} \right) \left[\frac{\frac{1}{2} L_1}{L_1} \left(\frac{U_1}{\frac{1}{2} U_1} \right)^{1/2} \right] \quad (\text{E14-5.6}) \\ &= 2.00 \left(\frac{1}{2} \right) \sqrt{2} = 1.414 \end{aligned}$$

Solving for X_2 gives us

$$X_2 = 0.76 \quad \underline{\text{Answer 2}}$$

Analysis: Consequently, we see that although the divided arrangement will have the advantage of a smaller pressure drop across the bed, it is a bad idea in terms of conversion. Recall that the series arrangement gave $X_1 = 0.865$; therefore ($X_2 < X_1$). Bad idea!! But every chemical engineering student in Jofostan knew that! Recall that if the reaction were reaction rate-limited, both arrangements would give the same conversion.

Bad idea!! Robert was right to worry.

Example 14–6 The Case of the Overenthusiastic Engineers

The same reaction as that in [Example 14-5](#) is being carried out in the same two reactors in series. A new engineer suggests that the rate of reaction could be increased by a factor of 2^{10} by increasing the reaction temperature from 400°C to 500°C , reasoning that the reaction rate doubles for every 10°C increase in temperature. Another engineer arrives on the scene and berates the new engineer with quotations from [Chapter 3](#) concerning this rule of thumb. She points out that it is valid only for a specific activation energy within a specific temperature range. She then suggests that he go ahead with the proposed temperature increase but should only expect an increase on the order of 2^3 or 2^4 . What do you think? Who is correct?



Robert worries if this temperature increase will be worth the trouble.

Solution

Because almost all surface reaction rates increase more rapidly with temperature than do diffusion rates, increasing the temperature will only increase the degree to which the reaction is mass transfer-limited.

We now consider the following two cases:

$$\text{Case 1: } T = 400^{\circ}\text{C} \quad X = 0.865$$

$$\text{Case 2: } T = 500^{\circ}\text{C} \quad X = ?$$

Taking the ratio of case 2 to case 1 and noting that the reactor length is the same for both cases ($L_1 = L_2$), we obtain

$$\frac{\ln \frac{1}{1-X_2}}{\ln \frac{1}{1-X_1}} = \frac{k_{c2}}{k_{c1}} \left(\frac{L_2}{L_1} \right) \frac{U_1}{U_2} = \frac{k_{c2}}{k_{c1}} \left(\frac{U_1}{U_2} \right) \quad (\text{E14-6.1})$$

The molar feed rate F_{T0} remains unchanged

$$F_{T0} = v_{01} \left(\frac{P_{01}}{RT_{01}} \right) = v_{02} \left(\frac{P_{02}}{RT_{02}} \right) \quad (\text{E14-6.2})$$

the pressure remains constant so

$$\frac{v_{01}}{T_1} = \frac{v_{02}}{T_2}$$

Because $v = A_c U$, the superficial velocity at temperature T_2 is

$$U_2 = \frac{T_2}{T_1} U_1 \quad (\text{E14-6.3})$$

J. D. G.



We now wish to learn the dependence of the mass transfer coefficient on temperature

$$k_c \propto \left(\frac{U^{1/2}}{d_p^{1/2}} \right) \left(\frac{D_{AB}^{2/3}}{v^{1/6}} \right) \quad (\text{E14-6.4})$$

Taking the ratio of case 2 to case 1 and realizing that the particle diameter is the same for both cases gives us

$$\frac{k_{c2}}{k_{c1}} = \left(\frac{U_2}{U_1} \right)^{1/2} \left(\frac{D_{AB2}}{D_{AB1}} \right)^{2/3} \left(\frac{v_1}{v_2} \right)^{1/6} \quad (\text{E14-6.5})$$

The temperature dependence of the gas-phase diffusivity is (from Table 14-3)

$$D_{AB} \propto T^{1.75} \quad (\text{E14-6.6})$$

For most gases, viscosity increases with increasing temperature according to the relation

$$\mu \propto T^{1/2}$$

From the ideal gas law

$$\rho \propto T^{-1}$$

Then

$$v = \frac{\mu}{\rho} \propto T^{3/2} \quad (\text{E14-6.7})$$

$$\frac{\ln \frac{1}{1-X_2}}{\ln \frac{1}{1-X_1}} = \frac{U_1}{U_2} \left(\frac{k_{c2}}{k_{c1}} \right) = \left(\frac{U_1}{U_2} \right)^{1/2} \left(\frac{D_{AB2}}{D_{AB1}} \right)^{2/3} \left(\frac{v_1}{v_2} \right)^{1/6} \quad (\text{E14-6.8})$$

$$= \left(\frac{T_1}{T_2} \right)^{1/2} \left[\left(\frac{T_2}{T_1} \right)^{1.75} \right]^{2/3} \left[\left(\frac{T_1}{T_2} \right)^{3/2} \right]^{1/6}$$

$$\begin{aligned} \frac{U_1 k_{c2}}{U_2 k_{c1}} &= \left(\frac{T_1}{T_2} \right)^{1/2} \left(\frac{T_2}{T_1} \right)^{7/6} \left(\frac{T_1}{T_2} \right)^{1/4} = \left(\frac{T_2}{T_1} \right)^{5/12} \\ &= \left(\frac{773}{673} \right)^{5/12} = 1.059 \end{aligned} \quad (\text{E14-6.9})$$

It's really important to know how to do this type of analysis.

Rearranging Equation (E14-6.1) in the form

$$\begin{aligned} \ln \frac{1}{1-X_2} &= \frac{k_{c2} U_1}{k_{c1} U_2} \ln \frac{1}{1-X_1} \\ \ln \frac{1}{1-X_2} &= 1.059 \left(\ln \frac{1}{1-0.685} \right) = 1.059 (2) \quad (\text{E14-6.10}) \\ X_2 &= 0.88 \quad \underline{\text{Answer}} \end{aligned}$$

Analysis: Consequently, we see that increasing the temperature from 400°C to 500°C increases the conversion by only 1.7%, that is, $X = 0.865$ compared to $X = 0.88$. Bad idea! Bad, bad idea! Both engineers would have benefited from a more thorough study of this chapter.

Bad idea!! Robert was right to worry.

For a packed catalyst bed, the temperature-dependence part of the mass transfer coefficient for a gas-phase reaction can be written as

$$k_c \propto U^{1/2} \left(D_{AB}^{2/3} / \nu^{1/6} \right) \quad (14-82)$$

$$k_c \propto U^{1/2} T^{11/12} \quad (14-83)$$

Taking the ratio of U to U_0 and T to T_0 and $k_{c0}(T_0, U_0)$ the mass transfer coefficient at any other T and U can be found from the Equation

$$k_c = k_{c0} \left(\frac{U}{U_0} \right)^{1/2} \left(\frac{T}{T_0} \right)^{11/12} \quad (14-84)$$

One can use Equation (14-81) when studying mass transfer-limited gas-phase reaction.

Depending on how one fixes or changes the molar feed rate, F_{T0} , U may also depend on the feed temperature.

As an engineer, it is extremely important that you reason out the effects of changing conditions, as illustrated in the preceding two examples.



Important concept

Example 14–7 Flow, Diffusion, and Reaction in a Packed Bed

Let's revisit a packed-bed reactor shown in Figure E14-4.1 in Example 14-4. We want to put the algorithm in a form where one can use Wolfram or Python to vary all the physical parameters and operating variables in order to study a first-order gas-phase reaction in a PBR. The reaction will be carried out isothermally and pressure drop is neglected.

Study the conversion and reaction rate profile for a reaction that is partially diffusion limited by first plotting the conversion as a function of catalyst weight up to a value $W = 100$ kg. Next use Wolfram to vary all the parameters and describe what you find.

Solution

1. Mole Balance

$$\frac{dX}{dW} = -r'_A / F_{A0} \quad (\text{E14-7.1})$$

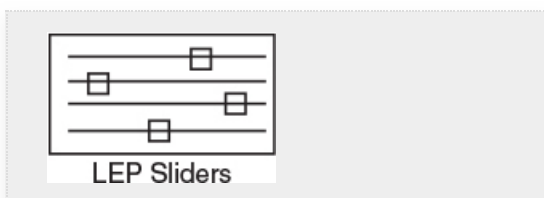
2. Rate Law

$$2A. \text{ First order, } -r''_A = k_r C_{As}$$

$$-r'_A = -r''_A * a'_c \quad (\text{E14-7.2})$$

At steady state the molar flux to the surface is equal to the rate of reaction on the surface

$$W_A = k_c (C_{A0} - C_{As}) = k_r C_{As} = -r''_A = \frac{k_c k_r}{k_r + k_c} C_A = k C_A \quad (\text{E14-7.3})$$



where

k_r = reaction-rate constant on the surface (m/s)

k_c = mass transfer coefficient (m/s)

$k = \frac{k_c k_r}{k_r + k_c}$ (m/s) overall transfer coefficient

a'_c = external surface area of the catalyst per unit mass of catalyst ($\text{m}^2/\text{kg-cat}$)

2B. Using the Thoenes and Kramer's correlation, Equations (14-76) and (14-77)

$$\text{Sh}' = 1.0(\text{Re}')^{1/2} \text{Sc}^{1/3} \quad (14-76)$$

$$\left[\frac{k_c d_p}{D_{AB}} \left(\frac{\phi}{1-\phi} \right) \frac{1}{\gamma} \right] = \left[\frac{U d_p \rho}{\mu (1-\phi) \gamma} \right] \left(\frac{\mu}{\rho D_{AB}} \right)^{1/3} \quad (14-77)$$

Correlation for k_c is

$$k_c = \frac{\text{Sh}' D_{AB}}{d_p} \frac{(1-\phi)\gamma}{\phi} \quad (\text{E14-7.4})$$

$$\text{Sh}' = 1.0 (\text{Re}')^{1/2} \text{Sc}^{1/3} \quad (\text{E14-7.5})$$

$$\text{Re}' = \frac{\text{Re}}{(1-\phi)\gamma} \quad (\text{E14-7.6})$$

$$\text{Re} = \frac{d_p U}{\nu} \quad (\text{E14-7.7})$$

$$\text{Sc} = \frac{\nu}{D_{AB}} \quad (\text{E14-7.8})$$

$$\nu = \frac{\mu}{\rho} \quad (\text{E14-7.9})$$

$$a'_c = 6 \frac{(1-\phi)}{d_p^* \rho_c} \quad (\text{E14-7.10})$$

3. Stoichiometry with $P = P_0$ and $T = T_0$

$$C_A = C_{A0} (1 - X) \quad (\text{E14-7.11})$$

4. Combine Polymath

We will now combine Equations (E14-7.1) through (E14-7.11) into Polymath, Wolfram, or Python to vary the parameters. The Polymath program is shown in Table E14-7.2 and the Wolfram solution in Figure E14-7.1.

5. Evaluate

The nominal values of the parameter to be varied are shown in Table E14-7.1.

TABLE E14-7.1 NOMINAL PARAMETER VALUES

<i>Parameters</i>	<i>Liquids</i>	<i>Gases</i>
ν	$10^{-6} \text{ m}^2/\text{s}$	$10^{-5} \text{ m}^2/\text{s}$
ρ	1000 kg/m^3	1 kg/m^3
D_{AB}	$10^{-8} \text{ m}^2/\text{s}$	$10^{-5} \text{ m}^2/\text{s}$
μ	10^{-3} kg/m/s	10^{-5} kg/m/s
U	1 m/s	100 m/s
d_p	10^{-3} m	10^{-2} m
k_r	0.5 m/s	5 m/s
A_c	$5 \cdot 10^{-2} \text{ m}^2$	$5 \cdot 10^{-2} \text{ m}^2$
γ	1	1
ϕ	0.4	0.4
ρ_c	3000 kg/m^3	3000 kg/m^3
C_{A0}	1 mol/m^3	$0.01 \text{ mol/m}^3 \text{ (Ca 1 atm)}$

Plot the conversion as a function of catalyst weight.

TABLE E14-7.2 POLYMATH PROGRAM FOR MASS
TRANSFER-LIMITED LIQUID-PHASE REACTION IN A PBR

Differential equations

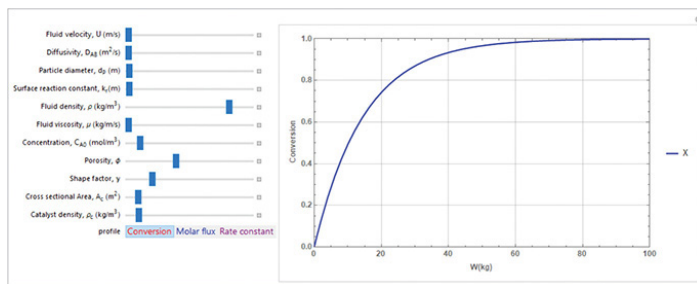
$$1 \quad d(X)/d(W) = -raprime/Fa0$$

Explicit equations

$$\begin{aligned} 1 \quad Ca0 &= 1 \\ 2 \quad \rho_0 &= 1000 \\ 3 \quad \rho_{oc} &= 3000 \\ 4 \quad dp &= 10^{-3} \\ 5 \quad DAB &= 10^{-8} \\ 6 \quad \mu &= 10^{-3} \\ 7 \quad \nu &= \mu/\rho_0 \\ 8 \quad \phi &= 0.4 \\ 9 \quad y &= 1 \\ 10 \quad Sc &= \nu/DAB \\ 11 \quad U &= 1 \\ 12 \quad Ca &= Ca0 \cdot (1-X) \\ 13 \quad kr &= 0.5 \\ 14 \quad Re &= dp \cdot U / \nu \\ 15 \quad Reprime &= Re / ((1-\phi) \cdot y) \\ 16 \quad Shprime &= (Reprime^{1/2}) \cdot (Sc^{1/3}) \\ 17 \quad kc &= Shprime \cdot DAB \cdot (1-\phi) \cdot y / (dp \cdot \phi) \\ 18 \quad k &= kc \cdot kr / (kc + kr) \\ 19 \quad ra &= -k \cdot Ca \\ 20 \quad Ac &= 5 \cdot 10^{-2} \\ 21 \quad Fa0 &= Ca0 \cdot U \cdot Ac \\ 22 \quad WA &= -ra \\ 23 \quad acprime &= 6 \cdot (1-\phi) / (dp \cdot \rho_{oc}) \\ 24 \quad raprime &= acprime \cdot ra \end{aligned}$$

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	Ac	0.05	0.05
2	acprime	1.2	1.2
3	Ca	1.	0.0011327
4	Ca0	1.	1.
5	DAB	1.0E-08	1.0E-08
6	dp	0.001	0.001
7	Fa0	0.05	0.05
8	k	0.0028263	0.0028263
9	kc	0.0028424	0.0028424
10	kr	0.5	0.5
11	mu	0.001	0.001
12	nu	1.0E-06	1.0E-06
13	phi	0.4	0.4
14	ra	-0.0028263	-3.201E-06
15	raprime	-0.0033916	-3.842E-06
16	Re	1000.	1000.
17	Reprime	1666.667	1666.667
18	rho	1000.	1000.
19	rho_c	3000.	3000.
20	Sc	100.	100.
21	Shprime	189.4921	189.4921
22	U	1.	1.
23	W	0	100.
24	WA	0.0028263	3.201E-06
25	X	0	0.9988673
26	y	1.	1.

**Figure E14-7.1** Wolfram solution.

Analysis: In this example we modeled a partially diffusion limited reaction in a PBR. The rest of the example is now up to you, the reader. Go to the LEP 14-7 and vary a number of physical parameters and operating variables, and write a set of observations and conclusions.

14.10 AND NOW... A WORD FROM OUR SPONSOR—SAFETY 14 (AWFOS–S14 SUGAR DUST EXPLOSION)

Dust Explosion at Imperial Sugar Company

According to the Chemical Safety Board, the yearly average number of dust explosions has been 5 per year over the last 5

years. In Examples 14-1 and 14-3, we discussed and calculated the rate of mass transfer of oxygen to small carbon dust particles allowing the particle to burn and possibly causing a dust explosion. Dust explosions can produce deadly consequences. On February 7, 2008, combustible fine sugar was ignited at the Imperial Sugar Company causing an explosion. Because the fine granulated sugar has high surface area, it has the potential to rapidly burn and explode. Prior to the explosion the dust collection system was not working properly; as a result fine sugar that had spilled over on the floor and collected on the ceiling and piping became airborne. When the belt transport system was enclosed, the airborne sugar dust found an ignition source and ignited. The explosion was fueled by the large accumulation of airborne sugar dust throughout the packaging plant. The fire and explosion caused 14 deaths and 38 injuries, including life-threatening burns.



© US Chemical Safety Board

Watch the Video:

(<https://www.csb.gov/imperial-sugar-company-dust-explosion-and-fire/>)

As chemical reaction engineers, it is important that we understand this accident, why it happened, and how it could have been prevented to ensure similar accidents may be prevented. In order to become familiar with a strategy for accident awareness and prevention, view the Chemical Safety Board video on the explosion and determine whether all the important concepts to prevent and mitigate the incident were captured in the BowTie diagram below.

Two other excellent videos on dust explosions are (<https://www.chemengonline.com/combustible-dust-fires-explosions-recent-data-lessons-learned/>) and (<https://www.aiche.org/academy/webinars/dust-explosion>). The BowTie diagram for the sugar dust plan explosion is shown in Figure 14-13.

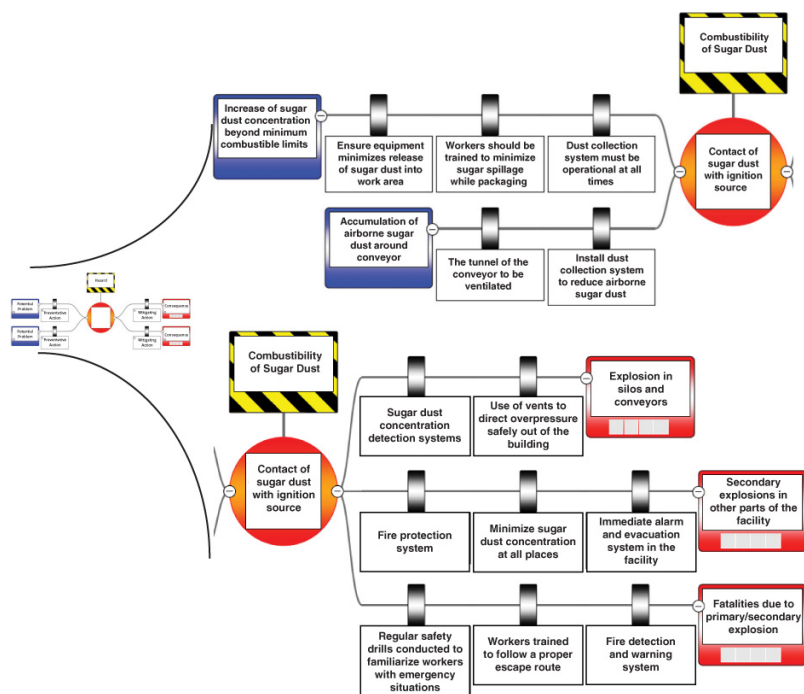


Figure 14-13 BowTie diagram for dust explosion.

Closure. After completing this chapter, the reader should be able to define and describe molecular diffusion and how it varies with temperature and pressure, the molar flux, bulk flow, the mass transfer coefficient, the Sherwood and Schmidt numbers, and the correlations for the mass transfer coefficient. The reader should be able to choose the appropriate correlation and calculate the mass transfer coefficient, the molar flux, and the rate of reaction. The reader

should also be able to describe the regimes and conditions under which mass transfer-limited reactions occur and when reaction-rate-limited reactions occur, and to make calculations of the rates of reaction and mass transfer for each case. One of the most important areas for the reader to apply the knowledge of this (and other chapters) is in his or her ability to ask and answer "What if . . ." questions.

SUMMARY

1. The molar flux of A in a binary mixture of A and B is

$$W_A = -D_{AB} \nabla C_A + y_A (W_A + W_B) \quad (\text{S14-1})$$

1. For equimolar counterdiffusion (EMCD) **or** for dilute concentration of the solute

$$W_A = J_A = -D_{AB} \nabla C_A \quad (\text{S14-2})$$

2. For diffusion through a stagnant gas

$$W_A = cD_{AB} \nabla \ln(1 - y_A) \quad (\text{S14-3})$$

3. For negligible diffusion

$$W_A = y_A W = y_A (W_A + W_B) = C_A U \quad (\text{S14-4})$$

2. The rate of mass transfer from the bulk fluid to a boundary at concentration C_{As} is

$$W_A = k_c (C_{Ab} - C_{As}) \quad (\text{S14-5})$$

where k_c is the mass transfer coefficient.

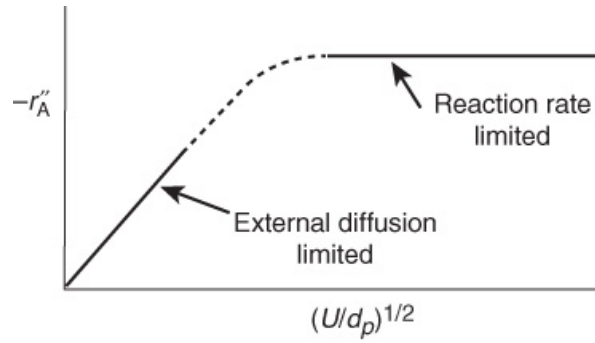
3. The Sherwood and Schmidt numbers are, respectively,

$$\text{Sh} = \frac{k_c d_p}{D_{AB}}$$

$$\text{Sc} = \frac{\nu}{D_{AB}}$$

Representative Values		(S14-6)
Liquid Phase	Gas Phase	
Re ~ 5000	Re ~ 500	(S14-7)
Sc ~ 4000	Sc ~ 1	
Sh ~ 500	Sh ~ 10	
$k_c = 10^{-2}$ m/s	$k_c = 5$ m/s	

4. If a heat transfer correlation exists for a given system and geometry, the mass transfer correlation may be found by replacing the Nusselt number by the Sherwood number and the Prandtl number by the Schmidt number in the existing heat transfer correlation.
5. Increasing the gas-phase velocity and decreasing the particle size will increase the overall rate of reaction for reactions that are externally mass transfer-limited.



6. The conversion for externally mass transfer-limited reactions can be found from the equation

$$\ln \frac{1}{1-X} = \frac{k_c a_c}{U} L \quad (\text{S14-8})$$

7. Back-of-the-envelope calculations should be carried out to determine the magnitude and direction that changes in process variables will have on conversion. **What if . . . ?**

CRE WEB SITE MATERIALS

(<http://www.umich.edu/~elements/6e/14chap/obj.html#/>)

Useful Links

Living
Example
Problems

Extra Help

Additional
Materials

Professional
Reference
Shelf

Computer
Simulation
Problem
Statements

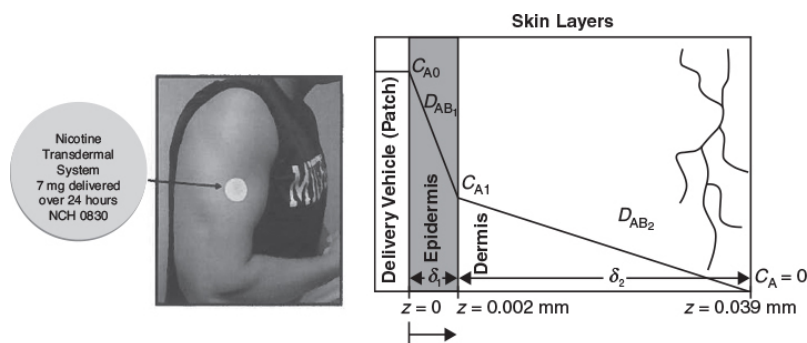
Evaluation

Self Tests

i>Clicker
Questions

• Additional Material on the Web site

Transdermal Drug Delivery Example



Transdermal drug delivery schematic.

QUESTIONS, SIMULATIONS, AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$A = \bullet \quad B = \blacksquare \quad C = \blacklozenge \quad D = \blacklozenge\blacklozenge$$

Questions

Q14-1_A QBR (*Question Before Reading*). Under what circumstances will the conversion predicted by mass transfer limitations be greater than that for surface reaction limitations?

Q14-2 Read over the problems at the end of this chapter. Make up an original problem that uses the concepts presented in this chapter. See Problem P5-1_A for the guidelines. To obtain a solution:



1. Make up your data and reaction.
2. Use a real reaction and real data.

The journals listed at the end of Chapter 1 may be useful for part (b).

Q14-3 (*Sergeant Ambercromby*). Capt. Apollo is piloting a shuttlecraft on his way to space station Klingon. Just as he is about to maneuver to dock his craft using the hydrazine system discussed in Example 14-2, the shuttle craft's thrusters do not respond properly and it crashes into the station, killing Capt. Apollo (*Star Wars* 7 (fall 2015)). An investigation reveals that Lt. Darkside prepared the packed beds used to maneuver the shuttle and Lt. Data prepared the hydrazine–helium

gas mixture. Foul play is suspected and Sgt. Ambercromby arrives on the scene to investigate.

1. What are the first three questions he asks?
2. Make a list of possible explanations for the crash, supporting each one by an equation or reason.

Q14-4 How would your answers change if the temperature was increased by 50°C, the particle diameter was doubled, and fluid velocity was cut in half? Assume properties of water can be used for this system.

Q14-5 How would your answers change in Example 14-3 if you had a 50–50 mixture of hydrazine and helium? If you increase d_p by a factor of 5?

Q14-6A After viewing the video, what was new to you with regard to dust explosions? Could you list three things one should do or have in place to prevent dust explosions?

Q14-7 Go to the LearnChemE screencast link for Chapter 14 (<http://www.learncheme.com/screencasts/kinetics-reactor-design>). View one or more of the screencast 5- to 6-minute videos and write a two-sentence evaluation of what you learned.

Q14-8 AWFOS–S14 View the CSB video to list two things in which dust explosions are different from those involving flammable liquids.

Computer Simulations and Experiments

P14-1B

1. **Example 14-1: Mass Transfer of Oxygen to a Burning Carbon Particle**

Wolfram and Python

1. Vary each slider to find the parameter to which the flux W_{Ar} is most sensitive.
2. What happens when the liquid diffusivity and viscosity are both increased simultaneously?
3. Vary the velocity as shown in Figure 14-5 and describe its effect on the flux.
4. Write a set of conclusions based on the above experiments.

2. Example 14-2: Rapid Liquid-Phase Reaction on the Surface of a Catalyst Wolfram and Python

1. Vary each of the parameters and tell which one the mass transfer coefficient (k_c) is most sensitive.
2. Change D_{AB} and U simultaneously both up and down and describe what you find.
3. Write a set of three conclusions from your experiments (i) and (ii).

3. Example 14-3: Combustion Time for a Single Particle Wolfram and Python

1. Compare the burning time for a 100 μm porous carbon particle with a 10% solid with t_c in [Example 14-3](#).
2. Vary all the parameters you can think of that would give a burning time of 500 ms.
3. Write a set of conclusions from your Wolfram experiments (i) and (ii).

4. Example 14-4: Mass Transfer Effects in Maneuvering a Space Satellite. *What if* you were asked for representative values for Re , Sc , Sh , and k_c for both liquid- and gas-phase systems for a velocity of 10 cm/s and a pipe diameter of 5 cm (or a packed-bed diameter of 0.2 cm)? What numbers would you give?

5. Example 14-5: The Case of Divide and Be Conquered. How would your answers change if the reaction were carried out in the liquid phase where kinematic viscosity, ν , varied as

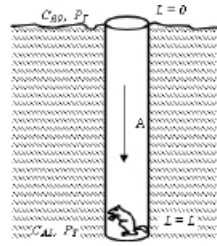
$$\nu(T_2) = \nu(T_1) \exp \left[-400 \text{ K} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right] ?$$

6. Example 14-7: Flow, Diffusion, and Reaction in a Packed Bed Wolfram and Python

1. Vary k_r and U and view X , W_A , and k as a function of W .
2. Vary D_{AB} and d_p and view k as a function of W .
3. Vary the ration (D_{AB}/ν) and describe what you find.
4. Vary the parameters by a factor of 10 above and below their nominal values and describe what you find (e.g., what were the most sensitive and least sensitive parameters? *Hint:* See Equation (14-81).
5. Write a set of conclusions based on all your experiments.

Problems





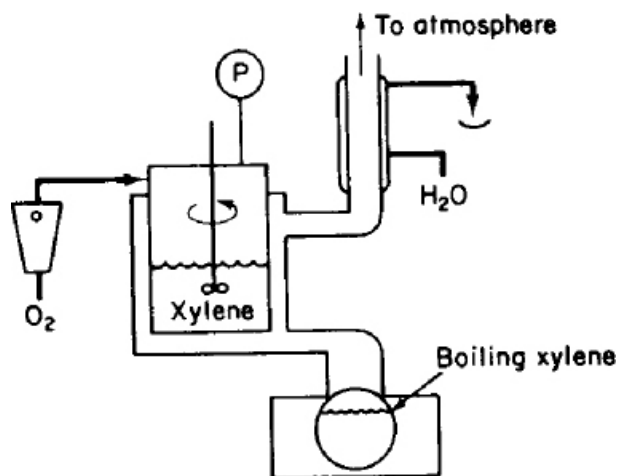
P14-2_B Assume the minimum respiration rate of a chipmunk is 1.5 micromoles of O_2 /min. The corresponding volumetric rate of gas intake is $0.05 \text{ dm}^3/\text{min}$ at STP.

1. What is the deepest a chipmunk can burrow a 3-cm diameter hole beneath the surface in Ann Arbor, Michigan? $D_{AB} = 1.8 \times 10^{-5} \text{ m}^2/\text{s}$
2. In Boulder, Colorado?
3. How would your answers to (a) and (b) change in the dead of winter when $T = 0^\circ\text{F}$?
4. Critique and extend this problem (e.g., CO_2 poisoning). Thanks to Professor Robert Kabel at Pennsylvania State University.

Hint: Review derivations and equations for W_A and W_B to see how they can be applied to this problem.

P14-3_B Pure oxygen is being absorbed by xylene in a catalyzed reaction in the experimental apparatus sketched in Figure P14-3_B. Under constant conditions of temperature and liquid composition, the following data were obtained:



Figure P14-3_B

Rate of Uptake of O ₂ (mL/h) for System Pressure (absolute)				
Stirrer Speed (rpm)	1.2 atm	1.6 atm	2.0 atm	3.0 atm
400	15	31	75	152
800	20	59	102	205
1200	21	62	105	208
1600	21	61	106	207

No gaseous products were formed by the chemical reaction. What would you conclude about the relative importance of liquid-phase diffusion and about the order of the kinetics of this reaction? (**California Professional Engineers Exam**)

P14-4_B Derive an equation for the time necessary to completely burn a 100 μm carbon particle as a function of D_0 . Also calculate the burning rate constant. Use the K_S values of the parameter values, for example, $C_{A\infty}$, given in Example 14-3.

1. diffusion controlled with $D_{AB} = 10^{-4} \text{ m}^2/\text{s}$
2. reaction controlled with $k_r = 0.01 \text{ m/s}$
3. combined reaction and diffusion controlled

Additional Information:

$$\rho_c = 188 \text{ mol/m}^3$$

P14-5C In a diving-chamber experiment, a human subject breathed a mixture of O_2 and He while small areas of his skin were exposed to nitrogen gas. After some time, the exposed areas became blotchy, with small blisters forming on the skin. Model the skin as consisting of two adjacent layers, one of thickness δ_1 and the other of thickness δ_2 . If counterdiffusion of He out through the skin occurs at the same time as N_2 diffuses into the skin, at what point in the skin layers is the sum of the partial pressures a maximum? If the saturation partial pressure for the sum of the gases is 101 kPa, can the blisters be a result of the sum of the gas partial pressures exceeding the saturation partial pressure and the gas coming out of the solution (i.e., the skin)?



Before answering any of these questions, derive the concentration profiles for N_2 and He in the skin layers.

Diffusivity of He and N_2 in the inner skin layer = $5 \times 10^{-7} \text{ cm}^2/\text{s}$ and $1.5 \times 10^{-7} \text{ cm}^2/\text{s}$, respectively.

Diffusivity of He and N_2 in the outer skin layer = $10^{-5} \text{ cm}^2/\text{s}$ and $3.3 \times 10^{-4} \text{ cm}^2/\text{s}$, respectively.

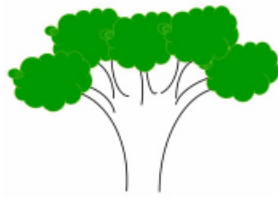
*External Skin
Boundary Partial
Pressure*

*Internal Skin
Boundary Partial
Pressure*

N_2	101 kPa	0
He	0	81 kPa
δ_1	20 μm	Stratum corneum
δ_2	80 μm	Epidermis

Hint: See Transdermal Drug Delivery in Expanded Material on the CRE Web site.

P14-6_B The decomposition of cyclohexane to benzene and hydrogen is mass transfer-limited at high temperatures. The reaction is carried out in a 5-cm-ID pipe 20 m in length packed with cylindrical pellets 0.5 cm in diameter and 0.5 cm in length. The pellets are coated with the catalyst only on the outside. The bed porosity is 40%. The entering volumetric flow rate is 60 dm^3/min .



Green engineering

1. Calculate the number of pipes necessary to achieve 99.9% conversion of cyclohexane from an entering gas stream of 5% cyclohexane and 95% H_2 at 2 atm and 500°C.
2. Plot conversion as a function of pipe length.
3. How much would your answer change if the pellet diameter and length were each cut in half?
4. How would your answer to part (a) change if the feed were pure cyclohexane?
5. What do you believe is the point of this problem? Is the focus really *green* CRE? How so?

P14-7_C Lead titanate, $PbTiO_3$, is a material having remarkable ferroelectric, pyroelectric, and piezoelectric properties [*J. Elec. Chem. Soc.*, 135, 3137 (1988)]. A thin film of

PbTiO₃ was deposited in a CVD reactor. The deposition rate is given below as a function of a temperature and flow rate over the film.

Flow Rate (SCCM)		Temperature (°C)	Deposition Rate (mg/cm ² · h)
500	650	0.2	
	750	0.8	
	800	1.2	
600	650	0.35	
	750	1.0	
	800	1.5	
750	650	0.53	
	750	1.45	
	800	2.0	
1000	650	0.55	
	750	1.5	
	800	2.0	

What are all the things, qualitative and quantitative, that you can learn from these data?

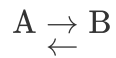
P14-8_B OEQ (Old Exam Question). A plant is removing a trace of Cl₂ from a waste-gas stream by passing it over a solid granulum absorbent in a tubular packed bed (Figure P14-8_B). At present, 63.2% removal is being accomplished, but it is believed that greater removal could be achieved if the flow rate were increased by a

factor of 4, the particle diameter were decreased by a factor of 3, and the packed tube length increased by 50%. What percentage of chlorine would be removed under the proposed scheme? (The chlorine transferring to the absorbent is removed completely by a virtually instantaneous chemical reaction.) (**Ans: 98%**)



Figure P14-8B

P14-9B OEQ (Old Exam Question). In a certain chemical plant, a reversible fluid-phase isomerization



is carried out over a solid catalyst in a tubular packed-bed reactor. If the reaction is so rapid that mass transfer between the catalyst surface and the bulk fluid is rate-limiting, show that the kinetics are described in terms of the bulk concentrations C_A and C_B by

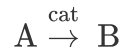
$$-r''_A = \frac{k_B[C_A - (1/K)C_B]}{1/K + k_B/k_A}$$

where $-r'_A$ = moles of A reacting per unit area catalyst per

k_A, k_B = transfer coefficients for A and B

K = equilibrium constant

It is desired to double the capacity of the existing plant by processing twice the feed of reactant A while maintaining the same fractional conversion of A to B in the reactor. How much larger a reactor, in terms of catalyst weight, would be required if all other operating variables are held constant? You may use the Thoenes–Kramers correlation for mass transfer coefficients in a packed bed.

P14-10_B The irreversible gas-phase reaction

is carried out adiabatically over a packed bed of solid catalyst particles. The reaction is first order in the concentration of A on the catalyst surface

$$-r'_{As} = k' C_{As}$$

The feed consists of 50% (mole) A and 50% inerts, and enters the bed at a temperature of 300 K. The entering volumetric flow rate is 10 dm³/s (i.e., 10000 cm³/s). The relationship between the Sherwood number and the Reynolds number is

$$\text{Sh} = 100 \text{Re}^{1/2}$$

As a first approximation, one may neglect pressure drop. The entering concentration of A is 1.0 M. Calculate the catalyst weight necessary to achieve 60% conversion of A for

1. isothermal operation.
2. adiabatic operation.

Additional information:

Kinematic viscosity: $\mu/\rho = 0.02 \text{ cm}^2/\text{s}$

Particle diameter: $d_p = 0.1 \text{ cm}$

Superficial velocity: $U = 10 \text{ cm/s}$

Catalyst surface area/mass of catalyst bed: $a = 60 \text{ cm}^2/\text{g-cat}$

Diffusivity of A: $D_e = 10^{-2} \text{ cm}^2/\text{s}$

Heat of reaction: $\Delta H_{\text{Rx}}^\circ = -10000 \text{ cal/g mol A}$

Heat capacities: $C_{pA} = C_{pB} = 25 \text{ cal/g mol} \cdot \text{K}$, C_{pS} (solvent) = $75 \text{ cal/g mol} \cdot \text{K}$

$k' (300 \text{ K}) = 0.01 \text{ cm}^3/\text{s} \cdot \text{g-cat}$ with $E = 4000 \text{ cal/mol}$

P14-11_B *Transdermal Drug Delivery*. See photo on page 781.

The principles of steady-state diffusion have been used in a number of drug-delivery systems. Specifically, medicated patches are commonly attached to the skin to deliver drugs for nicotine withdrawal, birth control, and motion sickness, to name a few. The U.S. transdermal drug-delivery is a multibillion dollar market. Equations similar to Equation (14-24) have been used to model the release, diffusion, and absorption of the drug from the patch into the body. The figure shown in the *Additional Material* and on page 781 shows a drug-delivery vehicle (patch) along with the concentration gradient in the epidermis and dermis skin layers.

1. Use a shell balance to show

$$\frac{dW_{Az}}{dz} = 0$$

2. Show the concentration profile in the epidermis layer

$$\frac{C_{A0} - C_A}{C_{A0} - C_{A1}} = \frac{z}{\delta_1}$$

3. Show the concentration profile in the dermis layer

$$\frac{C_A}{C_{A1}} = \frac{\delta_2 - z}{\delta_2 - \delta_1}$$

4. Equate the fluxes using $W_{A1} = -D_{A1} \frac{dC_A}{dz}$ and $W_{A2} = -D_{A2} \frac{dC_A}{dz}$ and to show

$$C_{A1} = \frac{D_{A1} \frac{C_{A0}}{\delta_1}}{\frac{D_{A2}}{\delta_2 - \delta_1} + \frac{D_{A1}}{\delta_1}}$$

5. What are the concentration profiles in the dermis and epidermis layers?
6. Show the flux in the dermis layer is

$$W_{Az} = \frac{D_{A2}}{\delta_2 - \delta_1} \left[\frac{D_{A1} \frac{C_{A0}}{\delta_1}}{\frac{D_{A2}}{\delta_2 - \delta_1} + \frac{D_{A1}}{\delta_1}} \right]$$

7. What is the flux in the epidermis layer?

P14-12_D (*Estimating glacial ages*) The following oxygen-18 data were obtained from soil samples taken at different depths in Ontario, Canada. Assuming that all the ^{18}O was laid down during the last glacial age and that the transport of ^{18}O to the surface takes place by molecular

diffusion, estimate the number of years since the last glacial age from the following data. Independent measurements give the diffusivity of ^{18}O in soil as $2.64 \times 10^{-10} \text{ m}^2/\text{s}$.



Figure P14-12_D Glaciers.

(surface)						
Depth (m)	0	3	6	9	12	18
^{18}O Conc. Ratio (C/C_0)	0	0.35	0.65	0.83	0.94	1.0

C_0 is the concentration of ^{18}O at 25 m. *Hint:* A knowledge of error function solutions may or may not be helpful. (Ans: $t = 5,616$ years)

P14-13_B OEQ (Old Exam Question). A spherical particle is dissolving in a liquid. The rate of dissolution is first order in the solvent concentration, C . Assuming that the solvent is in excess, show that the following conversion-time relationships hold.

Rate-Limiting Regime	Conversion–Time Relationship
Surface reaction	$1 - (1 - X)^{1/3} = \frac{\alpha t}{D_i}$
Mass transfer	

$$\frac{D_i}{2D^*} \left[1 - (1 - X)^{2/3} \right] = \frac{\alpha t}{D_i}$$

Mixed

$$[1 - (1 - X)]^{1/3} + \frac{D_i}{2D^*} \left[1 - (1 - X)^{2/3} \right] = \frac{\alpha t}{D_i}$$

P14-14_C Derive the diffusion and reaction equation in spherical coordinates to describe the dissolution of a drug in the form of a spherical pellet. Plot the drug concentration as a function distance r and time t . Also plot the flux and particle diameter as a function of time.

P14-15_B A powder is to be completely dissolved in an aqueous solution in a large, well-mixed tank. An acid must be added to the solution to render the spherical particle soluble. The particles are sufficiently small that they are unaffected by fluid velocity effects in the tank. For the case of excess acid, $C_0 = 2 \text{ M}$, derive an equation for the diameter of the particle as a function of time when

1. Mass transfer limits the dissolution: $-W_A = k_c C_{A0}$
2. Reaction limits the dissolution: $-r_A'' = k_r^A C_{A0}$
What is the time for complete dissolution in each case?
3. Now assume that the acid is not in excess and that mass transfer is limiting the dissolution. One mole of acid is required to dissolve 1 mol of solid. The molar concentration of acid is 0.1 M , the tank is 100 L , and 9.8 mol of solid is added to the tank at time $t = 0$. Derive an expression for the radius of the particles as a function of time and calculate the time for the particles to dissolve completely.
4. How could you make the powder dissolve faster? Slower?

Additional information:

$$D_e = 10^{-10} \text{ m}^2/\text{s}, \quad k = 10^{-18} / \text{s}$$

$$\text{initial diameter} = 10^{-5} \text{ m}$$

P14-16_B (*Pills*) An antibiotic drug is contained in a solid inner core and is surrounded by an outer coating that makes

it palatable. The outer coating and the drug are dissolved at different rates in the stomach, owing to their differences in equilibrium solubilities.

1. If $D_2 = 4$ mm and $D_1 = 3$ mm, calculate the time necessary for the pill to dissolve completely.
2. Assuming first-order kinetics ($k_A = 10 \text{ h}^{-1}$) for the absorption of the dissolved drug (i.e., in solution in the stomach) into the bloodstream, plot the concentration in grams of the drug in the blood per gram of body weight as a function of time when the following three pills are taken simultaneously:



Pill 1: $D_2 = 5$ mm, $D_1 = 3$ mm

Pill 2: $D_2 = 4$ mm, $D_1 = 3$ mm

Pill 3: $D_2 = 3.5$ mm, $D_1 = 3$ mm

3. Discuss how you would maintain the drug level in the blood at a constant level using different-size pills?
4. How could you arrange a distribution of pill sizes so that the concentration in the blood was constant over a period (e.g., 3 hr) of time?

Additional information:

Amount of drug in inner core = 500 mg

Solubility of outer layer at stomach conditions = 1.0 mg/cm^3

Solubility of inner layer at stomach conditions = 0.4 mg/cm^3

Volume of fluid in stomach = 1.2 L

Typical body weight = 75 kg

$Sh = 2$, $D_{AB} = 6 \times 10^{-4} \text{ cm}^2/\text{min}$



Green engineering

P14-17_B If disposal of industrial liquid wastes by incineration is to be a feasible process, it is important that the toxic chemicals be completely decomposed into harmless substances. One study carried out concerned the atomization and burning of a liquid stream of “principal” organic hazardous constituents (POHCs) [*Environ. Prog.*, 8, 152 (1989)]. The following data give the burning droplet diameter as a function of time (both diameter and time are given in arbitrary units):

Time	20	40	50	70	90	110
Diameter	9.7	8.8	8.4	7.1	5.6	4.0

What can you learn from these data?

SUPPLEMENTARY READING

1. The fundamentals of diffusional mass transfer may or may not be found in

R. B. BIRD, W. E. STEWART, and E. N. LIGHTFOOT, *Transport Phenomena*, 2nd ed. New York: Wiley, 2002, Chaps. 17 and 18.

S. Collins, *Mockingjay* (The Final Book of the Hunger Games). New York: Scholastic, 2014.

E. L. CUSSLER, *Diffusion Mass Transfer in Fluid Systems*, 3rd ed. New York: Cambridge University Press, 2009.

C. J. GEANKOPLIS, *Transport Processes and Unit Operations*. Upper Saddle River, NJ: Prentice Hall, 2003.

V. G. LEVICH, *Physicochemical Hydrodynamics*. Upper Saddle River, NJ: Prentice Hall, 1962, Chaps. 1 and 4.

2. Experimental values of the diffusivity can be found in a number of sources, two of which are

R. H. PERRY, D. W. GREEN, and J. O. MALONEY, *Chemical Engineers' Handbook*, 8th ed. New York: McGraw-Hill, 2007.

T. K. SHERWOOD, R. L. PIGFORD, and C. R. WILKE, *Mass Transfer*. New York: McGraw-Hill, 1975.

3. A number of correlations for the mass transfer coefficient can be found in

A. L. LYDERSEN, *Mass Transfer in Engineering Practice*. New York: Wiley-Interscience, 1983, Chap. 1.

W. L. MCCABE, J. C. SMITH, and P. HARRIOTT, *Unit Operations of Chemical Engineering*, 6th ed. New York: McGraw-Hill, 2000, Chap. 17.

15. Diffusion and Reaction

The breakfast of champions is not a cereal, it's your opposition.

—Nick Steitz

Overview. In this chapter, we will develop models for diffusion with reaction in single-phase and two-phase systems. We start off with a discussion of diffusion and reaction in catalyst pellets. In [Chapter 10](#), we assumed each point on the interior of the catalyst pellet's surface was accessible to the same concentration. However, when the reactants must diffuse inside the catalyst pellet's in order to react, we know the concentration at the pore mouth must be higher than that inside the pore. Consequently, the entire catalytic surface is not accessible to the same concentration; therefore, the rate of reaction throughout the pellet will vary. To account for variations in reaction rate throughout the pellet, we introduce a parameter known as the *internal effectiveness factor*, which is the ratio of the overall reaction rate in the pellet to the reaction rate at the external surface of the pellet.

The following topics will be discussed in this chapter:

- Diffusion and Reactions in Homogeneous Systems ([Section 15.1](#)).
- Diffusion and Reactions in Spherical Catalyst Pellets ([Section 15.2](#)).
- The Internal Effectiveness Factor ([Section 15.3](#)).
- Falsified Kinetics ([Section 15.4](#)).
- Overall Effectiveness Factor ([Section 15.5](#)).
- Estimation of Diffusion- and Reaction-Limited Regimes ([Section 15.6](#)).
- Mass Transfer and Reaction in a Packed Bed ([Section 15.7](#)).
- Determination of Limiting Situations from Reaction-Rate Data ([Section 15.8](#)).

After studying this chapter, you will be able to describe diffusion and reaction, determine when internal diffusion limits the overall rate of reaction for catalyst pellets, describe how to go about eliminating this limitation, and develop models for systems in which both diffusion and reaction play a role (e.g., catalysis, tissue growth).

The concentration in the internal surface of the pellet is less than that of the external surface.

In [Chapter 14](#), we discussed reactions limited by mass transfer from the bulk fluid through a boundary layer to a surface where the reaction rapidly takes place. In [Chapter 14](#), the reaction did not take place as the reactants diffused, however, in this chapter we consider diffusion with reaction. Here we

will model Steps 2 and 6 in Figure 15-1 (which is the same as Figure 14-1), where the molecules are reacting as they diffuse.

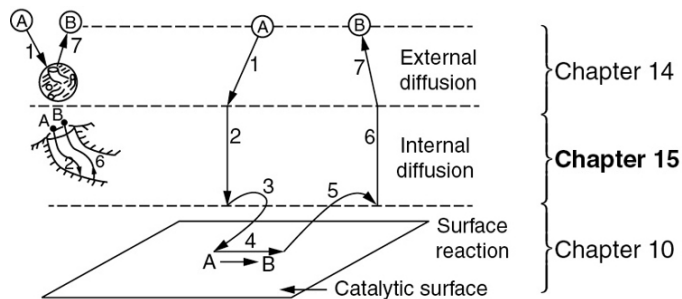


Figure 15-1 Steps in a heterogeneous catalytic reaction.

15.1 DIFFUSION AND REACTIONS IN HOMOGENEOUS SYSTEMS

For homogeneous systems, the mole balance on species A, Equation (14-1), for one-dimensional diffusion at steady state is

$$-\frac{dW_{Az}}{dz} + r_A = 0 \quad (15-1)$$

For diffusion through a stagnant film at dilute concentrations (i.e., $y_A \ll 1$), Equation (14-9) becomes

$$W_{Az} = -D_{AB} \frac{dC_A}{dz}$$

Substituting in Equation (14-1) one obtains

$$D_{AB} \frac{d^2 C_A}{dz^2} + r_A = 0 \quad (15-2)$$

Homogeneous diffusion and reaction

Understanding and modeling diffusion with chemical reaction is not only important for industrial catalysts but also has many other applications. These applications include medicine, cancer treatment using drug-laced particulates, and, as shown in the *Additional Material* on the CRE Web site (<http://www.umich.edu/~elements/6e/15chap/expanded.html>),

tissue engineering. In Problem P15-18_B, we discuss the diffusion and reaction of oxygen in cartilage.

We will now discuss solid–gas catalytic reactions and diffusion limitation in catalyst pellets.

15.2 DIFFUSION AND REACTIONS IN SPHERICAL CATALYST PELLETS

The following sections of this chapter will focus solely on the transport and reaction in heterogeneous systems with catalyst pellets. In a heterogeneous reaction sequence, mass transfer of reactants must first take place from the bulk fluid to the external surface of the pellet. The reactants then diffuse from the external surface into and through the pores within the pellet ($C_{As} > C_A(r)$), with reaction taking place only on the catalytic surface of the pores. A schematic representation of this two-step diffusion process is shown in Figures 10-6, 14-1, and 15-2.

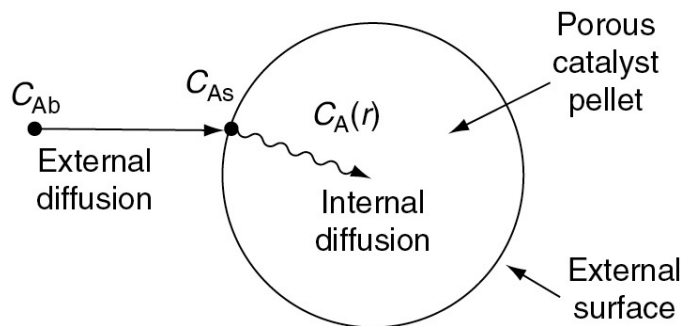


Figure 15-2 Mass transfer and reaction steps for a catalyst pellet..

In Chapter 14 we discussed *external diffusion*. In this section we will discuss *internal diffusion* and develop the internal effectiveness factor for spherical catalyst pellets. The development of models that treat individual pores and pellets of different shapes is undertaken in the problems at the end of this chapter. We will first look at the internal mass transfer resistance to either the reaction products or reactants that occurs between the external pellet surface and the interior of the pellet. To illustrate the salient principles of this model, we consider the irreversible isomerization



that occurs on the surface of the pore walls within the spherical pellet of radius R .

15.2.1 Effective Diffusivity

In order to reach and be catalyzed on the inner surface of the pellet, the reactant A must diffuse from a higher reactant concentration at the pellet external surface into and through the pores of pellets which are at a lower concentration as shown in Figure 15-2.

The pores in the pellet are not straight and cylindrical; rather, they are a series of tortuous, interconnecting paths of pore bodies and pore throats with varying cross-sectional areas. It would not be fruitful to describe diffusion within each and every one of the tortuous pathways individually; consequently, we shall define an effective diffusion coefficient so as to describe the average diffusion taking place at any interior position r in the pellet. We shall consider only radial variations in the concentration in a spherical catalyst pellet; the radial flux W_{Ar} will be based on the total area (voids and solid) normal to diffusion transport (i.e., $4\pi r^2$) rather than void area alone. This basis for W_{Ar} is made possible by proper definition of the effective diffusivity D_e .

The effective diffusivity accounts for the fact that:

1. Not all of the area normal to the direction of the flux is available (i.e., the area occupied by solids) for the molecules to diffuse.
2. The paths are tortuous.
3. The pores are of varying cross-sectional areas.

The effective diffusivity

An equation that relates the effective diffusivity D_e to either the bulk diffusivity D_{AB} or the Knudsen diffusivity D_K is

$$D_e = \frac{D_{AB}\phi_p\sigma_c}{\tilde{\tau}} \quad (15-3)$$

where

$$\bar{\tau} = \text{tortuosity}^1 = \frac{\text{Actual distance a molecule travels between two points}}{\text{Shortest distance between those two points}}$$

$$\phi_p = \text{pellet porosity} = \frac{\text{Volume of void space}}{\text{Total volume (voids and solids)}}$$

$$\sigma_c = \text{Constriction factor, see Figure 15-3 (a)}$$

¹ Some investigators lump the constriction factor and tortuosity into one factor, called the tortuosity factor, and set it equal to $\bar{\tau}/\sigma_c$. See C. N. Satterfield, *Mass Transfer in Heterogeneous Catalysis*, Cambridge, MA: MIT Press, 1970, pp. 33–47.

The constriction factor, σ_c , accounts for the variation in the cross-sectional area that is normal to diffusion.² It is a function of the ratio of maximum to minimum pore areas (Figure 15-3(a)). When the two areas, A_1 and A_2 , are equal, the constriction factor is unity, and when $\beta = 10$, the constriction factor is approximately 0.5.

² See E. E. Petersen, *Chemical Reaction Analysis*, Upper Saddle River, NJ: Prentice Hall, 1965, Chap. 3; C. N. Satterfield and T. K. Sherwood, *The Role of Diffusion in Catalysis*, Reading, MA: Addison-Wesley, 1963, Chap. 1.

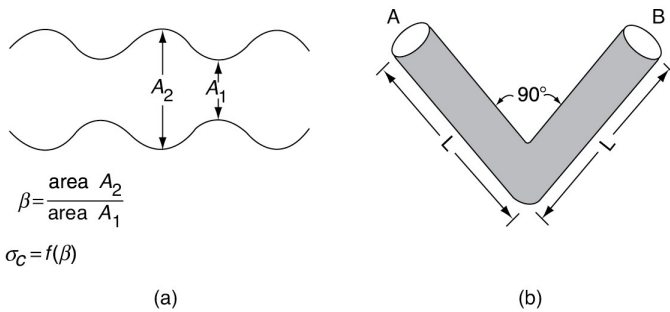


Figure 15-3 (a) Pore constriction; (b) pore tortuosity.

Example 15-1 Finding the Effective Diffusivity D_e

Using typical values of D_{AB} , ϕ_p , σ_c , and τ , estimate the effective diffusivity, D_e .

Solution

First, calculate the tortuosity for the hypothetical pore of length, L (Figure 15-3(b)), from the definition of $\tilde{\tau}$.

$$\tilde{\tau} = \frac{\text{Actual distance molecule travels from A to B}}{\text{Shortest distance between A and B}}$$

The shortest distance between points A and B for the idealized pore shown in Figure 15-3(b) is $\sqrt{2}L$. The actual distance the molecule travels from A to B is $2L$.

$$\tilde{\tau} = \frac{2L}{\sqrt{2}L} = \sqrt{2} = 1.414$$

Although this value is reasonable for $\tilde{\tau}$, values for $\tilde{\tau} = 6-10$ are not uncommon. Typical values of the constriction factor, the tortuosity, and the pellet porosity are, respectively, $\sigma_c = 0.8$, $\tilde{\tau} = 3.0$, and $\phi_p = 0.40$. A typical value of the gas-phase diffusivity is $D_{AB} = 10^{-6} \text{ m}^2/\text{s}$.

Using these values in Equation (15-3)

$$D_e = \frac{\phi_p \sigma_c}{\tilde{\tau}} D_{AB} \quad (15-3)$$

$$D_e = \frac{(0.4)0.8}{(3)} D_{AB} = 0.106 D_{AB}$$

therefore

$$D_e = 0.1 \cdot 10^{-6} \text{ m}^2/\text{s} = 10^{-7} \text{ m}^2/\text{s}$$

Analysis: The purpose of this example was to describe tortuosity and constriction factor in order to help the reader understand how these parameters decrease the effective diffusivity, D_e . We also see that a representative value of the effective diffusivity in the porous pellet is 10% of the gas-phase diffusivity.

15.2.2 Derivation of the Differential Equation Describing Diffusion and Reaction in a Single Spherical Catalyst Pellet

We now perform a steady-state mole balance on species A as it enters, leaves, and reacts in a spherical shell of inner radius r and outer radius $r + \Delta r$ of the pellet (**Figure 15-4**). Note that even though A is diffusing inward toward the center of the pellet, the *convention of our shell balance dictates that the flux be in the direction of increasing r* . We choose the flux of A to be positive in the direction of increasing r (i.e., the outward direction). Because A is actually diffusing inward, the flux of A will have some negative numerical value, such as $(-10 \text{ mol/m}^2\cdot\text{s})$, indicating that the flux is actually in the direction of decreasing r .

First, we will derive the concentration profile of reactant A in the pellet.

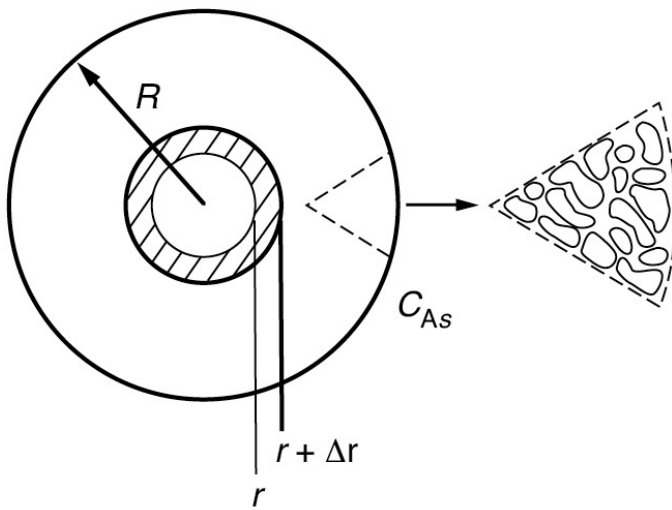


Figure 15-4 Shell balance on a catalyst pellet.

We now proceed to perform our shell balance on A. The area that appears in the balance equation is the total area (voids and solids) *normal* to the direction of the molar flux shown by the arrows in **Figure 15-3**.

$$\begin{aligned} \text{Rate of A in at } r &= W_{Ar} \cdot \text{Area} = W_{Ar} \times 4\pi r^2|_r \\ \text{Rate of A out at } (r + \Delta r) &= W_{Ar} \cdot \text{Area} = W_{Ar} \times 4\pi r^2|_{r+\Delta r} \end{aligned}$$

$$\begin{aligned}
 \left[\begin{array}{c} \text{Rate of} \\ \text{generation} \\ \text{of A within a} \\ \text{shell of thickness} \\ \Delta r \end{array} \right] &= \left[\frac{\text{Rate of reaction}}{\text{Mass of catalyst}} \right] \times \left[\frac{\text{Mass catalyst}}{\text{Volume}} \right] \times [\text{Volume of shell}] \\
 &= r'_A \times \rho_c \times 4\pi r_m^2 \Delta r \quad (15-4)
 \end{aligned}$$

where r_m is some mean radius between r and $r + \Delta r$ that is used to approximate the volume ΔV of the shell, and ρ_c is the density of the pellet.

Mole balance for diffusion and reaction inside the catalyst pellet

Mole balance

The mole balance over the shell thickness Δr is

$$\begin{aligned}
 (\text{In at } r) &- (\text{Out at } r + \Delta r) + (\text{Generation within } \Delta r) = 0 \\
 (W_{Ar} \times 4\pi r^2|_r) &- (W_{Ar} \times 4\pi r^2|_{r+\Delta r}) + (r'_A \rho_c \times \pi r_m^2 \Delta r) = 0 \quad (15-5)
 \end{aligned}$$

After dividing by $(-4\pi\Delta r)$ and taking the limit as $\Delta r \rightarrow 0$, we obtain the following differential equation

$$\frac{d(W_{Ar}r^2)}{dr} - r'_A \rho_c r^2 = 0 \quad (15-6)$$

Because 1 mol of A reacts under conditions of constant temperature and pressure to form 1 mol of B, we have Equimolar Counter Diffusion (EMCD) at constant total molar concentration (Section 14.2.1) and, therefore

The flux equation

where C_A is the number of moles of A per dm^3 of open-pore volume (i.e., volume of gas) as opposed to (mol/vol of gas and solids). In systems where we do not have EMCD in catalyst pores, it may still be possible to use Equation (15-7) if the reactant gases are present in dilute concentrations.

$$W_{Ar} = -D_e \frac{dC_A}{dr} \quad (15-7)$$

After substituting Equation (15-7) into Equation (15-6), we arrive at the following differential equation describing diffusion with reaction in a catalyst pellet

$$\frac{d \left[-D_e \left(\frac{dC_A}{dr} \right) r^2 \right]}{dr} - r^2 p_c - r'_A = 0 \quad (15-8)$$

We now need to incorporate the rate law. In the past, we have based the rate of reaction in terms of either per unit volume

$$-r_A [=] \left(\text{mol/dm}^3 \cdot \text{s} \right)$$

Inside the Pellet

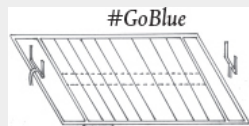
$$\begin{aligned} -r'_A &= S_a (-r''_A) \\ -r_A &= \rho_c (-r'_A) \\ -r_A &= \rho_c S_a (-r''_A) \end{aligned}$$

or per unit mass of catalyst

$$-r'_A [=] \left(\text{mol/g-cat} \cdot \text{s} \right)$$

When we study reactions on the internal surface area of catalysts, the rate of reaction and rate law are often based on per unit surface area

$$-r''_A [=] \left(\text{mol/m}^2 \cdot \text{s} \right)$$



As a result, the surface area of the catalyst per unit mass of catalyst

$$S_a [=] \left(\text{m}^2/\text{g-cat} \right)$$

is an important property of the catalyst. The rate of reaction per unit mass of catalyst, $-r'_A$, and the rate of reaction per unit surface area of catalyst are related through the equation

S_a : 10 grams of catalyst may cover as much surface area as a football field.

$$-r'_A = -r''_A S_a$$

A typical value of S_a might be $150 \text{ m}^2/\text{g}$ of catalyst.

The rate law

As mentioned previously, at high temperatures, the denominator of the catalytic rate law often approaches 1 as discussed in [Section 10.3.7](#). Consequently, for the moment, it is reasonable to assume that the surface reaction is of n th order in the gas-phase concentration of A within the pellet

$$-r''_A = -k''_n C_A^n \quad (15-9)$$

where the units of the rate constants for r_A , $-r'_A$, and $-r''_A$ are

$$-r''_A : \text{with } k''_n [=] \left(\frac{\text{m}^3}{\text{kmol}} \right)^{n-1} \frac{\text{m}}{\text{s}}$$

Similarly,

$$\begin{aligned} -r'_A : \text{with } k'_n &= S_a k''_n [=] \left(\frac{\text{m}^3}{\text{kmol}} \right)^{n-1} \frac{\text{m}^3}{\text{kg} \cdot \text{s}} \\ -r_A : \text{with } k_n &= k'_n \rho_c = \rho_c S_a k''_n [=] \left(\frac{\text{m}^3}{\text{kmol}} \right)^{n-1} \frac{1}{\text{s}} \end{aligned}$$

For a **first-order** catalytic reactor

per unit pellet surface area:	$k''_1 = [\text{m/s}]$
per unit mass of single pellet catalyst:	$k'_1 = k''_1 S_a = [\text{m}^3/\text{kg} \cdot \text{s}]$
per unit single pellet volume:	$k_1 = k''_1 S_a \rho_c = [\text{s}^{-1}]$

Substituting the rate-law equation (15-9) into Equation (15-8) gives

$$\frac{d[r^2(-D_e dC_A/dr)]}{dr} + r^2 \overbrace{k''_n S_a \rho_c}^{k_n} C_A^n = 0 \quad (15-10)$$

Letting k_n represent the terms under the bracket, differentiating the first term and dividing through by $-r^2 D_e$, Equation (15-10) becomes

$$\frac{d^2 C_A}{dr^2} + \frac{2}{r} \left(\frac{dC_A}{dr} \right) - \frac{k_n}{D_e} C_A^n = 0 \quad (15-11)$$

Differential equation and boundary conditions describing diffusion and reaction in a catalyst pellet

The boundary conditions are:

1. The concentration remains finite at the center of the pellet

$$C_A \text{ is finite at } r = 0$$

2. At the external surface of the catalyst pellet, the concentration is C_{As}

$$C_A = C_{As} \text{ at } r = R$$

15.2.3 Writing the Diffusion with the Catalytic Reaction Equation in Dimensionless Form

As engineers, we often put our governing equations in dimensionless form as it makes calculations much easier when we change numbers and units. Consequently, we now introduce dimensionless variables ψ and λ so that we may arrive at a parameter that is frequently discussed in catalytic reactions, the *Thiele modulus*. Let

$$\psi = \frac{C_A}{C_{As}} \quad (15-12)$$

$$\lambda = \frac{r}{R} \quad (15-13)$$

With the transformation of variables, the boundary condition

$$C_A = C_{As} \text{ at } r = R$$

becomes

$$\psi = \frac{C_A}{C_{As}} = 1 \text{ at } \lambda = 1$$

and the boundary condition

$$C_A \text{ is finite at } r = 0$$

becomes

$$\psi \text{ is finite at } \lambda = 0$$

We now rewrite the differential equation for the molar flux in terms of our dimensionless variables. Starting with

$$W_{Ar} = -D_e \frac{dC_A}{dr} \quad (15-7)$$

we use the chain rule to write

$$\frac{dC_A}{dr} = \left(\frac{dC_A}{d\lambda} \right) \frac{d\lambda}{dr} = \frac{d\psi}{d\lambda} \left(\frac{dC_A}{d\psi} \right) \frac{d\lambda}{dr} \quad (15-14)$$

Then differentiate Equation (15-12) with respect to ψ and Equation (15-13) with respect to r , and substitute the resulting expressions

$$\frac{dC_A}{d\psi} = C_{As} \quad \text{and} \quad \frac{d\lambda}{dr} = \frac{1}{R}$$

into Equation (15-14) to obtain

$$\frac{dC_A}{dr} = \frac{d\psi}{d\lambda} \frac{C_{As}}{R} \quad (15-15)$$

The flux of A in terms of the dimensionless variables, ψ and λ , is

The total rate of consumption of A inside the pellet, M_A (mol/s)

$$W_{Ar} = -D_e \frac{dC_A}{dr} = -\frac{D_e C_{As}}{R} \left(\frac{d\psi}{d\lambda} \right) \quad (15-16)$$

At steady state, the net flow of species A that enters into the pellet at the external pellet surface reacts completely within the pellet. The overall rate of reaction is therefore equal to the total molar flow of A into the catalyst pellet. The overall rate of reaction, M_A (mol/s), can be obtained by multiplying the molar flux into the pellet at the outer surface by the external surface area of the pellet, $4\pi R^2$

All the reactant that diffuses into the pellet is consumed (a black hole?).

$$M_A = -4\pi R^2 W_{Ar} \Big|_{r=R} = +4\pi R^2 D_e \frac{dC_A}{dr} \Big|_{r=R} = 4\pi R D_e C_{As} \frac{d\psi}{d\lambda} \Big|_{\lambda=1} \quad (15-17)$$

Consequently, to determine the overall rate of reaction, which is given by Equation (15-17), we first solve Equation (15-11) for C_A , differentiate C_A with respect to r , and then substitute the resulting expression into Equation (15-17).

Differentiating the concentration gradient, Equation (15-15), yields

$$\frac{d^2 C_A}{dr^2} = \frac{d}{dr} \left(\frac{dC_A}{dr} \right) = \frac{d}{d\lambda} \left(\frac{d\psi}{d\lambda} \frac{C_{As}}{R} \right) \frac{d\lambda}{dr} = \frac{d^2 \psi}{d\lambda^2} \left(\frac{C_{As}}{R} \right) \quad (15-18)$$

After dividing by C_{As}/R^2 , the dimensionless form of Equation (15-11) is written as

$$\frac{d^2 \psi}{d\lambda^2} + \frac{2}{\lambda} \frac{d\psi}{d\lambda} - \frac{k_n R^2 C_{As}^{n-1}}{D_e} \psi^n = 0$$

Then

Dimensionless form of equations describing diffusion and reaction

$$\frac{d^2 \psi}{d\lambda^2} + \frac{2}{\lambda} \left(\frac{d\psi}{d\lambda} \right) - \phi_n^2 \psi^n = 0 \quad (15-19)$$

where

$$\phi_n^2 = \frac{k_n R^2 C_{As}^{n-1}}{D_e} \quad (15-20)$$

The Thiele Modulus

The square root of the coefficient of ψ^n in Equation 15-19 (i.e., ϕ_n) is called the Thiele modulus (pronounced *th ē -lē*). The Thiele modulus, ϕ_n , will always contain a subscript (e.g., n), which refers to the reaction order and distinguishes this symbol from the symbol for porosity, ϕ , used in the Ergun pressure drop equation and defined in Chapter 5, which has no subscript. The quantity ϕ_n^2 is a measure of the ratio of “a” surface reaction rate to “a” rate of diffusion through the catalyst pellet

$$\phi_n^2 = \frac{k_n R^2 C_{As}^{n-1}}{D_e} = \frac{k_n R C_{As}^n}{D_e [(C_{As} - 0) / R]} = \frac{\text{"a" surface reaction rate}}{\text{"a" diffusion rate}} \quad (15-20)$$

Limiting conditions:

When the Thiele modulus is large, internal diffusion usually limits the overall rate of reaction; when ϕ_n is small, the surface reaction is usually rate-limiting. If, for the first-order reaction



the reaction were surface reaction rate limited with respect to the adsorption of A and desorption of B, and if A and B were weakly adsorbed (i.e., low surface coverage), we can write the apparent first-order reaction rate law per unit volume of pellet as

$$-r_A = k_1 C_A$$

where k_1 is the rate constant for a single catalyst pellet.

Recalling $k_1 = S_a \rho_c k''$ we could also write the rate in terms of pellet catalytic surface area ($\text{mol/m}^2 \cdot \text{s}$)

$$-r_A'' = k_1'' C_A \left(\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right) \quad (15-21)$$

The units of k_1'' are $\text{m}^3/\text{m}^2 \cdot \text{s}$ ($= \text{m/s}$).

For a first-order reaction, Equation (15-19) becomes

$$\frac{d^2 \psi}{d\lambda^2} + \frac{2}{\lambda} \frac{d\psi}{d\lambda} - \phi_1^2 \psi = 0 \quad (15-22)$$

the Thiele modulus for this first-order reaction is

$$\phi_1 = R \sqrt{\frac{k_1'' \rho_c S_a}{D_e}} = R \sqrt{\frac{k_1}{D_e}} \quad (15-23)$$

where

Always check to make sure the units are consistent.

$$k_1 = k_1'' \rho_c S_a \quad [=] \quad \left(\frac{\text{m}}{\text{s}} \cdot \frac{\text{g}}{\text{m}^3} \cdot \frac{\text{m}^2}{\text{g}} \right) = 1/\text{s}$$

$$\frac{k_1}{D_e} \quad [=] \quad \left(\frac{1/\text{s}}{\text{m}^2/\text{s}} \right) = \frac{1}{\text{m}^2}$$

$$\phi_1 = R \sqrt{\frac{k_1}{D_e}} \quad [=] \quad \text{m} \left(\frac{\text{s}^{-1}}{\text{m}^2/\text{s}} \right)^{1/2} = \frac{1}{1} (\text{Dimensionless})$$

The boundary conditions are

$$\boxed{\text{B.C. 1 : } \psi = 1 \quad \text{at } \lambda = 1} \quad (15-24)$$

$$\boxed{\text{B.C. 2 : } \psi \text{ is finite} \quad \text{at } \lambda = 0} \quad (15-25)$$

15.2.4 Solution to the Differential Equation for a First-Order Reaction

Differential equation (15-22) is readily solved with the aid of the transformation $y = \psi\lambda$:

$$\frac{d\psi}{d\lambda} = \frac{1}{\lambda} \left(\frac{dy}{d\lambda} \right) - \frac{y}{\lambda^2}$$

$$\frac{d^2\psi}{d\lambda^2} = \frac{1}{\lambda} \left(\frac{d^2y}{d\lambda^2} \right) - \frac{2}{\lambda^2} \left(\frac{dy}{d\lambda} \right) + \frac{2y}{\lambda^3}$$

With these transformations, Equation (15-22) reduces to

$$\frac{d^2y}{d\lambda^2} - \phi_1^2 y = 0 \quad (15-26)$$

This differential equation has the following solution (see [Appendix A.3](#)):

$$y = A_1 \cosh \phi_1 \lambda + B_1 \sinh \phi_1 \lambda$$

In terms of ψ ,

$$\psi = \frac{A_1}{\lambda} \cosh \phi_1 \lambda + \frac{B_1}{\lambda} \sinh \phi_1 \lambda$$

The arbitrary constants A_1 and B_1 can easily be evaluated with the aid of the boundary conditions. At $\lambda = 0$, $\cosh \phi_1 \lambda \rightarrow 1$, $(1/\lambda) \rightarrow \infty$, and $\sinh \phi_1 \lambda \rightarrow 0$. The second boundary condition requires ψ to be finite at the center (i.e., $\lambda = 0$), therefore A_1 must be zero.

The constant B_1 is evaluated from B.C. 1 (i.e., $\psi = 1$, $\lambda = 1$) and the dimensionless concentration profile is

Dimensionless concentration profile

$$\psi = \frac{C_A}{C_{As}} = \frac{1}{\lambda} \left(\frac{\sinh \phi_1 \lambda}{\sinh \phi_1} \right) \quad (15-27)$$

Figure 15-5 shows the concentration profile for three different values of the Thiele modulus, ϕ_1 . Small values of the Thiele modulus indicate surface reaction controls and a significant amount of the reactant diffuses well into the pellet interior without reacting. As a result, the concentration profile is very shallow, with the concentration at the center of the pellet being close to that at the external surface. That is, virtually the entire internal surface is accessible to the reactant concentration C_{As} . Large values of the Thiele modulus indicate that the surface reaction is rapid and that the reactant is consumed very close to the external pellet surface and very little penetrates into the interior of the pellet. Consequently, if the porous pellet is to be plated with a precious metal catalyst (e.g., Pt), it should only be plated in the immediate vicinity of the external surface when large values of ϕ_n characterize the diffusion and reaction. That is, it would be a waste of the precious metal to plate the entire insides of the pellet when internal diffusion is limiting because the reacting gases are consumed near the outer pellet surface and never reach the metal catalyst near the pellet's center. Consequently, the reacting gases would never contact the center portion of the pellet.

Dimensionless concentration profile

#WasteOfMoney

For large values of the Thiele modulus, internal diffusion limits the rate of reaction.

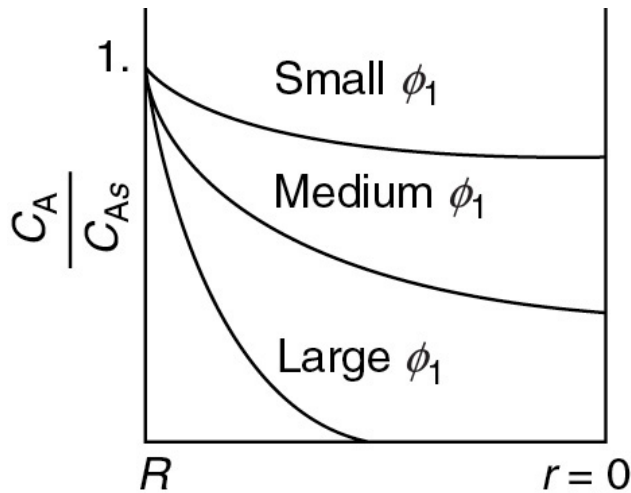


Figure 15-5 Concentration profile in a spherical catalyst pellet.

15.3 THE INTERNAL EFFECTIVENESS FACTOR

In [Figure 15-5](#) we saw that the concentration varied with the pellet radius. Consequently, for all but zero-order reactions, the rate will also vary throughout the pellet. In order to account for this variation in rates, we introduce the *internal effectiveness factor*.

15.3.1 Isothermal First-Order Catalytic Reactions

The magnitude of the effectiveness factor (ranging from 0 to 1) indicates the relative importance of diffusion and reaction limitations. The internal effectiveness factor is defined as

η is a measure of how far the reactant diffuses into the pellet before reacting.

$$\eta = \frac{\text{Actual overall rate of reaction}}{\text{Rate of reaction that would result if entire interior surface were exposed to the external pellet surface conditions } C_{As}, T_s} \quad (15-28)$$

The overall rate, $-r'_A$, is also referred to as the observed rate of reaction $[-r_A(\text{obs})]$. In terms of symbols, the effectiveness factor is

$$\eta = \frac{-r_A}{-r_{As}} = \frac{-r'_A}{-r'_{As}} = \frac{-r''_A}{-r''_{As}}$$

To derive the effectiveness factor for a first-order reaction, it is easiest to work in reaction rates of moles per unit time, M_A , rather than in moles per unit time per volume of catalyst (i.e., $-r_A$). Consequently, we multiply the numerator and denominator of Equation (15-28) by the volume, V , of the catalyst pellet.

$$\eta = \frac{-r_A}{-r_{As}} = \frac{-r_A \times \text{Volume of catalyst particle}}{-r_{As} \times \text{Volume of catalyst particle}} = \frac{M_A}{M_{As}}$$

First, we shall consider the denominator, M_{As} , the molar rate to the surface. If the entire surface were exposed to the concentration at the external surface of the pellet, C_{As} , the rate for a first-order reaction would be

$M_{As} = (\text{Rate at external surface per unit volume}) \times (\text{Volume of catalyst pellet})$

$$M_{As} = -r_{As} \times \left(\frac{4}{3} \pi R^3 \right) = k_1 C_{As} \left(\frac{4}{3} \pi R^3 \right) \quad (15-29)$$

The subscript s indicates that the rate $-r_{As}$ is evaluated at the conditions (e.g., concentration, temperature) present at the **external** surface of the pellet (i.e., $\lambda = 1$).

The *actual rate of reaction* is the rate at which the reactant diffuses into the pellet at the outer surface; that is, all of A that diffuses into the pellet at the outer surface reacts and no A diffuses back out. (It behaves as a “black hole.”) We recall Equation (15-17) on page 799 for the actual rate of reaction

The actual rate of reaction

$$M_A = 4\pi R D_e C_{As} \left. \frac{d\psi}{d\lambda} \right|_{\lambda=1} \quad (15-17)$$

Differentiating Equation (15-27) and then evaluating the result at $\lambda = 1$ yields

$$\left. \frac{d\psi}{d\lambda} \right|_{\lambda=1} = \left(\frac{\phi_1 \cosh \lambda \phi_1}{\lambda \sinh \phi_1} - \frac{1}{\lambda^2} \frac{\sinh \lambda \phi_1}{\sinh \phi_1} \right)_{\lambda=1} = (\phi_1 \coth \phi_1 - 1) \quad (15-30)$$

Substituting Equation (15-30) into (15-17) gives us

$$M_A = 4\pi R D_e C_{As} (\phi_1 \coth \phi_1 - 1) \quad (15-31)$$

We now substitute Equations (15-29) and (15-31) into Equation (15-28) to obtain an expression for the effectiveness factor

$$\begin{aligned} \eta &= \frac{M_A}{M_{As}} = \frac{M_A}{(-r_{As}) \left(\frac{4}{3} \pi R^3 \right)} = \frac{4\pi R D_e C_{As}}{k_1 C_{As} \frac{4}{3} \pi R^3} (\phi_1 \coth \phi_1 - 1) \\ &= 3 \underbrace{\frac{1}{k_1 R^2 / D_e}}_{\phi_1^2} (\phi_1 \coth \phi_1 - 1) \end{aligned}$$

Internal effectiveness factor for a first-order reaction in a spherical catalyst pellet

$$\eta = \frac{3}{\phi_1^2} (\phi_1 \coth \phi_1 - 1) \quad (15-32)$$

A plot of the internal effectiveness factor as a function of the Thiele modulus is shown in Figure 15-6. Figure 15-6(a) shows η as a function of the Thiele modulus, ϕ_s , for a spherical catalyst pellet for reactions of zero, first, and second order. Figure 15-6(b) corresponds to a first-order reaction occurring in three differently shaped pellets of volume V_p and external surface area A_p , and where the Thiele modulus for a first-order reaction, ϕ_1 , is defined differently for each shape. When volume change accompanies a reaction (i.e., $\epsilon \neq 0$), the corrections shown in Figure 15-7 apply to the effectiveness factor for a first-order reaction.

The Thiele Modulus is a very important parameter that helps us identify when either *diffusion* is rate limiting (Large ϕ_n) or *reaction* is rate limiting (Small ϕ_n). We observe that as the particle diameter becomes very small, ϕ_n decreases, so that the internal effectiveness factor approaches 1 and the reaction is surface reaction-limited. On the other hand, when the Thiele modulus ϕ_n is large (e.g., ~ 30), the internal effectiveness factor η is small (e.g., ~ 0.1), and the reaction is diffusion-limited within the pellet. Consequently, factors influencing the rate of external mass transport such as fluid velocity will have a negligible effect on the overall reaction rate when the reaction is either internal surface reaction rate limited or

internal diffusion limited. For large values of the Thiele modulus, one can expand $\coth \phi_1$ in Equation (15-32) in a Taylor series and show that the effectiveness factor can be written as

If $\phi > 2$

$$\text{then } \eta \approx \frac{3}{\phi_1^2} [\phi_1 - 1]$$

If $\phi > 20$

$$\text{then } \eta \approx \frac{3}{\phi_1}$$

$$\eta \simeq \frac{3}{\phi_1} = \frac{3}{R} \sqrt{\frac{D_e}{k_1}} \quad (15-33)$$

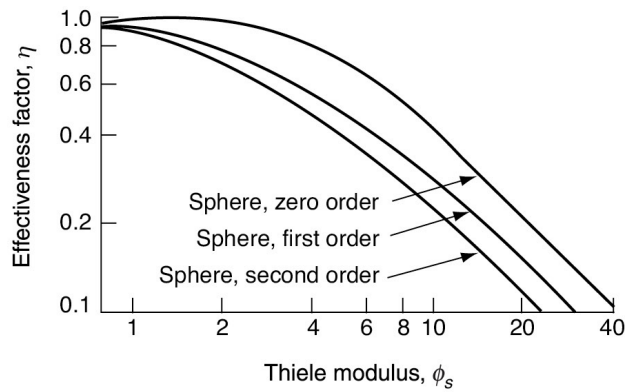
To express the overall rate of reaction in terms of the Thiele modulus, we rearrange Equation (15-28) and use the rate law for a first-order reaction in Equation (15-29)

$$\begin{aligned} -r_A &= \left(\frac{\text{Actual reaction rate}}{\text{Reaction rate at } C_{As}} \right) \times (\text{Reaction rate at } C_{As}) \\ &= \eta (-r_{As}) \end{aligned}$$

For a first-order reaction

$$-r_A = \eta (k_1 C_{As}) \quad (15-34)$$

Limited regimes

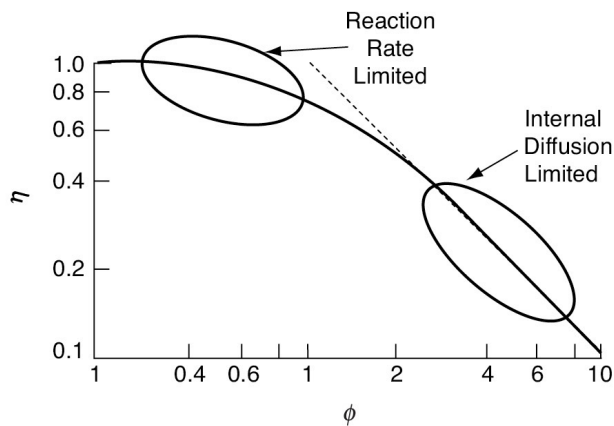


Zero order $\phi_{s0} = R\sqrt{k_0'' S_a \rho_c / D_e C_{A0}} = R\sqrt{k_0 / D_e C_{A0}}$

First order $\phi_{s1} = R\sqrt{k_1'' S_a \rho_c / D_e} = R\sqrt{k_1 / D_e}$

Second order $\phi_{s2} = R\sqrt{k_2'' S_a \rho_c C_{A0} / D_e} = R\sqrt{k_2 C_{A0} / D_e}$

(a)



Sphere $\phi_1 = (R/3)\sqrt{k_1'' S_a \rho_c / D_e} = \frac{R}{3}\sqrt{k_1 / D_e}$

Cylinder $\phi_1 = (R/2)\sqrt{k_1'' S_a \rho_c / D_e} = \frac{R}{2}\sqrt{k_1 / D_e}$

Slab $\phi_1 = L\sqrt{k_1'' S_a \rho_c / D_e} = L\sqrt{k_1 / D_e}$

(b)

Figure 15-6 (a) Effectiveness factor plot for n th-order kinetics on spherical catalyst particles. [Satterfield, C. N. "Mass Transfer in Heterogeneous Catalysis," *AIChE Journal* 16(3) 509–510 (1970). With permission of the American Institute of Chemical Engineers. Copyright © 1970 AIChE. All rights reserved.] (b) First-order reaction in different pellet geometries. [Aris, R. *Introduction to the Analysis of*

Chemical Reactors, 1965, p. 131; reprinted by permission of Pearson Education, Upper Saddle River, NJ.]

Combining Equations (15-33) and (15-34), the overall rate of reaction for a first-order, internal-diffusion-limited reaction is

Note that for catalytic packed beds the rate varies inversely with the particle diameter of the catalyst.

$$-r_A = \frac{3}{R} \sqrt{D_e k_1} C_{As} = \frac{3}{R} \sqrt{D_e S_a \rho_c k_1} C_{As}$$

15.3.2 Effectiveness Factors with Volume Change with Reaction

When there is volume change, $\varepsilon \neq 0$, we use a correction factor to account for this change. The correction is obtained from a plot of the ratio of effective factors

$$\frac{\eta'}{\eta} = \frac{\text{Factor in the presence of volume change}}{\text{Factor in the absence of volume change}}$$

as a function of ε for various values of the Thiele modulus. This plot is given in [Figure 15-7](#).

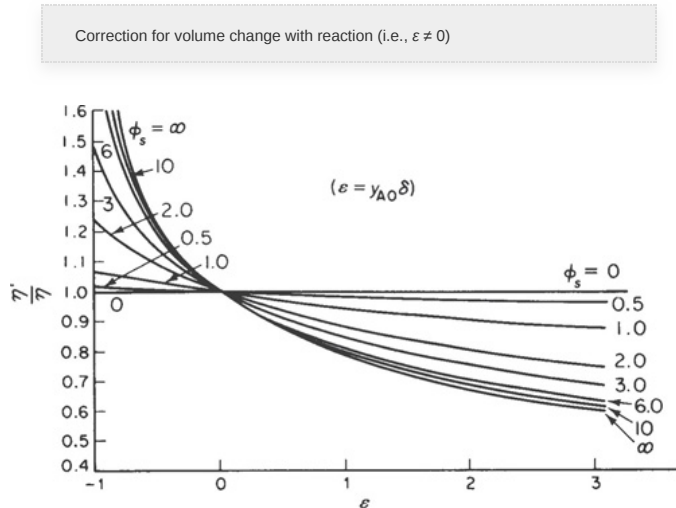


Figure 15-7 Effectiveness factor ratios for first-order kinetics on spherical catalyst pellets for various values of the Thiele modulus of a sphere, ϕ_s , as a function of volume change. [From V. W. Weekman and R. L. Goring, "Influence of Volume Change on Gas-Phase Reactions in Porous Catalysts." *J. Catal.*, 4(2), 260 (1965).]

For example, if the Thiele modulus were 10 for the gas-phase reaction $A \rightarrow 2B$ with ($\varepsilon = 1$), then the effectiveness factor with volume change would be $\eta' = 0.8 \eta$.

15.3.3 Internal-Diffusion-Limited Reactions Other Than First Order

How can the rate of reaction be increased?

To increase the reaction rate, $-r'_A$, for internal-diffusion-limited reactions, we can (1) decrease the radius R (make pellets smaller); (2) increase the temperature; (3) increase the concentration; and (4) increase the internal surface area. For reactions of order n , we have from Equation (15-20)

$$\phi_n^2 = \frac{k_n'' S_a \rho_c R^2 C_{As}^{n-1}}{D_e} = \frac{k_n R^2 C_{As}^{n-1}}{D_e} \quad (15-20)$$

For large values of the Thiele modulus, the effectiveness factor is

$$\eta = \left(\frac{2}{n+1} \right)^{1/2} \frac{3}{\phi_n} = \left(\frac{2}{n+1} \right)^{1/2} \frac{3}{R} \sqrt{\frac{D_e}{k_n}} C_{As}^{(1-n)/2} \quad (15-35)$$

Consequently, for reaction orders greater than 1, the effectiveness factor decreases with increasing concentration at the external pellet surface. We will use this equation when we discuss *Falsified Kinetics*.

15.3.4 Weisz–Prater Criterion for Internal Diffusion Limitations

The Weisz–Prater criterion uses measured values of the rate of reaction, $-r'_A$ (obs), to determine whether internal diffusion is limiting the reaction. This criterion can be developed intuitively for a first-order reaction by first rearranging Equation (15-32) in the form

$$\eta \phi_1^2 = 3 (\phi_1 \coth \phi_1 - 1) \quad (15-36)$$

The left-hand side of Equation (15-36) is the Weisz–Prater parameter, WP:

Showing where the Weisz–Prater comes from

$$WP = \eta \times \phi_1^2 \quad (15-37)$$

$$WP = \frac{\text{Observed (actual) reaction rate}}{\text{Reaction rate evaluated at } C_{As}} \times \frac{\text{Reaction rate evaluated at } C_{As}}{\text{"a" diffusion rate}}$$

$$WP = \frac{\text{Actual reaction rate}}{\text{"a" diffusion rate}}$$

Explore WP using Wolfram LEP P15-3 on the Web site

Substituting for

$$\eta = \frac{-r'_A (\text{obs})}{-r'_{As}} \quad \text{and} \quad \phi_1^2 = \frac{-r'_A S_a \rho_c R^2}{D_e C_{As}} = \frac{-r'_A \rho_c R^2}{D_e C_{As}}$$

in Equation (15-59) we obtain

$$WP = \frac{-r'_A (\text{obs})}{-r'_{As}} \left(\frac{-r'_A \rho_c R^2}{D_e C_{As}} \right) \quad (15-38)$$

$$WP = \eta \phi_1^2 = \frac{-r'_A (\text{obs}) \rho_c R^2}{D_e C_{As}} \quad (15-39)$$

Are there any internal diffusion limitations indicated from the Weisz–Prater criterion?

All the terms in the rhs of Equation (15-39) are either measured or known. Consequently, we can calculate WP to learn whether there are any diffusion limitations.

If

$$WP \ll 1$$

No internal diffusion limitations

there are no diffusion limitations and consequently no concentration gradient exists within the pellet.

However, if

$$WP \gg 1$$

Severe internal diffusion limitations

internal diffusion limits the reaction severely. Ouch!

Example 15-2 Estimating the Thiele Modulus and Effectiveness Factor

The first-order reaction



was carried out over two different-sized pellets. The pellets were contained in a spinning basket reactor that was operated at sufficiently high rotation speeds that external mass transfer resistance was negligible. The results of two experimental runs made under identical conditions are given in [Table E15-2.1](#).

These two experiments yield an enormous amount of information.

1. Estimate the Thiele modulus and effectiveness factor for each pellet.
2. How small should the pellets be made to virtually eliminate all internal diffusion resistance, for example, $\eta = 0.95$?

TABLE E15-2.1 DATA FROM A SPINNING BASKET REACTOR

<u>Measured Rate (obs) (mol/g-cat · s) × 10⁵ Pellet Radius (m)</u>		
Run 1	3.0	0.01
Run 2	15.0	0.001

Solution

(a) Combining Equations (15-36) and (15-39), we obtain

$$WP = \frac{-r'_A(\text{Obs}) R^2 \rho_c}{D_e C_{As}} = \eta \phi_1^2 = 3(\phi_1 \coth \phi_1 - 1) \quad (\text{E15-2.1})$$

Letting the subscripts 1 and 2 refer to runs 1 and 2, we apply Equation (E15-2.1) to runs 1 and 2 and then take the ratio to obtain

$$\frac{-r'_{A_2} R_2^2}{-r'_{A_1} R_1^2} = \frac{\phi_{12} \coth \phi_{12} - 1}{\phi_{11} \coth \phi_{11} - 1} \quad (\text{E15-2.2})$$

The terms ρ_c , D_e , and C_{As} cancel because the runs were carried out under identical conditions. The Thiele modulus is

$$\phi_1 = R \sqrt{\frac{-r'_{As} \rho_c}{D_e C_{As}}} \quad (\text{E15-2.3})$$

Taking the ratio of the Thiele moduli for runs 1 and 2, we obtain

$$\frac{\phi_{11}}{\phi_{12}} = \frac{R_1}{R_2} \quad (\text{E15-2.4})$$

or

$$\phi_{11} = \frac{R_1}{R_2} \phi_{12} = \frac{0.01 \text{ m}}{0.001 \text{ m}} \phi_{12} = 10\phi_{12} \quad (\text{E15-2.5})$$

Substituting for ϕ_{11} in Equation (E15-2.2) above and evaluating and R for runs 1 and 2 gives us

$$\left(\frac{15 \times 10^{-5}}{3 \times 10^{-5}} \right) \frac{(0.001)^2}{(0.01)^2} = \frac{\phi_{12} \coth \phi_{12} - 1}{10\phi_{12} \coth(10\phi_{12}) - 1} \quad (\text{E15-2.6})$$

$$0.05 = \frac{\phi_{12} \coth \phi_{12} - 1}{10\phi_{12} \coth(10\phi_{12}) - 1} \quad (15-2.7)$$

We now have one equation and one unknown. Solving Equation (E15-2.7) we find that

$\phi_{12} = 1.65$	for $R_2 = 0.001 \text{ m}$
Then	
$\phi_{11} = 10\phi_{12} = 16.5$	for $R_1 = 0.01 \text{ m}$

The corresponding effectiveness factors

Given two experimental points, one can predict the particle size where internal mass transfer does not limit the rate of reaction.

$$\text{For } R_2 : \eta_2 = \frac{3(\phi_{12} \coth \phi_{12} - 1)}{\phi_{12}^2} = \frac{3(1.65 \coth 1.65 - 1)}{(1.65)^2} = 0.856$$

$$\text{For } R_1 : \eta_1 = \frac{3(16.5 \coth 16.5 - 1)}{(16.5)^2} \approx \frac{3}{16.5} = 0.182$$

(b) Next we calculate the particle radius needed to virtually eliminate internal diffusion control (say, $\eta = 0.95$)

$$0.95 = \frac{3(\phi_{13} \coth \phi_{13} - 1)}{\phi_{13}^2} \quad (\text{E15-2.8})$$

The solution to Equation (E15-2.8) yields $\phi_{13} = 0.9$

$$R_3 = R_1 \frac{\phi_{13}}{\phi_{11}} = (0.01) \left(\frac{0.9}{16.5} \right) = 5.5 \times 10^{-4} \text{ m}$$

A particle size of 0.55 mm is necessary to virtually eliminate diffusion control (i.e., $\eta = 0.95$).

Only two data points were necessary.

Analysis: This example is important because it shows us how, with only two measurements and some assumptions, we can determine internal diffusion limitations for the two pellet sizes, and predict the pellet size necessary to completely eliminate internal diffusion.

15.4 FALSIFIED KINETICS

You may not be measuring what you think you are.

There are circumstances under which the measured reaction order and activation energy are not the true values. Consider the case in which we obtain reaction-rate data in a differential reactor at two different temperatures, T_1 and T_2 , where precautions are taken to virtually eliminate external mass transfer resistance (i.e., $C_{As} = C_{Ab}$). From these data, we construct a log-log plot of the measured rate of reaction $-r'_A$ as a function of the gas-phase concentration, C_{As} (Figure 15-8). The slope of this plot is the apparent reaction order n' and the measured rate law takes the form

Measured rate:

$$-r'_{Am} = k'_n C_{As}^{n'} \quad (15-40)$$

We will now proceed to relate this measured reaction order n' to the true reaction order n . Using the definition of the effectiveness factor, noting that the

Measured rate with apparent reaction order n'

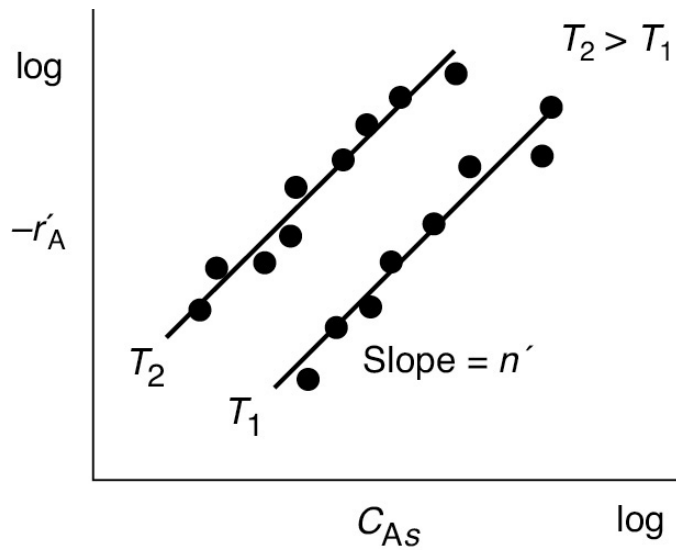


Figure 15-8 Determining the apparent reaction order ($-r_A = \rho_b (-r'_A)$).

actual rate, $-r'_A$, is the product of η and the rate of reaction evaluated at the external surface, $k_n C_{As}^n$, for example,

Actual rate:

$$-r'_A = \eta(-r'_{As}) = \eta(k_n C_{As}^n) \quad (15-41)$$

For large values of the Thiele modulus, ϕ_n , where internal mass transfer is limiting, we can use Equation (15-35) to substitute into Equation (15-41) to obtain

$$-r'_A = \frac{3}{\phi_n} \sqrt{\frac{2}{n+1}} k_n C_{As}^n = \frac{3}{R} \sqrt{\frac{D_e}{k_n}} C_{As}^{1-n} \sqrt{\frac{2}{n+1}} k_n C_{As}^n$$

Simplifying

$$-r'_A = \frac{3}{R} \sqrt{\frac{2D_e}{(n+1)}} k_n^{1/2} C_{As}^{(n+1)/2} \quad (15-42)$$

We equate the true reaction rate, Equation (15-42), to the measured reaction rate, Equation (15-40), to get

$$-r'_A = \sqrt{\frac{2}{n+1}} \left(\frac{3}{R} \sqrt{D_e} k_n^{1/2} C_{As}^{(n+1)/2} \right) = \overbrace{k'_n C_{As}^{n'}}^{\text{Measured Apparent}} \quad (15-43)$$

The functional dependence of the reaction rate on concentration **must** be the same for both the measured rate and the theoretically predicted rate

$$C_{As}^{(n+1)/2} = C_{As}^{n'}$$

therefore the measured apparent reaction order n' (n_{Apparent}) is related to the true reaction order n (n_{True}) by

The true and the apparent reaction order

$$n' = \frac{1+n}{2} \quad (15-44)$$

In addition to an apparent reaction order, there is also an apparent activation energy, E_{App} . This value is the activation energy we would calculate using the experimental data from the slope of a plot of $\ln(-r'_A)$ as a function of $(1/T)$ at a fixed concentration of A. Substituting for the measured and true specific reaction rates in terms of the activation energy gives

$$\underbrace{k'_n = A_{\text{App}} e^{-E_{\text{App}}/RT}}_{\text{Measured}} : \underbrace{k_n = A_T e^{-E_T/RT}}_{\text{True}}$$

into Equation (15-43), we find that

$$n_{\text{true}} = 2n_{\text{apparent}} - 1$$

$$-r'_A = \left(\frac{3}{R} \sqrt{\frac{2}{n+1}} D_e \right) A_T^{1/2} \left[\exp \left(\frac{-E_T}{RT} \right) \right]^{1/2} C_{As}^{(n+1)/2} = A_{\text{App}} \left[\exp \left(\frac{-E_{\text{App}}}{RT} \right) \right] C_{As}^{n'}$$

Taking the natural log of both sides gives us

$$\ln \left[\frac{3}{R} \sqrt{\frac{2}{n+1}} D_e A_T^{1/2} C_{As}^{(n+1)/2} \right] - \frac{E_T}{2RT} = \ln [A_{\text{App}} C_{As}^{n'}] - \frac{E_{\text{App}}}{RT} \quad (15-45)$$

where E_T is the true activation energy.

As with the dependence of reaction rate on concentration, the temperature dependence must be the same for the analytical rate. Comparing the temperature-dependent terms on the right- and left-hand sides of Equation (15-45), we see that the true activation energy is equal to twice the apparent activation energy.

The true activation energy

$$E_T = 2E_{\text{App}} \quad (15-46)$$

Important industrial consequence of falsified kinetic runaway reactions. Safety considerations!

This measurement of the apparent reaction order and activation energy results primarily when internal diffusion limitations are present and is referred to as *disguised* or *falsified kinetics*. Serious consequences could occur if the laboratory data were taken in the disguised regime and the reactor were operated in a different regime. For example, what if the particle size were reduced so that internal diffusion limitations became negligible? The higher activation energy, E_T , could cause the reaction to be much more temperature sensitive, and there is the possibility for *runaway reaction conditions* causing an explosion to occur.

15.5 OVERALL EFFECTIVENESS FACTOR

For first-order reactions, we can use an overall effectiveness factor to help us analyze diffusion, flow, and reaction in packed beds. We now consider a situation where external **and** internal resistance to mass transfer to and within the pellet are of the same order of magnitude (Figure 15-9). At steady state, the transport of the reactant(s) from the bulk fluid to the external surface of the catalyst is equal to the net rate of reaction of the reactant within and on the pellet.

Here, both internal and external diffusion are important.

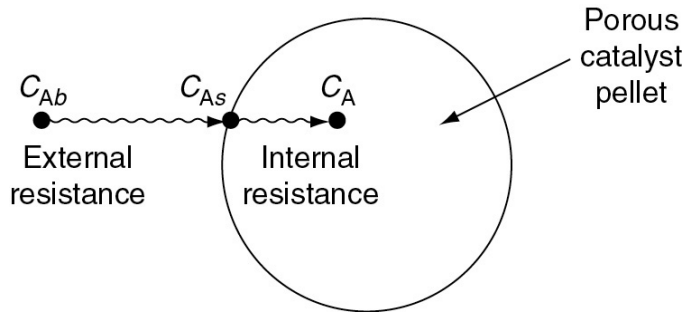


Figure 15-9 Mass transfer and reaction steps.

The molar rate of mass transfer from the bulk fluid to the *external* surface is

$$\begin{aligned}
 \text{Molar rate} &= (\text{Molar flux } C_{Ab} \text{ to } C_{As}) \cdot (\text{External surface area}) \\
 M_A &= W_{Ar} \cdot (\text{External surface area/Volume}) (\text{Reactor volume}) \\
 &= W_{Ar} \cdot a_c \Delta V \quad (15-47)
 \end{aligned}$$

where a_c is the external surface area per unit reactor volume (cf. [Chapter 14](#)) and ΔV is the reactor volume.

This molar rate of mass transfer to the surface, M_A , is also equal to the net (total) rate of reaction *on and within* the pellet

$$M_A = (-r_A'') \times (\text{External area} + \text{Internal area})$$

$$\begin{aligned}
 \text{External area} &= \frac{\text{External area}}{\text{Reactor volume}} \times \text{Reactor volume} \\
 &= a_c \Delta V
 \end{aligned}$$

$$\begin{aligned}
 \text{Internal area} &= \frac{\text{Internal area}}{\text{Mass of catalyst}} \times \frac{\text{Mass of catalyst}}{\text{Volume of catalyst}} \times \frac{\text{Volume of catalyst}}{\text{Reactor volume}} \times \text{Reactor volume} \\
 &= S_a \times \rho_c \times (1 - \phi) \times \Delta V \\
 &= \left[\frac{\text{m}^2}{\text{g}} \times \frac{\text{g}}{\text{m}^3} \times \text{m}^3 \right] \\
 &= S_a \overbrace{\rho_c (1 - \phi)}^{\rho_b} \Delta V \\
 &= S_a \rho_b \Delta V
 \end{aligned}$$

$$\begin{aligned}
 \rho_b &= \text{Bulk density} \\
 &= \rho_c (1 - \phi) \\
 \phi &= \text{porosity}
 \end{aligned}$$

See nomenclature note in Example 15-4.

Recall that ρ_c is the density of catalyst pellet, kg per volume of pellet and ρ_b is the bulk density of catalyst in the reactor, kg-cat per reactor volume.

We now combine the above equations for external surface area and internal surface area with Equations (15-47) to obtain total molar flow into all the catalyst in volume ΔV

$$\boxed{M_A = -r_A'' [a_c \Delta V + S_a \rho_b \Delta V]} \quad (15-48)$$

Combining Equations (15-47) and (15-48), and canceling the volume ΔV , we see the flux to the pellet surface, $W_{Az}a_c$, is equal to the rate of consumption of A *in and on* the catalyst.

$$W_{Az}a_c = -r_A'' \cdot (a_c + S_a \rho_b)$$

For most catalysts, the internal surface area is much greater than the external surface area (i.e., $S_a \rho_b \gg a_c$), in which case we have

$$W_{Az}a_c = -r_A'' S_a \rho_b$$

Comparing units on the r.h.s. and l.h.s. of Equation (15-49), we find no inconsistencies, that is,

$$\left[\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \cdot \frac{\text{m}^2}{3} \right] = \left[\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \left(\frac{\text{m}^2}{\text{g}} \right) \frac{\text{g}}{\text{m}^3} \right]$$

where $-r_A''$ is the overall rate of reaction within and on the pellet per unit surface area, $-r_A'$ is the rate of reaction per mass of catalyst

$$-r_A' = -r_A'' S_a$$

and $-r_A$ is the overall rate per volume of reactor, that is,

$$-r_A = r_A'' \rho_b$$

then

$$\boxed{W_{Az}a_c = -r_A = -r_A'' S_a \rho_b} \quad (15-49)$$

with the corresponding units for each term in Equation (15-49) shown below.

$$\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \times \frac{\text{m}^2}{\text{m}^3} = \frac{\text{mol}}{\text{m}^3 \cdot \text{s}} = \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \times \frac{\text{m}^2}{\text{g-cat}} \times \frac{\text{g-cat}}{\text{m}^3}$$

Again, we find no inconsistencies.

The relationship for the rate of mass transport to the external catalyst surface is

$$M_A = W_{Ar} a_c \Delta V = k_c (C_{Ab} - C_{As}) a_c \Delta V \quad (15-50)$$

$$\left[\frac{\text{mol}}{\text{s}} \right] = \left[\left(\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right) \left(\frac{\text{m}^2}{\text{m}^3} \right) \text{m}^3 \right] = \left[\left(\frac{\text{m}}{\text{s}} \right) \left(\frac{\text{mol}}{\text{m}^3} \right) \left(\frac{\text{m}^2}{\text{m}^3} \right) \text{m}^3 \right]$$

Again, comparing units on the l.h.s. and r.h.s., *no inconsistencies*

where k_c is the external mass transfer coefficient (m/s) discussed in [Section 14.4](#). Because internal diffusion resistance is also significant, not all of the interior surface of the pellet is accessible to the concentration at the external surface of the pellet, C_{As} . We have already learned that the effectiveness factor is a measure of the internal surface accessibility (see [Equation \(15-41\)](#)):

$$-r_A = -r_{As} \eta$$

$$\left[\begin{array}{c} \text{Actual} \\ \text{rate} \end{array} \right] = \left[\begin{array}{c} \text{Rate at} \\ \text{surface} \\ \text{conditions} \end{array} \right] \left[\frac{\text{Actual rate}}{\text{Rate at surface conditions}} \right]$$

Assuming that the surface reaction is first order with respect to A, we can utilize the internal effectiveness factor to write

$$-r_A = \eta k_1 C_{As} \quad (15-51)$$

Recall that

$$(k_1 = k_1'' S_a \rho_b)$$

We need to eliminate the surface concentration from any equation involving the rate of reaction or rate of mass transfer, because C_{As} cannot be measured by standard techniques. To accomplish this elimination, we use [Equations \(15-49\)](#), [\(15-50\)](#), and [\(15-51\)](#) in order to equate the mass transfer rate of A to the pellet surface, $-W_{Ar} a_c$, to the rate of consumption of A within the pellet, $\eta k_1 C_{As}$

$$W_{Ar}a_c = \eta k_1 C_{As}$$

Then substitute for $W_{Ar}a_c$ using Equation (15-50)

$$k_c a_c (C_{Ab} - C_{As}) = \eta k_1 C_{As} \quad (15-52)$$

Solving for C_{As} , we obtain

$$C_{As} = \frac{k_c a_c}{k_c a_c + \eta k_1} C_{Ab} \quad (15-53)$$

Concentration at the pellet surface as a function of bulk gas concentration

Substituting for C_{As} in Equation (15-51) gives

$$-r_A = \frac{\eta k_1 k_c a_c C_{Ab}}{k_c a_c + \eta k_1} \quad (15-54)$$

In discussing the surface accessibility, we defined the internal effectiveness factor η with respect to the concentration at the external surface of the pellet, C_{As} , as

$$\eta = \frac{\text{Actual overall rate of reaction}}{\text{Rate of reaction that would result if entire interior surface were exposed to the external pellet surface conditions, } C_{As}, T_s} \quad (15-28)$$

Two different effectiveness factors

We now define an overall effectiveness factor that is based on the bulk concentration

$$\Omega = \frac{\text{Actual overall rate of reaction}}{\text{Rate that would result if the entire surface were exposed to the bulk conditions, } C_{Ab}, T_b} \quad (15-55)$$

Dividing the numerator and denominator of Equation (15-54) by $k_c a_c$, we obtain the net rate of reaction, $-r_A$, in terms of the bulk fluid concentration, which is a measurable quantity:

$$-r_A = \frac{\eta}{1 + \frac{\eta k_1}{k_c a_c}} k_1 C_{Ab} \quad (15-56)$$

The actual rate of reaction is related to the reaction rate evaluated at the bulk concentration of A. Consequently, the overall rate of reaction in terms of the bulk concentration C_{Ab} is

$$-r_A = \Omega (-r_{Ab}) = \Omega k_1 C_{Ab} \quad (15-57)$$

where the overall effectiveness factor is

Overall effectiveness factor for a first-order reaction

$$\Omega = \frac{\eta}{1 + \frac{\eta k_1}{k_c a_c}} \quad (15-58)$$

Let's look at some limiting situations for the overall effectiveness factor. First note that the rates of reaction based on surface and bulk concentrations are related by

$$-r_A = \Omega (-r_{Ab}) = \eta (-r_{As}) \quad (15-59)$$

where

$$\begin{aligned} -r_{As} &= k_1 C_{As} \\ -r_{Ab} &= k_1 C_{Ab} \end{aligned}$$

The actual rate can be expressed in terms of the rate per unit volume, $-r_A$, the rate per unit mass, $-r'_A$, and the rate per unit surface area, $-r''_A$, which are related by the equation

$$-r_A = -r'_A \rho_b = -r''_A S_a \rho_b$$

Recall that k''_1 is given in terms of the catalyst surface area ($\text{m}^3/\text{m}^2 \cdot \text{s}$), k'_1 is given in terms of catalyst mass ($\text{m}^3/\text{g-cat} \cdot \text{s}$), and k_1 (1/s) is given in terms of reactor volume

$$k_1 = \rho_b k'_1 = \rho_b \cdot S_a \cdot k''_1$$

We saw in [Chapter 14](#) that as the velocity of the fluid increases, the external mass transfer coefficient k_c increases (cf. Equation 14-46). Consequently, for large flow rates resulting in large values of the external mass transfer coefficient k_c , we can neglect the ratio in the denominator

High flow rates of fluid

$$\Omega = \frac{\eta}{1 + \frac{\eta k_1}{k_c a_c}} \approx \eta$$

Neglect

and the overall effectiveness factor approaches the internal effectiveness factor

$$\boxed{\Omega \equiv \eta} \quad (15-60)$$

Now let's consider the case where the ratio of $\left(\frac{\eta k_1}{k_c a_c}\right)$ is very small, then

$$\Omega = \frac{\eta}{1 + \frac{\eta k_1}{k_c a_c}}$$

Neglect 1

External diffusion limits

The overall effectiveness factor for external diffusion control is

$$\boxed{\Omega = \frac{k_c a_c}{k_1}} \quad (15-61)$$

15.6 ESTIMATION OF DIFFUSION- AND REACTION-LIMITED REGIMES

Dial soap

In many instances it is of interest to obtain “quick and dirty” estimates to learn which is the rate-limiting step in a heterogeneous reaction.

15.6.1 Mears Criterion for External Diffusion Limitations

The Mears criterion, like the Weisz–Prater criterion, uses the measured rate of reaction, $-r'_A$, (kmol/kg-cat·s) to learn whether *external mass transfer* from the bulk gas phase to the catalyst surface can be neglected.³ The Mears number, MR, is

³ D. E. Mears, *Ind. Eng. Chem. Process Des. Dev.*, 10, 541 (1971). Other interphase transport-limiting criteria can be found in *AIChE Symp. Ser.* 143 (S. W. Weller, ed.), 70 (1974).

Is external diffusion limiting?

$$MR = \frac{-r'_A \text{ (obs)} \rho_b R n}{k_c C_{Ab}} \quad (15-62)$$

The Mears number can be used to establish external mass transfer limitations

Here, we measure $-r'_A \text{ (obs)}$, C_{Ab} , ρ_b , R and n , and then calculate k_c to determine MR, where

n = reaction order

R = catalyst particle radius, m

ρ_b = bulk density of catalyst bed, kg/m³
 $= (1 - \phi)\rho_c$ (ϕ = porosity)

ρ_c = solid density of catalyst pellet, kg/m³

C_{Ab} = bulk reactant concentration, mol/dm³

k_c = mass transfer coefficient, m/s

Mears proposed that when

$$MR < 0.15$$

external mass transfer effects can be neglected and no concentration gradient exists between the bulk gas and external surface of the catalyst pellet. This proposal by Mears was endorsed unanimously by the Jofostan legislature. The mass transfer coefficient can be calculated from the appropriate correlation, such as that of Thoenes–Kramers, for the flow conditions through the bed.

Mears also proposed that the bulk fluid temperature, T , will be virtually the same as the temperature at the external surface of the pellet when

$$T_b \cong T_s$$

$$\left| \frac{-\Delta H_{\text{Rx}}(-r'_A)\rho_b RE}{hT^2 R_g} \right| < 0.15 \quad (15-63)$$

where

- h = heat transfer coefficient between gas and pellet, $\text{kJ/m}^2 \cdot \text{s} \cdot \text{K}$
 R_g = gas constant, $8.314 \text{ J/mol} \cdot \text{K}$
 ΔH_{Rx} = heat of reaction, kJ/mol
 E = activation energy, kJ/kmol

and the other symbols are as in Equation (15-62).

15.7 MASS TRANSFER AND REACTION IN A PACKED BED

We now consider the same isomerization taking place in a packed bed of catalyst pellets rather than on one single pellet (see Figure 15-10). The concentration C_{Ab} is the bulk gas-phase concentration of A at any point along the length of the bed.

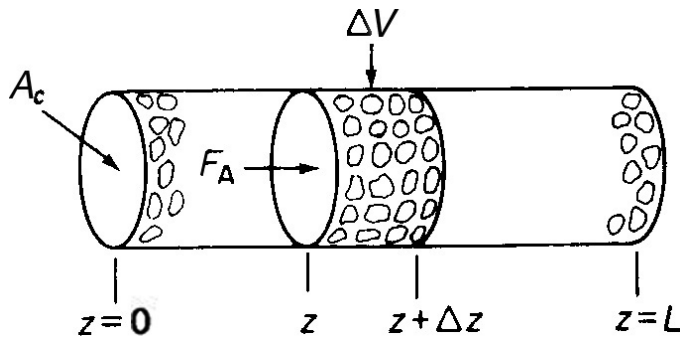


Figure 15-10 Packed-bed reactor.

We shall perform a balance on species A over the volume element, ΔV , neglecting any radial variations in concentration and assuming that the bed is operated at steady state. The following symbols will be used in developing our model:

- A_c = cross-sectional area of the tube containing the catalyst, dm^2
 C_{Ab} = bulk gas concentration of A, mol/dm^3
 ρ_b = bulk density of the catalyst bed, g/dm^3
 v_0 = volumetric flow rate, dm^3/s
 U = superficial velocity $= v_0/A_c$, dm/s

Mole Balance

A mole balance on ΔV , the volume element ($A_c \Delta z$), yields

$$\begin{aligned} [\text{Rate in}] - [\text{Rate out}] + [\text{Rate of formation of A}] &= 0 \\ A_c W_{Az}|_z - A_c W_{Az}|_{z+\Delta z} + r'_A \rho_b A_c \Delta z &= 0 \end{aligned}$$

Dividing by $A_c \Delta z$ and taking the limit as $\Delta z \rightarrow 0$ yields

$$-\frac{dW_{Az}}{dz} + \overbrace{r'_A \rho_b}^{r_A} = 0 \quad (15-64)$$

Combining Equation (14-4) and (14-6), we get

$$W_{Az} = -D_{AB} \frac{dC_{Ab}}{dz} + y_{Ab} (W_{Az} + W_{Bz})$$

Also, writing the bulk flow term in the form

$$B_{Az} = y_{Ab} (W_{Az} + W_{Bz}) = y_{Ab} cU = UC_{Ab}$$

Equation (15-64) can be written in the form

$$D_{AB} \frac{d^2 C_{Ab}}{dz^2} - U \frac{dC_{Ab}}{dz} + r_A = 0 \quad (15-65)$$

Now we will see how to use η and Ω to calculate conversion in a packed bed.

The term $D_{AB}(d^2 C_{Ab}/dz^2)$ is used to represent either *diffusion* and/or *dispersion* in the axial direction. Consequently, we shall use the symbol D_a for the dispersion coefficient to represent either or both of these cases. We will come back to this form of the diffusion equation when we discuss dispersion in Chapter 18 (cf. Equation (18-16)). The overall reaction rate, $-r_A$, is a function of the reactant concentration within the catalyst. This overall rate can be related to the rate of reaction of A that would exist if the entire surface were exposed to the bulk concentration C_{Ab} through the overall effectiveness factor Ω

$$-r_A = -r_{Ab} \Omega \quad (15-57)$$

For the first-order reaction considered here

$$-r_A = \Omega k_1 C_{Ab} \quad (15-66)$$

Substituting this equation for $-r_A$ into Equation (15-65), we form the differential equation describing diffusion with a first-order reaction in a catalyst bed

$$D_a \frac{d^2 C_{Ab}}{dz^2} - U \frac{dC_{Ab}}{dz} - \Omega k_1 C_{Ab} = 0 \quad (15-67)$$

Flow and first-order reaction in a packed bed

As will be shown in Chapter 18, the solution to Equations (15-67) and (18-16) can be quite complicated depending on the boundary conditions and assumptions. Consequently for now, we will only discuss one approximate solution. We shall solve this equation for the case in which the flow rate through the bed is very large and the axial diffusion can be neglected. Young and Finlayson have shown that axial dispersion can be neglected when⁴

⁴ L. C. Young and B. A. Finlayson, *Ind. Eng. Chem. Fund.*, 12, 412.

Criterion for neglecting axial dispersion/diffusion

$$\frac{-r_{A(\text{obs})} d_p}{U_0 C_{Ab}} < \frac{U_0 d_p}{D_a} \quad (15-68)$$

where U_0 is the superficial velocity, d_p is the particle diameter, and D_a is the effective axial dispersion coefficient. In Chapter 18 we will consider solutions to the complete form of Equation (15-67).

Neglecting axial dispersion with respect to forced axial convection

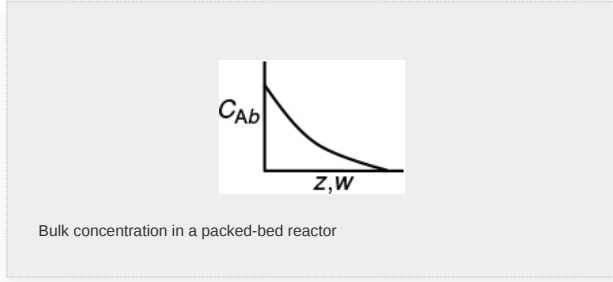
$$\left| U \frac{dC_{Ab}}{dz} \right| \gg \left| D_a \frac{d^2 C_{Ab}}{dz^2} \right|$$

Equation (15-67) can be arranged in the form

$$\frac{dC_{Ab}}{dz} = - \frac{\Omega k_1 C_{Ab}}{U} \quad (15-69)$$

With the aid of the boundary condition at the entrance of the reactor

$$C_{Ab} = C_{Ab0} \quad \text{at } z = 0$$

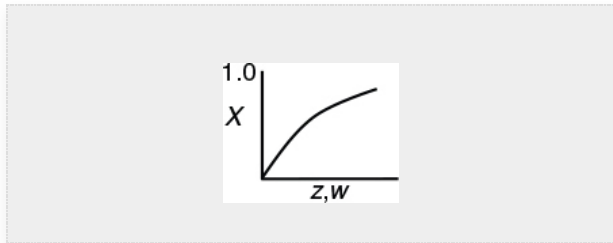


$$C_{Ab} = C_{Ab0} \exp \left[-\frac{\Omega k_1 z}{U} \right] \quad (15-70)$$

Recall we can easily relate the distance z to the catalyst weight down the reactor, W , using the bulk density, ρ_b , that is,

$$W = \rho_b A_c z$$

The conversion at the reactor's exit, $z = L$, is



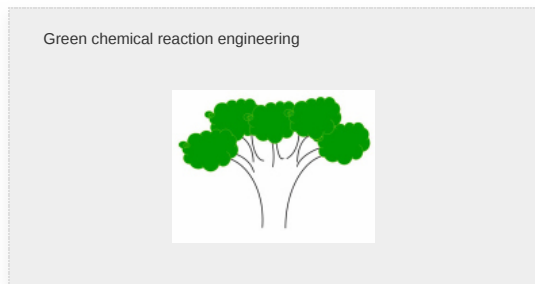
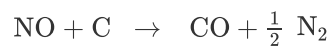
$$X = 1 - \frac{C_{Ab}}{C_{Ab0}} = 1 - \exp \left[-\frac{k_1 \Omega L}{U} \right] \quad (15-71)$$

The sketch of the corresponding conversion profile is shown in the margin.

Example 15–3 Reducing Nitrous Oxides in a Plant's Effluent[†]

[†]This is a **Stop and Smell the Roses** Example. Exploring this LEP Example with Wolfram and/or Python that will give you a fantastic intuitive feel of the parameters and conditions that result in internal and external diffusion limitations.

We have seen that Nitric Oxide (NO) plays an important role in smog formation and there are great incentives for reducing its concentration in the atmosphere. It is proposed to reduce the concentration of NO in an effluent stream from a plant by passing it through a packed bed of spherical, porous carbonaceous solid pellets. A 2% NO and 98% air mixture flows at a rate of $1 \times 10^{-6} \text{ m}^3/\text{s}$ ($0.001 \text{ dm}^3/\text{s}$) through a 2-in.-ID tube packed with porous solid pellets at a temperature of 1173 K and a pressure of 101.3 kPa. The reaction



is pseudo first order in NO because of the excess of carbon surface area; that is,

$$-r'_{\text{NO}} = k_1'' S_a C_{\text{NO}}$$

and occurs primarily in the pores inside the pellet, where

$$S_a = \text{Internal surface area} = 530 \text{ m}^2/\text{g}$$

$$k_1'' = 4.42 \times 10^{-10} \text{ m}^3/\text{m}^2 \cdot \text{s}$$

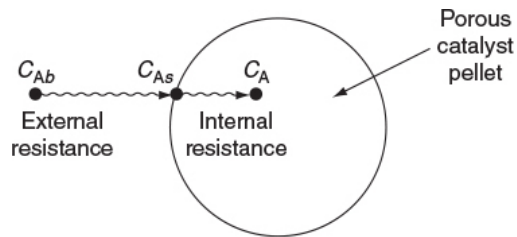
$$k_1' = k_1'' S_a = [4.42 \times 10^{-10} \text{ m}^3/\text{m}^2 \cdot \text{s}] \left[530 \frac{\text{m}^2}{\text{g}} \right] = 2.34 \times 10^{-7} \text{ m}^3/\text{g} \cdot \text{s}$$

From those values of k_1'' and k_1' we find

$$k_1 = \rho_b k_1' = (1.4 \times 10^{-6} \text{ g}/\text{m}^3) (2.34 \times 10^{-7} \text{ m}^3/\text{g} \cdot \text{s}) = 0.328 \text{ s}^{-1}$$



1. Derive an equation to find the conversion profiles, $X = f(W)$.
2. Calculate the Thiele modulus ϕ_1 and the η internal effectiveness factor.
3. Calculate the Weisz–Prater parameter, WP. Is internal mass transfer limiting?
4. Calculate the overall effectiveness factor, Ω
5. Calculate the Mears parameter, MR. Is external mass transfer limiting?
6. Calculate the weight of solid porous catalyst necessary to reduce the NO concentration of 0.004%, which is below the Environmental Protection Agency's limit.



Additional information:

At 1173 K, the fluid properties are

$$\begin{aligned}\nu &= \text{Kinematic viscosity} = 1.53 \times 10^{-8} \text{ m}^2/\text{s} \\ D_e &= \text{Effective diffusivity} = 1.82 \times 10^{-8} \text{ m}^2/\text{s} \\ D_{AB} &= \text{Gas diffusivity} = 2.0 \times 10^{-8} \text{ m}^2/\text{s}\end{aligned}$$

Also see the Web site www.rowan.edu/greenengineering

The properties of the catalyst and bed are

$$\begin{aligned}\rho_c &= \text{Density of catalyst particle} = 2.8 \text{ g/cm}^3 = 2.8 \times 10^6 \text{ g/m}^3 \\ \phi &= \text{Bed porosity} = 0.5 \\ \rho_b &= \text{Bulk density of bed} = \rho_c(1 - \phi) = 1.4 \times 10^6 \text{ g/m}^3 \\ R &= \text{Pellet radius} = 3 \times 10^{-3} \text{ m} \\ \gamma &= \text{Sphericity} = 1.0\end{aligned}$$

Solution

1. Find X and the $W = f(X)$

It is desired to reduce the NO concentration from 2.0% to 0.004%. Neglecting any volume change at these low concentrations gives us the exit conversion

$$X = \frac{C_{Ab0} - C_{Ab}}{C_{Ab0}} = \frac{2 - 0.004}{2} = 0.998$$

where A represents NO.

The variation of NO down the length of the reactor is given by Equation (15-69). Replacing k_1 by $k'_1\rho_b$

$$\frac{dC_{Ab}}{dz} = -\frac{\Omega k_1 C_{Ab}}{U} = -\Omega \frac{k'_1 \rho_b C_{Ab}}{U} \quad (15-69)$$

Multiplying the denominator on the right and left hand sides of Equation (15-69) by the cross-sectional area, A_c , and realizing that the weight of the catalyst up to a point z in the bed is

$$\begin{array}{c} \text{(Mole balance)} \\ + \\ \text{(Rate law)} \\ + \\ \text{(Overall effectiveness factor)} \end{array}$$

$$W = \rho_b A_c z$$

the variation of NO concentration with solids is

$$\frac{dC_{Ab}}{dW} = -\frac{\Omega k'_1 C_{Ab}}{A_c U} \quad (\text{E15-3.1})$$

Because NO is present in dilute concentrations (i.e., $y_{A0} \ll 1$), we shall take $\varepsilon \ll 1$ and set $A_c U = v_0$. We integrate Equation (E15-3.1) using the boundary condition that when $W = 0$, then $C_{Ab} = C_{Ab0}$

$$X - \left(1 - \frac{C_{Ab}}{C_{Ab0}}\right) = 1 - \exp\left(-\frac{\Omega k'_1 W}{v_0}\right) \quad (\text{E15-3.2})$$

where

$$\Omega = \frac{\eta}{1 + \eta \frac{k'_1 \rho_b}{k_c a_c}} \quad (15-58)$$

Rearranging, we have

$$W = \frac{v_0}{\Omega k'_1} \ln \frac{1}{1 - X} \quad (E15-3.3)$$

2. Calculating the internal effectiveness factor for spherical pellets in which a first-order reaction is occurring, we obtained

$$\eta = \frac{3}{\phi_1^2} (\phi_1 \coth \phi_1 - 1) \quad (15-32)$$

As a first approximation, we shall neglect any changes in the pellet size resulting from the reactions of NO with the porous carbon. The Thiele modulus for this system is⁵

⁵ L. K. Chan, A. F. Sarofim, and J. M. Beer, *Combust. Flame*, 52, 37.

$$\phi_1 = R \sqrt{\frac{k'_1 \rho_c}{D_e}} = R \sqrt{\frac{k''_1 S_a \rho_c}{D_e}} \quad (E15-3.4)$$

where

$$R = \text{pellet radius} = 3 \times 10^{-3} \text{ m}$$

$$D_e = \text{effective diffusivity} = 1.82 \times 10^{-8} \text{ m}^2/\text{s}$$

$$\rho_c = \text{catalyst pellet density} = 2.8 \text{ g/cm}^3 = 2.8 \times 10^6 \text{ g/m}^3$$

$$k''_1 = \text{specific reaction rate (m/s)} = 4.42 \times 10^{-10} \text{ m}^3/\text{m}^2/\text{s}$$

Substituting in Equation (E15-3.4)

$$\phi_1 = 0.003 \text{ m} \sqrt{\frac{(4.42 \times 10^{-10} \text{ m/s})(530 \text{ m}^2/\text{g})(2.8 \times 10^6 \text{ g/m}^3)}{1.82 \times 10^{-8} \text{ m}^2/\text{s}}}$$

$$\phi = 18$$

Because ϕ_1 is large

$$\eta \cong \frac{3}{\phi_1} = \frac{3}{18} = 0.167$$

3. Calculate WP

$$\begin{aligned}\text{WP} &= \eta \phi_1^2 \\ &= (0.167)(18)^2 = 54.\end{aligned}$$

WP \gg 1 and internal diffusion limits the reaction

4. Calculate the overall effectiveness factor (a) To calculate we first need to calculate the external mass transfer coefficient, we will use the Thoenes–Kramers correlation. From Chapter 14 we recall

(a) To calculate Ω we first need to calculate the external mass transfer coefficient, we will use the Thoenes–Kramers correlation. From Chapter 14 we recall

$$\text{Sh}' = (\text{Re}')^{1/2} \text{Sc}^{1/3} \quad (14-76)$$

For a 2-in.-ID pipe, $A_c = 2.03 \times 10^{-3} \text{ m}^2$. The superficial velocity is

$$U = \frac{v_0}{A_c} = \frac{10^{-6} \text{ m}^3/\text{s}}{2.03 \times 10^{-3} \text{ m}^2} = 4.93 \times 10^{-4} \text{ m/s}$$

Procedure

Calculate
Re'
Sc
Then
Sh'
Then
 k_c

Assuming a shape factor of 1.0

$$\text{Re}' = \frac{U d_p}{(1 - \phi) \nu} = \frac{(4.93 \times 10^{-4} \text{ m/s})(6 \times 10^{-3} \text{ m})}{(1 - 0.5)(1.53 \times 10^{-8} \text{ m}^2/\text{s})} = 386.7$$

Nomenclature note: ϕ with subscript 1, ϕ_1 = Thiele modulus
 ϕ without subscript, ϕ = porosity

$$SC = \frac{\nu}{D_{AB}} = \frac{1.53 \times 10^{-8} \text{ m}^2/\text{S}}{2.0 \times 10^{-8} \text{ m}^2/\text{S}} = 0.765$$

$$Sh' = (0.386)^{1/2} (0.765)^{1/3} = (19.7)(0.915) = 18.0$$

$$k_c = \frac{1-\phi}{\phi} \left(\frac{D_{AB}}{d_p} \right) Sh' = \frac{0.5}{0.5} \left(\frac{2.0 \times 10^{-8} \text{ (m}^2/\text{s)}}{6.0 \times 10^{-3} \text{ m}} \right) (18.0)$$

$$k_c = 6 \times 10^{-5} \text{ m/s}$$

(b) *Calculating the external area per unit reactor volume*, we obtain

$$a_c = \frac{6(1-\phi)}{d_p} = \frac{6(1-0.5)}{6 \times 10^{-3} \text{ m}} \quad (\text{E15-3.5})$$

$$= 500 \text{ m}^2/\text{m}^3$$



This example is long and detailed. Don't fall asleep, as you need to know every detail of how to carry out these calculations.

5. Evaluating the overall effectiveness factor.

Substituting into Equation (15-58), we have

$$\Omega = \frac{\eta}{1 + \eta k_1'' S_a \rho_b / k_c a_c}$$

$$\Omega = \frac{0.167}{1 + \frac{(0.167) (4.4 \times 10^{-10} \text{ m}^3/\text{m}^2 \cdot \text{s}) (530 \text{ m}^2/\text{g}) (1.4 \times 10^6 \text{ g/m}^3)}{((6 \times 10^{-5}) \text{ m/s}) (500 \text{ m}^2/\text{m}^3)}}$$

$$\Omega = \frac{0.167}{1 + 1.83} = 0.059$$

In this example we see that both the external and internal resistances to mass transfer are significant.

6. *Calculate the Mears criterion, MR, to see if mass transfer limits the reaction.*

$$MR = \frac{-r_A' \rho_b Rn}{k_c C_{Ab}} = \frac{\Omega (-r_{Ab}) Rn}{k_c C_{Ab}}$$

$$= \frac{\Omega k'_1 C_{Ab} \rho_b R}{k_c C_{Ab}} = \frac{\Omega k'_1 \rho_b R}{k_c}$$

$$= \frac{(0.059) (2.34 \times 10^{-7} \text{ m}^3/\text{g}\cdot\text{s}) \left(1.4 \times 10^{-6} \frac{\text{g}}{\text{m}^3}\right) (3 \times 10^{-3} \text{ m})}{6 \times 10^{-5} \text{ m/s}}$$

MR = 0.97

MR (i.e., 0.97 > 0.15) and diffusion limits the reaction.

7. (a) **Calculating the weight of solid catalyst, W, necessary to achieve 99.8% conversion.** Substituting into Equation (E15-3.3), we obtain

$$W = \frac{1 \times 10^{-6} \text{ m}^3/\text{s}}{(0.059) (4.42 \times 10^{-10} \text{ m}^3/\text{m}^2 \cdot \text{s}) (530 \text{ m}^2/\text{g})} \ln \frac{1}{1 - 0.998}$$

W = 450 g

(b) **The reactor length, L, is**

This catalyst weight and corresponding reactor length are rather small and as such we could easily increase the feed rate to the reactor.

$$L = \frac{W}{A_c \rho_b} = \frac{450 \text{ g}}{(2.03 \times 10^{-3} \text{ m}^2) (1.4 \times 10^6 \text{ g/m}^3)}$$

L = 0.16 m

Analysis: One of the purposes of this example was to show how to carry out detailed calculations to size a reactor (i.e., calculate z or V or W) to achieve a specified conversion, when both external and internal diffusion resistances affect the rate of reaction. These calculations are tedious and detailed, and it was my feeling that we should show and know all the intermediate calculations, for example, a_c , η and Ω , so that the reader will have a better understanding of how to make such calculations in the future.

15.8 DETERMINATION OF LIMITING SITUATIONS FROM REACTION-RATE DATA

For external mass transfer–limited reactions in packed beds, the rate of reaction per unit mass of catalyst at a point in the bed is

$$-r'_A = k_c a_c C_A \quad (15-72)$$

Variation of reaction rate with system variables

The correlation for the mass transfer coefficient, Equation (14-77), shows that k_c is directly proportional to the square root of the velocity and inversely proportional to the square root of the particle diameter

$$k_c \propto \frac{U^{1/2}}{d_p^{1/2}} \quad (15-73)$$

We recall from Equation (E15-3.5), $a_c = 6(1 - \phi)/d_p$, that the variation of external surface area with catalyst particle size is

$$a_c \propto \frac{1}{d_p}$$

We now combine Equations (15-72) and (15-73) to obtain

$$-r'_A \propto \frac{U^{1/2}}{d_p^{3/2}} \quad (15-74)$$

Consequently, for *external mass transfer–limited reactions*, the rate is proportional to the velocity to the one-half power and is inversely proportional to the particle diameter to the three-halves power.

From Equation (14-83), we see that for gas-phase external mass transfer– limited reactions, the rate increases approximately linearly with temperature.

Many heterogeneous reactions are diffusion limited.

When *internal diffusion limits* the rate of reaction, we observe from Equation (15-42) that the rate of reaction varies inversely with particle diameter, is independent of velocity, and exhibits an exponential temperature dependence that is not as strong as

that for surface-reaction-controlling reactions. For surface-reaction-limited reactions, the rate is independent of particle size and is a strong function of temperature (exponential). [Table 15-1](#) summarizes the dependence of the rate of reaction on the velocity through the bed, particle diameter, and temperature for the three types of limitations that we have been discussing.

Very important table

TABLE 15-1 LIMITING CONDITIONS

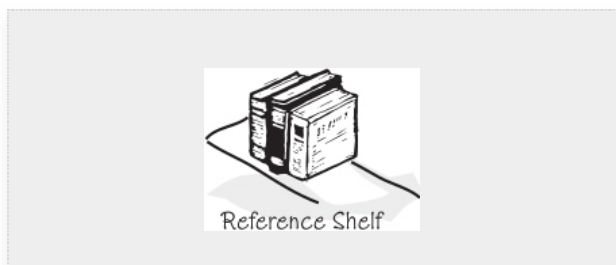
Type of LimitationVariation of Reaction Rate with:			
	Velocity	Particle Size	Temperature
External diffusion	$U^{1/2}$	$(d_p)^{-3/2}$	\approx Linear
Internal diffusion	Independent	$(d_p)^{-1}$	Exponential
Surface reaction	Independent	Independent	Exponential

The exponential temperature dependence for internal diffusion limitations is usually not as strong a function of temperature as is the dependence for surface reaction limitations (cf. [Section 15.4](#)). If we would calculate an activation energy between 8 and 24 kJ/mol, chances are that the reaction would be strongly diffusion-limited. An activation energy of 200 kJ/mol, however, suggests that the reaction is surface reaction rate–limited.

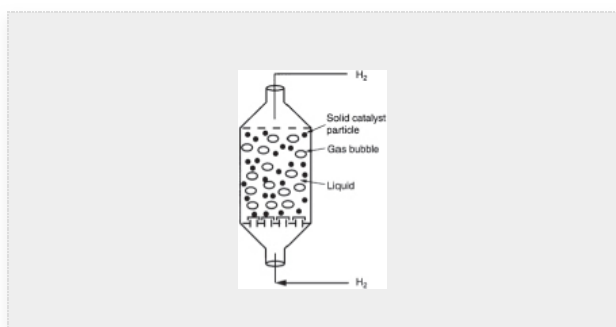
15.9 MULTIPHASE REACTORS IN THE PROFESSIONAL REFERENCE SHELF

Multiphase reactors are reactors in which two or more phases are necessary to carry out the reaction. The majority of multiphase reactors involve gas and liquid phases that contact a solid. In the case of the slurry and trickle bed reactors, the reaction between the gas and the liquid takes place on a solid

catalyst surface (see Table 15-2). However, in some reactors the liquid phase is an inert medium for the gas to contact the solid catalyst. The latter situation arises when a large heat sink is required for highly exothermic reactions. In many cases, the catalyst life is extended by these milder operating conditions.



The multiphase reactors discussed in the previous editions of this book are the slurry reactor, fluidized bed, and the trickle bed reactor. The material for the slurry reactors, trickle bed reactors, and fluidized bed reactors described below has been typeset for easy reading on the Web and can be easily printed out from the Professional Reference Shelf for this Chapter 15 (<http://www.umich.edu/~elements/6e/15chap/prof.html>). The trickle bed reactor, which has reaction and transport steps similar to the slurry reactor, is discussed in the first edition of this book and on the CRE Web site along with the bubbling fluidized bed. In slurry reactors, the catalyst is suspended in the liquid, and gas is bubbled through the liquid. A slurry reactor may be operated in either a semibatch or continuous mode.



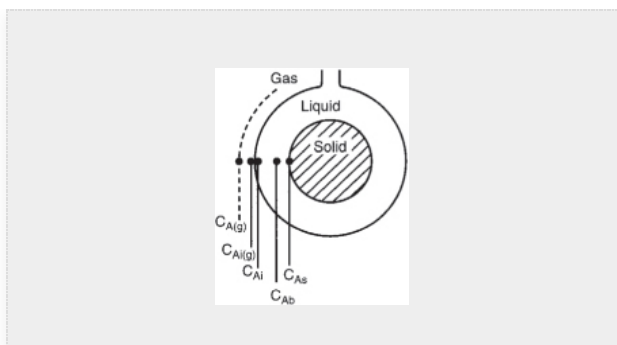


TABLE 15-2 APPLICATIONS OF THREE-PHASE REACTORS

1. *Slurry reactor*

A. Hydrogenation

A. of fatty acids over a supported nickel catalyst

B. of 2-butyne-1,4-diol over a Pd-CaCO₃ catalyst

C. of glucose over a Raney nickel catalyst

B. Oxidation

A. of C₂H₄ in an inert liquid over a PdCl₂-carbon catalyst

B. of SO₂ in inert water over an activated carbon catalyst

C. Hydroformation

of CO with high-molecular-weight olefins on either a cobalt or ruthenium complex bound to polymers

D. Ethynylation

Reaction of acetylene with formaldehyde over a CaCl_2 -supported catalyst

2. Trickle bed reactors

A. Hydrodesulfurization

B. Removal of sulfur compounds from crude oil by reaction with hydrogen on Co-Mo on alumina

C. Hydrogenation

A. of aniline over a Ni-clay catalyst

B. of 2-butyne-1,4-diol over a supported Cu-Ni catalyst

C. of benzene, α -CH₃ styrene, and crotonaldehyde

D. of aromatics in napthenic lube oil distillate

D. Hydrodenitrogenation

A. of lube oil distillate

B. of cracked light furnace oil

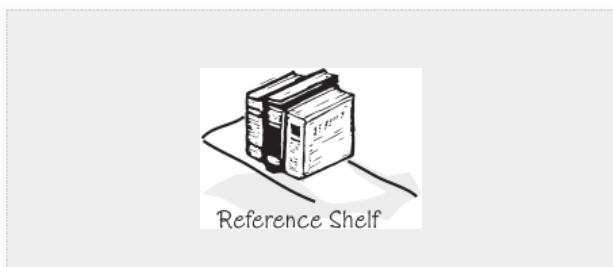
E. Oxidation

A. of cumene over activated carbon

B. of SO₂ over carbon

Source: Satterfield, C. N. *AIChE Journal.*, 21, 209 (1975); P. A. Ramachandran and R. V. Chaudhari, *Chem. Eng.*, 87(24), 74 (1980); R. V. Chaudhari and P. A. Ramachandran, *AIChE Journal.*, 26, 177 (1980). With permission of the American Institute of Chemical Engineers. Copyright © 1980 AIChE. All rights reserved.

15.9.1 Slurry Reactors

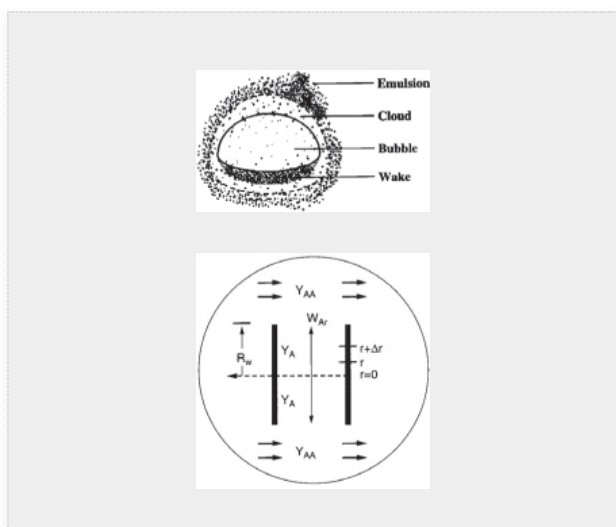


A complete description of the slurry reactor and the transport and reaction steps is given on the CRE Web site, along with the design equations and a number of examples. Methods to determine which of the transport and reaction steps are rate limiting are included. See *Professional Reference Shelf R12.1* (<http://www.umich.edu/~elements/6e/15chap/pdf/slurry.pdf>) for the complete text.

15.9.2 Trickle Bed Reactors

The CRE Web site (in Additional Material → Expanded Material) includes all the material on trickle bed reactors from the first edition of this book. A comprehensive example problem for trickle bed reactor design is included. See *Professional Reference Shelf R15.2* (<http://www.umich.edu/~elements/6e/15chap/pdf/trickle.pdf>).

15.10 FLUIDIZED BED REACTORS



The Kunii–Levenspiel model for fluidization is given on the CRE Web site (in Additional Material → Expanded Material) along with a comprehensive example problem. The rate-limiting transport steps are also discussed. See *Professional Reference Shelf R15.3* (<http://www.umich.edu/~elements/6e/15chap/pdf/FluidizedBed.pdf>).

15.11 CHEMICAL VAPOR DEPOSITION (CVD)

Chemical vapor deposition in boat reactors is discussed and modeled (see in Additional Material → Expanded Material on the CRE Web site). The equations and parameters that affect wafer thickness and shape are derived and analyzed. This material is taken directly from the second edition of this book. See *Professional Reference Shelf R15.4* (<http://www.umich.edu/~elements/6e/15chap/pdf/CVD.pdf>).

15.12 AND NOW... A WORD FROM OUR SPONSOR—SAFETY 15 (AWFOS—S15 CRITICAL THINKING QUESTIONS APPLIED TO SAFETY)

The 2017 April issue of *Chemical Engineering*[†] has a great article on safety and on a number of critical thinking and creative thinking questions that should be asked. Socratic questioning is at the heart of critical thinking and we shall use R.W. Paul’s Six Types of Socratic (i.e., Critical Thinking) Questions shown in Table 15-3 as a basis for our discussion.[‡] A critical aspect of process safety is “anticipating” what could go wrong in a chemical process and ensuring it won’t go wrong. We are going to use an actual life example to discuss critical thinking.

[†] <https://www.chemengonline.com/key-questions-guide-effective-selection-personal-protective-equipment-PPE-safety-chemicalsafety/?s=april+2017>

[‡] Paul, R. W., Critical Thinking, Foundation for Critical Thinking, Santa Rosa, CA, 1992.

Actual Case History:^{*} *A large tank containing ethylene oxide has been insulated and is out in the plant. There is uncertainty as to whether or not corrosion has taken place under the insulation. To strip the insulation and check for corrosion would require shutting the plant down for 3 weeks. Because such a shutdown would affect the supply chain and many customers, the shutdown would be very costly, ca. 5 million dollars.*

^{*} Written in conjunction with Joel Young, BASF, Wyandotte, MI.

Let’s apply R. W. Paul’s Six Types of Critical Thinking Questions to this situation to help us decide whether or not to strip the insulation.

TABLE 15-3 R.W. PAUL’S SIX TYPES OF CRITICAL THINKING QUESTIONS (CTQs) AND EXAMPLES** STORAGE TANK INSULATION

Type of CTQ	Example Phrases of CTQ	CTQ Safety Examples
1. Questions about the question or problem statement: The purpose of this question is to determine why the question was asked, who asked it,	<ul style="list-style-type: none"> What is the 	Why do you think I questioned you about corrosion

<i>and why the question or problem needs to be solved.</i>	<p>main question you want to answer ?</p> <ul style="list-style-type: none">• What is the point of this question?• Why do you think I ask this question?• Why is it important you learn the answer to that question?• How does this question relate to our discussion?	<p>under the insulation, considering the storage tank is only 10 years old?</p>
<p>2. Questions for clarification: <i>The purpose of this question is to identify missing or unclear information in the problem statement or question.</i></p>	<ul style="list-style-type: none">• What do you mean by that?• What information do we	<p>Are there industry-identified case histories about corrosion occurring under insulation?</p>

	<p>need to answer this question?</p> <ul style="list-style-type: none">• How does that relate to our discussion?• What do we already know about that?	
<p>3. Questions that probe assumptions: <i>The purpose of this question is to identify any misleading or false assumptions.</i></p>	<ul style="list-style-type: none">• What could we assume instead ?• How does one verify or disapprove that assumption?• Explain why . . . (Explain how . . .)• What would happen if . . . ?	<p>How did you assume stripping the insulation is the only method to check for corrosion?</p>

	<ul style="list-style-type: none"> What is the basis of this assumption? 	
<p>4. Questions that probe reasons and evidence: <i>The purpose of this question is to explore whether facts and observations support an assertion.</i> · What would be an example?</p>	<ul style="list-style-type: none"> Why is . . . happening? What is analogous to . . . ? What do you think causes . . . ? Why? What evidence is there to support your answer ? 	<p>What evidence do you have that corrosion may have occurred in this tank in the last 10 years?</p>
<p>5. Questions that probe viewpoints and perspectives: <i>The purpose of this question is to learn how things are viewed or judged and consider things not only in a relative perspective but also as a whole.</i> · What is a counterargument for ____?</p>	<ul style="list-style-type: none"> What are the strengths and weaknesses of that viewpoint? What are the 	<p>What are counterarguments for taking all the insulation off and inspecting the tank?</p>

	<p>similarities and differences between your point of view and compare the other person's point of view?</p> <ul style="list-style-type: none">• Compare _____ and _____ with regard to _____.• What is your perspective on why it happened?	
<p>6. Questions that probe implications and consequences: <i>The purpose of this question is to help understand the inferences or deductions and the end result if the inferred action is carried out.</i> · What are the consequences if that assumption turns out to be false?</p>	<ul style="list-style-type: none">• What will happen if the trend continues?• Is there a more logical inference we might make in	<p>What are consequences of ethylene oxide leaking into the atmosphere on people, equipment, and the environment?</p>

	<p>this situation?</p> <ul style="list-style-type: none"> • Could you explain how you reached that conclusion? • Given all the facts, is that really the best possible conclusion? 	
--	--	--

*** See pages 58–59, H. S. Fogler, S. E. LeBlanc, and B. R. Rizzo, *Strategies for Creative Problem Solving*, 3rd ed. Boston, MA: Prentice Hall, 2014.

HSF favorite types of critical thinking questions are (1) Why do you think I asked this question? (2) What information do we need to answer this question? (3) Could you explain your reasoning for making that choice? (4) Can you give me an example? (5) What is a counterargument for your suggestion? (6) What are the consequences if your assumption is false?

Closure. After completing this chapter, the reader should be able to derive differential equations describing diffusion and reaction; discuss the meaning of the internal effectiveness factor, η , and its relationship to the Thiele modulus; and discuss the overall effectiveness factor, Ω . The reader should be able to identify the regions of external and internal mass transfer limitations and reaction-rate limitations by applying the Weisz–Prater criterion and Mears criterion. The reader should be able to apply the overall effectiveness factor to a packed-bed reactor to calculate the conversion at the exit of the reactor. In **Chapter 18**, we will introduce radial variations in temperature and concentration while previous chapters in this text considered only plug-flow profiles. Using COMSOL we can readily generate $C(r, z)$ and $T(r, z)$ for tubular reactors. In summary on these Living Example Problems, the best way to get a good understanding of reactors with heat effects is to download and run the Polymath, MATLAB, Wolfram, Python, and COMSOL programs from the CRE Web site.

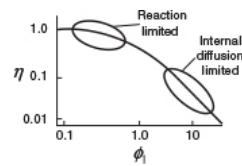
SUMMARY

1. The concentration profile for a first-order reaction occurring in a spherical catalyst pellet is

$$\frac{C_A}{C_{As}} = \frac{R}{r} \left[\frac{\sinh(\phi_1 r/R)}{\sinh \phi_1} \right] \quad (\text{S15-1})$$

where ϕ_1 is the Thiele modulus. For a first-order reaction

$$\phi_1^2 = \frac{k_1}{D_e} R^2 \quad (\text{S15-2})$$



2. The effectiveness factors are

$$\begin{aligned} \text{Internal effectiveness factor} &= \eta = \frac{\text{Actual rate of reaction}}{\text{Reaction rate if entire interior surface is exposed to concentration at the external pellet surface}} \end{aligned}$$

$$-r_A = \eta (-r_{As})$$

$$\begin{aligned} \text{Overall effectiveness factor} &= \Omega = \frac{\text{Actual rate of reaction}}{\text{Reaction rate if entire surface area is exposed to bulk concentration}} \end{aligned}$$

$$-r_A = \Omega (-r_{Ab})$$

3. For large values of the Thiele modulus for an n^{th} order reaction

$$\eta = \left(\frac{2}{n+1} \right)^{1/2} \frac{3}{\phi_n} \quad (\text{S15-3})$$

4. For internal diffusion control, the true reaction order is related to the measured reaction order by

$$n_{\text{true}} = 2n_{\text{apparent}} - 1 \quad (\text{S15-4})$$

The true and apparent activation energies are related by

$$E_{\text{true}} = 2E_{\text{app}} \quad (\text{S15-5})$$

5. A. The Weisz–Prater Parameter

$$\text{WP} = \phi_1^2 \eta = \frac{-r'_A (\text{observed}) \rho_c R^2}{D_e C_{As}} \quad (\text{S15-6})$$

The Weisz–Prater criterion dictates that

If $\text{WP} \ll 1$ no internal diffusion limitations present

If $\text{WP} \gg 1$ internal diffusion limitations present

B. The Mears Criterion for Neglecting External Diffusion and Heat Transfer

The Mears number is

$$\text{MR} = \frac{-r'_A (\text{obs}) \rho_b R n}{k_c C_{Ab}} \quad (\text{S15-7})$$

There will be no external diffusion limitations **if**

$$\text{MR} < 0.15 \quad (\text{S15-8})$$

And there will be no temperature gradients **if**

$$\left| \frac{-\Delta H_{\text{Rx}} (-r'_A) (\rho_b R E)}{h T^2 R_g} \right| < 0.15 \quad (\text{S15-9})$$

CRE WEB SITE MATERIALS

([HTTP://WWW.UMICH.EDU/~ELEMENTS/6E/15CHAP/OBJ.HTML#/](http://www.umich.edu/~elements/6e/15chap/obj.html#/))

Useful Links

Living
Example
Problems

Extra Help

Additional
Materials

Professional
Reference
Shelf

Computer
Simulation
Problem
Statements

Evaluation

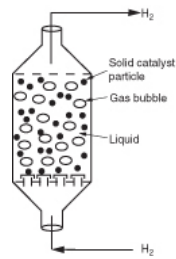
Self Tests

Clicker
Questions

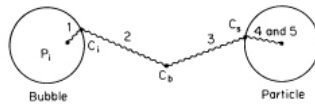
• Professional Reference Shelf

R15.1. Slurry Reactors

(<http://www.umich.edu/~elements/6e/15chap/pdf/slurry.pdf>)



Transport Steps and Resistances



A. Description of the Use of Slurry Reactors

Example R15-1 Industrial Slurry Reactor

B. Reaction and Transport Steps in a Slurry Reactor

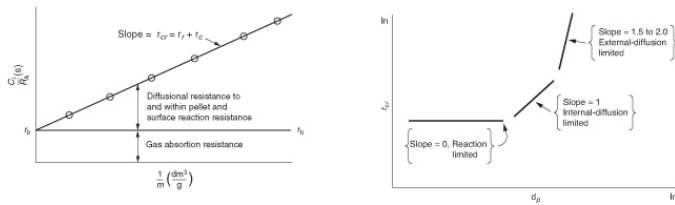
$$\frac{C_i}{R_A} = \frac{1}{k_b a_b} + \frac{1}{m} \left(\frac{1}{k_b a_b} + \frac{1}{k\eta} \right)$$

C. Determining the Rate-Limiting Step

A. Effect of Loading, Particle Size, and Gas Adsorption

B. Effect of Shear Example R15-2 Determining the Controlling Resistance

D. Slurry Reactor Design

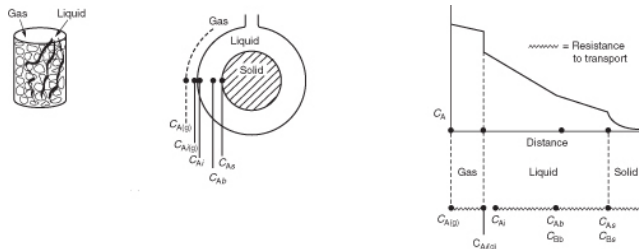


Example R15-3 Slurry Reactor Design

R15.2. Trickle Bed Reactors

(<http://www.umich.edu/~elements/6e/15chap/prof-trickle.html#seca>)

A. Fundamentals



B. Limiting Situations

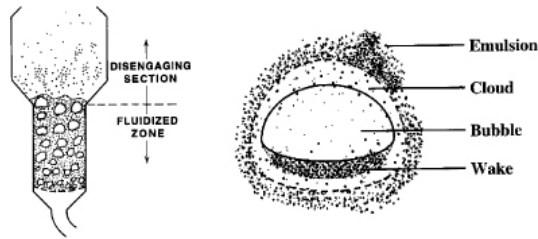
C. Evaluating the Transport Coefficients

$$-r'_A = \frac{1/H}{\underbrace{\frac{(1-\phi)\rho_c}{Hk_g a_i} + \frac{(1-\phi)\rho_c}{k_i a_i} + \frac{1}{k_c a_p} + \frac{1}{\eta k C_{Bs}}}}_{k_{vg}} C_A(g) \quad \frac{\text{mol}}{\text{g-cat} \cdot \text{s}}$$

R15.3. Fluidized Bed Reactors

(<http://www.umich.edu/~elements/6e/15chap/prof-fluidized.html>)

A. Descriptive Behavior of the Kunii–Levenspiel Bubbling Bed Model



B. Mechanics of Fluidized Beds

Example R15-4 Maximum Solids Hold-Up

C. Mass Transfer in Fluidized Beds

D. Reaction in a Fluidized Bed

E. Solution to the Balance Equations for a First-Order Reaction

$$W = \frac{\rho_c A_c u_b (1 - \epsilon_{mf}) (1 - \delta)}{k_{cat} K_R} \ln \frac{1}{1 - X}$$

$$K_R = \gamma_b + \frac{1}{\frac{k_{cat}}{K_{bc}} + \frac{1}{\gamma_c + \frac{1}{\frac{1}{\gamma_e} + \frac{k_{cat}}{K_{ce}}}}}$$

Example R15-5 Catalytic Oxidation of Ammonia

F. Limiting Situations

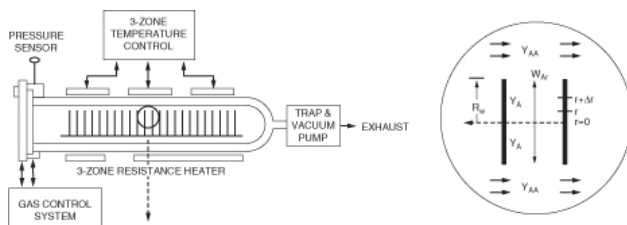
Example R15-6 Calculation of the Resistances

Example R15-7 Effect of Particle Size on Catalyst Weight for a Slow Reaction

Example R15-8 Effect of Catalyst Weight for a Rapid Reaction

R15.4. Chemical Vapor Deposition Reactors

(<http://www.umich.edu/~elements/6e/15chap/prof-cvd.html>)



A. Chemical Reaction Engineering in Microelectronic Processing

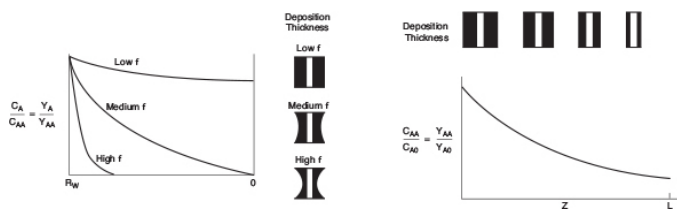
B. Fundamentals of CVD

C. Effectiveness Factors for Boat Reactors

$$\eta = \frac{2I_1(\phi_1)}{\phi_1 I_0(\phi_1)}$$

Example R15-9 Diffusion Between Wafers

Example R15-10 CVD Boat Reactor



QUESTIONS, SIMULATIONS, AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$A = \bullet \quad B = \blacksquare \quad C = \blacklozenge \quad D = \blacklozenge\blacklozenge$$

Questions

Q15-1_A QBR (*Question Before Reading*). What are two factors that affect the rate of diffusion inside a porous catalyst pellet the most?

Q15-2 Make up an original problem using the concepts presented in Section _____ (your instructor will specify the section). Extra credit will be given if you obtain and use real data from the literature. (See Problem P5-1_A for the guidelines.)

Q15-3 What if you consider an exothermic reaction in which internal diffusion limits the rate of reaction? Can you explain how the internal effectiveness factor could be

greater than one, that is, $\eta > 1$? *Hint:* See nonisothermal reactors on Web under Additional Material.

- Q15-4** What if the temperature in the CRE Web site Professional Reference Shelf Example R15.2 were increased? How would the relative resistances in the slurry reactor change?
- Q15-5** What if you were asked for all the things that could go wrong in the operation of a slurry reactor as described in the Professional Reference Shelf for Chapter 15? What would you say?
- Q15-6** What if someone had used the falsified kinetics parameters (i.e., wrong E , wrong n)? Can you explain why one might have a runaway reaction? Under what circumstances would the catalyst weight be over-designed or underdesigned? What are other positive or negative effects that could occur?
- Q15-7_A** Go to the LearnChemE screencast link for Chapter 15 (<http://www.learncheme.com/screencasts/kinetics-reactor-design>). View the two screencasts: **(1)** “Diffusion and Reaction in a Cylindrical Porous Catalyst,” **(a)** What is the equation for the amount reacting in 1 cm; and **(2)** “Effectiveness Factor for spherical Catalyst,” **(b)** Write the effectiveness factor in terms of the Thiele Modulus. For these two screencasts list two of the most important points.
- Q15-8** AWFOS-S15 Six Types of Critical Thinking Questions
1. Write a Critical Thinking Question for each type of CTQ for the Monsanto Incident, [Example 13-2](#).
 2. Write another question for each CTQ for the case history concerning ethylene oxide in the insulated storage tank.

Computer Simulations and Experiments

P15-1_B

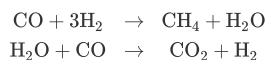
1. **Example 15-1: Finding the Effective Diffusivity of D_e**
Wolfram
 1. Can you think up a question about the sliders that would be somewhat interesting? I am not sure I can, that's why there is no specific question here.
2. **Example 15-3: Reducing Nitrous Oxides in a Plant's Effluent.** This is a **Stop and Smell the Roses Simulation**.
Wolfram
 1. Which parameter has the larger impact in reducing internal diffusion limitations, pellet radius or internal surface area?



2. Vary and list at least three parameters which can be changed to achieve approximately 90% conversion for a new flow rate of $10^{-5} \text{ m}^3/\text{s}$.
3. Which combination of parameter values causes the surface reaction rate to become the closest to the internal diffusion rate, that is, $WP \sim 1$?
4. For the base case, calculate the percent of the total resistance for each of the individual resistances of external diffusion, internal diffusion, and surface reaction.
5. Qualitatively, how would each of your percentages change if the temperature were increased significantly?
6. Vary various parameters to see the effect of each parameter on Mears number, MR and write a set of conclusions.
7. What variable affects the internal effectiveness factor the most?
8. What variable affects the overall effectiveness factor the most?
9. What variable affects the Mears criteria (MR) the most?
10. What variable affects the Weisz–Prater (WP) the most?
11. Apply the Weisz–Prater criteria to a particle 0.005 m in diameter.
12. Write a set of conclusions for your experiments (i) through (xi).

Polymath

1. How would your answers in (i) through (v) change if the reaction were zero order with $k_0 = 9 \times 10^{-4} \text{ mol/g}\cdot\text{s}$. *Hint: What are the new equations for η and Ω ?*
2. *Overall Effectiveness Factor.* Calculate the percent of the total resistance for the resistance of external diffusion, internal diffusion, and surface reaction. Qualitatively, how would each of your percentages change?
3. What if you applied the Mears and Weisz–Prater criteria to Examples 15-4 and 15-3? What would you find? What would you learn if $\Delta H_{R_{\text{rx}}}^\circ = -25 \text{ kcal/mol}$, $h = 100 \text{ Btu/h} \cdot \text{ft}^2 \cdot ^\circ\text{F}$, and $E = 20 \text{ kcal/mol}$?
4. What if your internal surface area decreased with time because of sintering (see Section 10.7). Describe how your effectiveness factor would change and the rate of reaction change with time if $k_d = 0.01 \text{ h}^{-1}$ and $\eta = 0.01$ at $t = 0$? Explain, being as quantitative as possible when you can.
5. What if you were to assume that the resistance to gas absorption in the CRE Web site *Professional Reference Shelf R15.1* was the same as in *Professional Reference Shelf R15.3* and that the liquid-phase reactor volume in *Professional Reference Shelf R15.3* was 50% of the total? Could you determine the limiting resistance? If so, what is it? What other things could you calculate in *Professional Reference Shelf R15.1* (e.g., selectivity, conversion, molar flow rates in and out)? *Hint: Some of the other reactions that occur include*



Problems

P15-2_B OEQ (Old Exam Question). Concept problem:

The catalytic reaction



takes place within a fixed bed containing spherical porous catalyst X22. Figure P15-2_B shows the overall rates of reaction at a point in the reactor as a function of temperature for various entering total molar flow rates, F_{T0} .

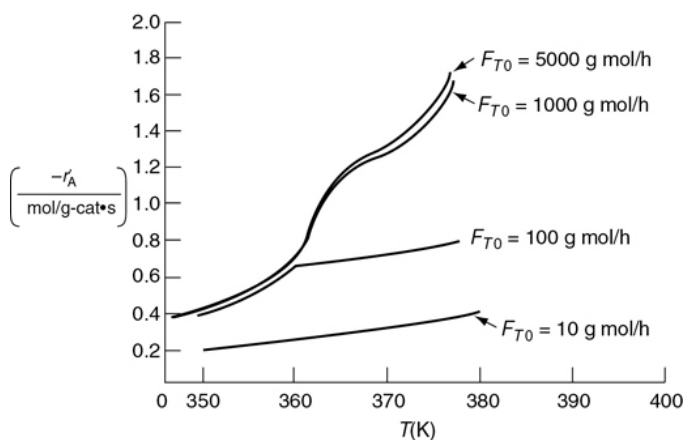
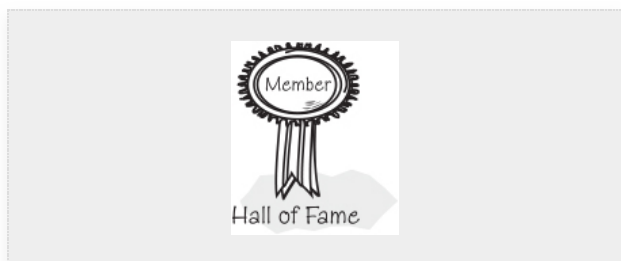


Figure P15-2_B Reaction rates in a catalyst bed.

1. Is the reaction limited by external diffusion?
2. If your answer to part (a) was “yes,” under what conditions of those shown (i.e., T , F_{T0}) is the reaction limited by external diffusion?
3. Is the reaction “reaction-rate-limited”?
4. If your answer to part (c) was “yes,” under what conditions of those shown (i.e., T , F_{T0}) is the reaction limited by the rate of the surface reactions?
5. Is the reaction limited by internal diffusion?
6. If your answer to part (e) was “yes,” under what conditions of those shown (i.e., T , F_{T0}) is the reaction limited by the rate of internal diffusion?
7. For a flow rate of 10 g mol/h, determine (if possible) the overall effectiveness factor, $\Omega = \eta$, at 360 K.
8. Estimate (if possible) the internal effectiveness factor, η , at 367 K. (**Ans:** $\eta = 0.86$)
9. If the concentration at the external catalyst surface is 0.01 mol/dm^3 , calculate (if possible) the concentration at $r = R/2$ inside the porous catalyst at 367 K. (Assume a first-order reaction.)

Additional information:

Gas properties: Bed properties:Diffusivity: $0.1 \text{ cm}^2/\text{s}$ Tortuosity of pellet: 1.414Density: 0.001 g/cm^3 Bed permeability: 1 millidarcyViscosity: $0.0001 \text{ g/cm}\cdot\text{s}$ Porosity = 0.3

P15-3_B OEQ (Old Exam Question). *Concept problem:* The reaction



is carried out in a differential packed-bed reactor at different temperatures, flow rates, and particle sizes. The results shown in **Figure P15-3_B** were obtained.

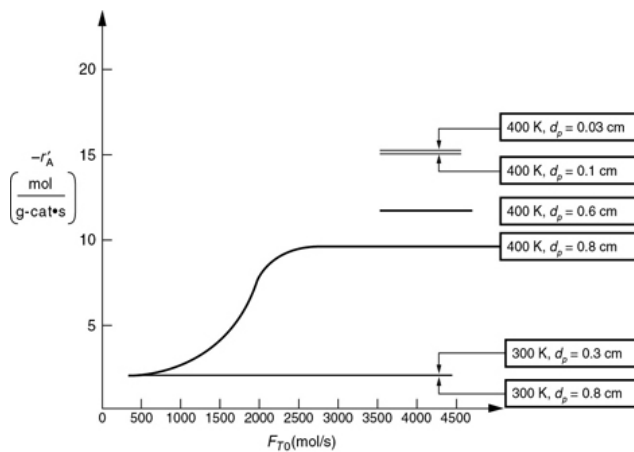


Figure P15-3_B Reaction rates in a catalyst bed.

1. What regions (i.e., conditions d_p , T , F_{T0}) are external mass transfer-limited?

2. What regions are reaction rate-limited?
3. What region is internal-diffusion-controlled?
4. What is the internal effectiveness factor at $T = 400$ K and $d_p = 0.8$ cm?
(Ans: $\eta = 0.625$)

P15-4_A OEQ (Old Exam Question). *Concept problem:* Curves A, B, and C in Figure P15-4_A show the variations in reaction rate for three different reactions catalyzed by solid catalyst pellets. What can you say about each reaction?

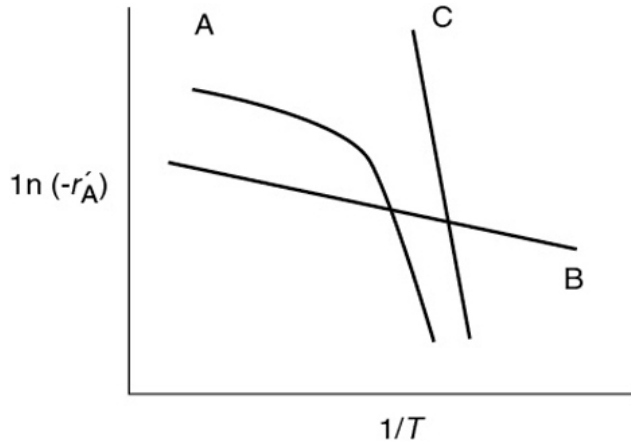


Figure P15-4_A Temperature dependence of three reactions.

P15-5_B OEQ (Old Exam Question). A first-order heterogeneous irreversible reaction is taking place within a spherical catalyst pellet that is plated with platinum throughout the pellet (see Figure 15-3). The reactant concentration halfway between the external surface and the center of the pellet (i.e., $r = R/2$) is equal to one-tenth the concentration of the pellet's external surface. The concentration at the external surface is 0.001 g mol/dm³, the diameter ($2R$) is 2×10^{-3} cm, and the diffusion coefficient is 0.1 cm²/s.



1. What is the concentration of reactant at a distance of 3×10^{-4} cm in from the external pellet surface? (Ans: $C_A = 2.36 \times 10^{-4}$ mol/dm³)
2. To what diameter should the pellet be reduced if the effectiveness factor is to be 0.8? (Ans: $d_p = 6.8 \times 10^{-4}$ cm. Critique this answer!)
3. If the catalyst support were not yet plated with platinum, how would you suggest that the catalyst support be plated *after* it had been reduced by grinding?

P15-6_B The swimming rate of a small organism (*J. Theoret. Biol.*, 26, 11 (1970)) is related to the energy released by the hydrolysis of adenosine triphosphate (ATP) to

adenosine diphosphate (ADP). The rate of hydrolysis is equal to the rate of diffusion of ATP from the midpiece to the tail (see Figure P15-6B). The diffusion coefficient of ATP in the midpiece and tail is $3.6 \times 10^{-6} \text{ cm}^2/\text{s}$. ADP is converted to ATP in the midsection, where its concentration is $4.36 \times 10^{-5} \text{ mol/cm}^3$. The cross-sectional area of the tail is $3 \times 10^{-10} \text{ cm}^2$.

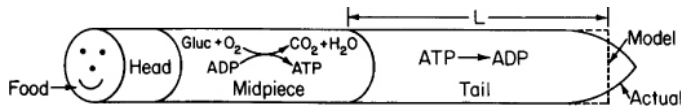


Figure P15-6B Swimming of an organism.

Application
Pending
for Problem
Hall of
Fame

1. Derive an equation for diffusion and reaction in the tail.
2. Derive an equation for the effectiveness factor in the tail.
3. Taking the reaction in the tail to be of zero order, calculate the length of the tail. The rate of reaction in the tail is $23 \times 10^{-18} \text{ mol/s}$.
4. Compare your answer with the average tail length of $41 \text{ }\mu\text{m}$. What are possible sources of error?

P15-7B A first-order, heterogeneous, irreversible reaction is taking place within a catalyst pore that is plated with platinum entirely along the length of the pore (Figure P15-7B). The reactant concentration at the plane of symmetry (i.e., equal distance from the pore mouth) of the pore is equal to one-tenth the concentration at the pore mouth. The concentration at the pore mouth is 0.001 mol/dm^3 , the pore length ($2L$) is $2 \times 10^{-3} \text{ cm}$, and the diffusion coefficient is $0.1 \text{ cm}^2/\text{s}$.

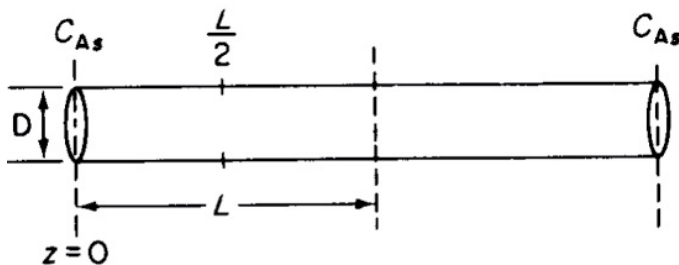


Figure P15-7B Single catalyst pore.

1. Derive an equation for the effectiveness factor.
2. What is the concentration of reactant at $L/2$?
3. To what length should the pore length be reduced if the effectiveness factor is to be 0.8?

4. If the catalyst support were not yet plated with platinum, how would you suggest the catalyst support be plated *after* the pore length, L , had been reduced by grinding?

P15-8_B *Extension of Problem P15-7_B.* The elementary isomerization reaction



is taking place on the walls of a cylindrical catalyst pore (see Figure P15-7_B.) In one run, a catalyst poison P entered the reactor together with the reactant A. To estimate the effect of poisoning, we assume that the poison renders the catalyst pore walls near the pore mouth ineffective up to a distance z_1 , so that no reaction takes place on the walls in this entry region.

1. Show that before poisoning of the pore occurred, the effectiveness factor was given by

$$\eta = \frac{1}{\phi} \tanh \phi$$

where

$$\phi = L \sqrt{\frac{2k}{rD_e}}$$

with

k = reaction-rate constant (length/time)

r = pore radius (length)

D_e = effective molecular diffusivity (area/time)

2. Derive an expression for the concentration profile and also for the molar flux of A in the ineffective region, $0 < z < z_1$, in terms of z_1 , D_{AB} , C_{A1} , and C_{As} . Without solving any further differential equations, obtain the new effectiveness factor η' for the poisoned pore.

P15-9_A A first-order reaction is taking place inside a porous catalyst. Assume dilute concentrations and neglect any variations in the axial (x) direction.

1. Derive an equation for both the internal and overall effectiveness factors for the rectangular porous slab shown in Figure P15-9_A.
2. Repeat part (a) for a cylindrical catalyst pellet where the reactants diffuse inward in the radial direction. (C-level problem, i.e., P15-9_C(b).)

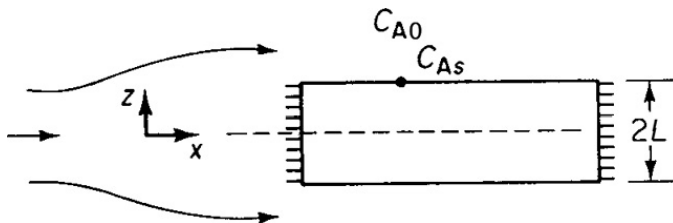
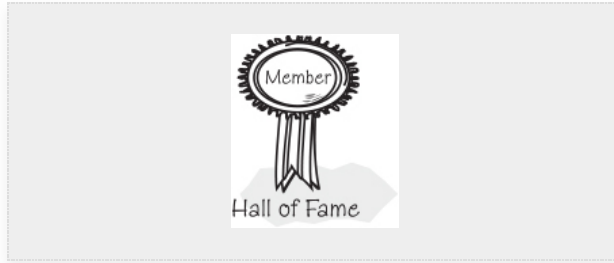


Figure P15-9_A Flow over porous catalyst slab.

P15-10_B The irreversible reaction



is taking place in the same porous catalyst slab shown in Figure P15-9A.



The reaction is zero order in A.

1. Show that the concentration profile using the symmetry B.C. is

$$\frac{C_A}{C_{As}} = 1 + \phi_0^2 \left[\left(\frac{z}{L} \right)^2 - 1 \right] \quad (\text{P15-10.1})$$

where

$$\phi_0^2 = \frac{kL^2}{2D_e C_{As}} \quad (\text{P15-10.2})$$

2. For a Thiele modulus of 1.0, at what point in the slab is the concentration zero? For $\phi_0 = 4$?
3. What is the concentration you calculate at $z = 0.1 L$ and $\phi_0 = 10$ using Equation (P15-10.1)? What do you conclude about using this equation?
4. Plot the dimensionless concentration profile $\psi = C_A/C_{As}$ as a function of $\lambda = z/L$ for $\phi_0 = 0.5, 1, 5$ and 10 . *Hint:* there are regions where the concentration is zero. Show that $\lambda_C = (1 - 1/\phi_0)$ is the start of this region where the gradient and concentration are both zero. (L. K. Jang, R. L. York, J. Chin, and L. R. Hile, *Inst. Chem. Engr.*, 34, 319 (2003).) Show that $\psi = \phi_0^2 \lambda^2 - 2\phi_0(\phi_0 - 1)\lambda + (\phi_0 - 1)^2$ for $\lambda_C \leq \lambda < 1$.
5. The effectiveness factor can be written as

$$\eta = \frac{\int_0^L -r_A A_c dz}{-r_{As} A_c L} = \frac{\int_0^{z_c} -r_A A_c dz + \int_{z_c}^L -r_A A_c dz}{-r_{As} A_c L} \quad (\text{P15-0.3})$$

where z_C (λ_C) is the point at which both the concentration gradients and flux go to zero, and A_c is the cross-sectional area of the slab. Show for a zero-order reaction that

$$\eta = \begin{cases} 1 & \text{for } \phi_0 \leq 1.0 \\ 1 - \lambda_C = \frac{1}{\phi_0} & \text{for } \phi_0 \geq 1 \end{cases} \quad (\text{P15-10.4})$$

6. Make a sketch for η versus ϕ_0 similar to the one shown in Figure 15-5.
7. Repeat parts (a) through (f) for a spherical catalyst pellet.
8. What do you believe to be the point of this problem?

P15-11C The second-order decomposition reaction



is carried out in a tubular reactor packed with catalyst pellets 0.4 cm in diameter. The reaction is internal-diffusion-limited. Pure A enters the reactor at a superficial velocity of 3 m/s, a temperature of 250°C, and a pressure of 500 kPa. Experiments carried out on smaller pellets where surface reaction is limiting yielded a specific reaction rate of 0.05 m⁶/mol·g-cat·s. Calculate the length of bed necessary to achieve 80%

conversion. Critique the numerical answer. (**Ans:** $L = 2.8 \times 10^{-5} \text{ m}$)

Additional information:

Effective diffusivity: $2.66 \times 10^{-8} \text{ m}^2/\text{s}$ Pellet density: $2 \times 10^6 \text{ g/m}^3$

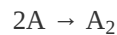
Ineffective diffusivity: $0.00 \text{ m}^2/\text{s}$ Internal surface area: $400 \text{ m}^2/\text{g}$

Bed porosity: 0.4

P15-12_C Derive the concentration profile and effectiveness factor for cylindrical pellets 0.2 cm in diameter and 1.5 cm in length. Neglect diffusion through the ends of the pellet.

1. Assume that the reaction is a first-order isomerization. *Hint:* Look for a Bessel function.
2. Rework Problem P15-11_C for these pellets.

P15-13_C OEQ (Old Exam Question). *Falsified Kinetics.* The irreversible gas-phase dimerization



is carried out at 8.2 atm in a stirred contained-solids reactor to which only pure A is fed. There are 40 g of catalyst in each of the four spinning baskets. The following runs were carried out at 227°C:

Total Molar Feed Rate, F_{T0} (g mol/min)	1	2	4	6	11	20
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Mole Fraction A in Exit, y_A	0.2	0.3	0.4	0.5	0.7	0.8
	1	3	0	7	0	1

The following experiment was carried out at 237°C:

$$F_{T0} = 9 \text{ g mol/min} \quad y_A = 0.097$$

1. What are the apparent reaction order and the apparent activation energy?
2. Determine the true reaction order, specific reaction rate, and activation energy.
3. Calculate the Thiele modulus and effectiveness factor.
4. What pellet diameter should be used to make the catalyst more effective?
5. Calculate the rate of reaction on a rotating disk made of the catalytic material when the gas-phase reactant concentration is 0.01 g mol/L and the temperature is 227°C. The disk is flat, nonporous, and 5 cm in diameter.

Additional information:

Effective diffusivity: 0.23 cm ² /s	Radius of catalyst pellets: 1 cm
Surface area of porous catalyst: 49 m ² /g-cat	Color of pellets: blushing peach
Density of catalyst pellets: 2.3 g/cm ³	

P15-14_B Derive Equation (15-39). *Hint:* Multiply both sides of Equation (15-25) for n th order reaction; that is,

$$\frac{d^2 y}{d\lambda^2} - \phi_n^2 y^n = 0$$

by $2dy/d\lambda$, rearrange to get

$$\frac{d}{d\lambda} \left(\frac{dy}{d\lambda} \right)^2 = \phi_n^2 y^n 2 \frac{dy}{d\lambda}$$

and solve using the boundary conditions $dy/d\lambda = 0$ at $\lambda = 0$.

P15-15_C You will need to read about slurry reactions on the Web site's *Additional Material*. The following table was obtained from the data taken in a slurry reactor for the hydrogenation of methyl linoleate to form methyl oleate.

	$L + H_2 \rightarrow O$
S	= solubility of H_2 in the liquid mixture, mol/dm ³
m	= catalyst charge, g/dm ³
$-r'_L$	= rate of reaction of methyl linoleate, mol/dm ³ • min

Catalyst Size $S/ - r'_L$ (min) $1/m$ (dm^3/g)

A 4.2 0.01

A 7.5 0.02

B 1.5 0.01

B 2.5 0.03

B 3.0 0.04

1. Which catalyst size has the smaller effectiveness factor?
2. If catalyst size A is to be used in the reactor at a concentration of 50 g/dm^3 , would a significant increase in the reaction be obtained if a more efficient gas sparger were used?
3. If catalyst size B is to be used, what is the minimum catalyst charge that should be used to ensure that the combined diffusional resistances for the pellet are less than 50% of the total resistance?

P15-16C You will need to read about slurry reactions on the Web site's *Additional Material*. The catalytic hydrogenation of methyl linoleate to methyl oleate was carried out in a laboratory-scale slurry reactor in which hydrogen gas was bubbled up through the liquid containing spherical catalyst pellets. The pellet density is 2 g/cm^3 . The following experiments were carried out at 25°C :



Partial Pressure of H_2 (atm)	Solubility of H_2 (g mol/dm^3)	H_2 Rate of Reaction ($\text{g mol/dm}^3 \cdot \text{min}$)	Catalyst Charge (g/dm^3)	Catalyst Particle Size (μm)
--	--	--	-------------------------------------	--

1	3	0.007	0.014	3.0	12
2	18	0.042	0.014	0.5	50
3	3	0.007	0.007	1.5	50

1. It has been suggested that the overall reaction rate can be enhanced by increasing the agitation, decreasing the particle size, and installing a more efficient sparger. With which, if any, of these recommendations do you agree? Are there other ways that the overall rate of reaction might be increased? Support your decisions with calculations.
2. Is it possible to determine the effectiveness factor from the data above? If so, what is it?
3. For economical reasons concerning the entrainment of the small solid catalyst particles in the liquid, it is proposed to use particles an order of magnitude larger. The following data were obtained from these particles at 25°C:

R_{Partial}	u	Pressure of H_2 (atm)	Solubility of H_2 (g mol/dm ³)	H_2 Rate of Reaction (g mol/dm ³ • min)	Catalyst Charge (g/dm ³)	Catalyst Particle Size (μm)
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4	3	0.007	0.00233	2.0	750
---	---	-------	---------	-----	-----

The Thiele modulus is 9.0 for the 750- μm particle size in run 4. Determine (if possible) the external mass transfer coefficient, k_c , and the percent (of the overall) of the external mass transfer resistance to the catalyst pellet.

P15-17_B *Applications of Diffusion and Reaction to Tissue Engineering.* The equations describing diffusion and reaction in porous catalysts also can be used to derive rates of tissue growth and have been studied by Professor Kristi Anseth and her students at the University of Colorado. One important area of tissue growth is in cartilage tissue in joints such as the knee. Over 200,000 patients per year receive knee joint replacements. Alternative strategies include the growth of cartilage to repair the damaged knee.

One approach is to deliver cartilage-forming cells in a hydrogel to the damaged area such as the one shown in Figure WP15-1.1 in additional material on the CRE Web site.

Here, the patient's own cells are obtained from a biopsy and embedded in a hydrogel, which is a cross-linked polymer network that is swollen in water. In order for the cells to survive and grow new tissue, many properties of the gel must be tuned to allow diffusion of important species in and out (e.g., nutrients *in* and cell-secreted extracellular molecules such as collagen *out*). Because there is no blood flow through the cartilage, oxygen transport to the cartilage cells is primarily by diffusion. Consequently, the design must be such that the gel can maintain the necessary rates of diffusion of nutrients (e.g., O_2) into the hydrogel. These rates of exchange in the gel depend on the geometry and the thickness of the gel. To illustrate the application of chemical reaction engineering principles to tissue engineering, we will examine the diffusion and consumption of one of the nutrients, oxygen.

Our examination of diffusion and reaction in catalyst pellets showed that in many cases the reactant concentration near the center of the particle was virtually zero. If this condition were to occur in a hydrogel, the cells at the center would die. Consequently, the gel thickness needs to be designed to allow rapid transport of oxygen.

Let's consider the simple gel geometry shown in Figure P15-17B. We want to find the gel

thickness at which the minimum oxygen consumption rate is 10^{-13} mol/cell/h $\left(k = \frac{10^{-3} \text{ mol } O_2}{\text{dm}^3 \text{ h}}\right)$.

The cell density in the gel is 10^{10} cells/dm³, the bulk concentration of oxygen C_{A0} ($z = 0$) is 2×10^{-4} mol/dm³, and the diffusivity, D_{AB} , is 10^{-5} cm²/s.

1. Show that the dimensionless form of concentration and length, $\psi = C_A/C_{A0}$, and $\lambda = z/L$, differential mole balance on O_2 gives

$$\frac{d^2\psi}{d\lambda^2} - \frac{kL^2}{D_{AB}C_{A0}}\psi = 0$$

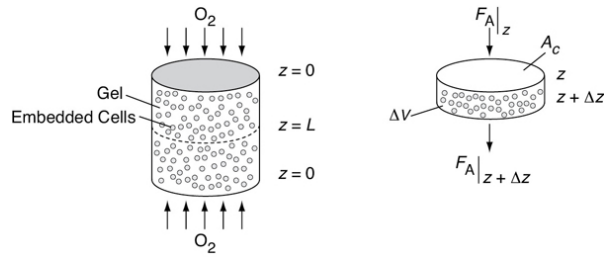


Figure P15-17B Schematic of cartilage cell system.

2. Show the dimensionless O_2 concentration profile in the gel is

$$\psi = \frac{C_A}{C_{A0}} = \phi_0 \lambda (\lambda - 2) + 1$$

where

$$\lambda = z/L$$

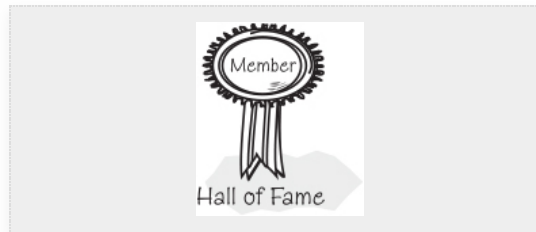
$$\phi_0 = \left(\frac{k}{2D_{AB}C_{A0}} \right) L^2$$

3. Solve the gel thickness when the concentration at $z = 0$ and $C_A = 0.1$ mmole/dm³.
4. How would your answers change if the reaction kinetics were (1) first order in the O_2 concentration with $k_1 = 10^{-2} \text{ h}^{-1}$? (**D** level of difficulty)
5. Carry out a quasi-steady-state analysis using Equation (WE15-1.19) from the Web site

(http://www.umich.edu/~elements/6e/15chap/expanded_ch15_tissue.pdf)

, along with the overall balance

$$\frac{dN_w}{dt} = v_c W_{O_2} \Big|_{z=0} A_c$$



to predict the O_2 flux and collagen build-up as a function of time.

6. Sketch ψ versus λ at different times.
7. Sketch λ_c as a function of time. *Hint:* $V = A_c L$. Assume $\alpha = 10$ and the stoichiometric coefficient for oxygen to collagen, v_c , is 0.05 mass fraction of cell/mol O_2 . $A_c = 2 \text{ cm}^2$.

Section 15.9 through 15.11 have been typeset and can be read and/or printed out from the Web site

(<http://www.umich.edu/~elements/6e/15chap/prof.html>).

Homework problems for slurry reactors, trickle bed reactors, fluidized bed reactors, and CVD boat reactors can be found at <http://www.umich.edu/~elements/6e/15chap/add.html>.

SUPPLEMENTARY READING

1. There are a number of books that discuss internal diffusion in catalyst pellets; however, one of the first books that should be consulted on this and other topics on heterogeneous catalysis is

L. LAPIDUS AND N. R. AMUNDSON, *Chemical Reactor Theory: A Review*, Upper Saddle River, NJ: Prentice Hall, 1977.

In addition, see

R. ARIS, *Elementary Chemical Reactor Analysis*. Upper Saddle River, NJ: Prentice Hall, 1989, Chap. 6. Old, but one should find the references listed at the end of this reading particularly useful.

JOSEPH J. FOGLER, AKA, JOFO, *A Chemical Reaction Engineers Guide to the Country of Jofostan*. To be self published, hopefully by 2025.

D. LUSS, "Diffusion—Reaction Interactions in Catalyst Pellets," p. 239 in *Chemical Reaction and Reactor Engineering*. New York: Marcel Dekker, 1987.

The effects of mass transfer on reactor performance are also discussed in

FRANK C. COLLINS AND GEORGE E. KIMBALL, "Diffusion Controlled Reaction Rates," *Journal of Colloid Science*, Vol. 4, Issue 4, August 1949, Pages 425-437.

2. 2. Diffusion with homogeneous reaction is discussed in

G. ASTARITA AND R. OCONE, *Special Topics in Transport Phenomena*. New York: Elsevier, 2002.

Gas-liquid reactor design is also discussed in

Y. T. SHAH, *Gas-Liquid-Solid Reactor Design*. New York: McGraw-Hill, 1979.

3. 3. Modeling of CVD reactors is discussed in

DANIEL DOBKIN AND M. K. ZUKRAW, *Principles of Chemical Vapor Deposition*. The Netherlands: Kluwer Academic Publishers, 2003.

D. W. HESS, K. F. JENSEN, and T. J. ANDERSON, "Chemical Vapor Deposition: A Chemical Engineering Perspective," *Rev. Chem. Eng.*, 3, 97, 1985.

4. 4. Multiphase reactors are discussed in

P. A. RAMACHANDRAN AND R. V. CHAUDHARI, *Three-Phase Catalytic Reactors*. New York: Gordon and Breach, 1983.

A. E. RODRIGUES, J. M. COLO, and N. H. SWEED, eds., *Multiphase Reactors*, Vol. 1: *Fundamentals*. Alphen aan den Rijn, The Netherlands: Sitjhoff and Noordhoff, 1981.

A. E. RODRIGUES, J. M. COLO, and N. H. SWEED, eds., *Multiphase Reactors*, Vol. 2: *Design Methods*. Alphen aan den Rijn, The Netherlands: Sitjhoff and Noordhoff, 1981.

Y. T. SHAH, B. G. KELKAR, S. P. GODBOLE, and W. D. DECKWER, "Design Parameters Estimations for Bubble Column Reactors" (journal review), *AIChE J.*, 28, 353 (1982).

The following *Advances in Chemistry Series* volume discusses a number of multiphase reactors:

H. S. FOGLER, ed., *Chemical Reactors*, ACS Symp. Ser. 168.
Washington, DC: American Chemical Society, 1981, pp. 3–255.

5. 5. Fluidization

DAIZO KUNII AND OCTAVE LEVENSPIEL, *Fluidization Engineering*,
2nd ed. (Butterworths Series in Chemical Engineering Deposition).
Stoneham, MA: Butterworth-Heinemann, 1991.

In addition to Kunii and Levenspiel's book, many correlations can be
found in

J. F. DAVIDSON, R. CLIFF, and D. HARRISON, *Fluidization*, 2nd ed.
Orlando: Academic Press, 1985.

J. G. YATES, *Fundamentals of Fluidized-Bed Chemical Processes*, 3rd ed.
London: Butterworth, 1983.

16. Residence Time Distributions of Chemical Reactors[†]

Nothing in life is to be feared. It is only to be understood.

—Marie Curie

[†] Dr. Peter Danckwerts is considered the father of *Residence Time Distributions* in Chemical Reactors. After WWII, in which he served defusing unexploded bombs in London, he began developing the concepts of Residence Times, which he published in the early 1950s. Lucky for us he was careful during his WWII service.

Overview. In this chapter, we learn about nonideal reactors; that is, reactors that do not follow the models we have developed for ideal CSTRs, PFRs, and PBRs. After studying this chapter, the reader will be able to describe:

- What the residence time distribution (RTD) is and how it can be used in analyzing reactors (Section 16.1).
- Measurement of the RTD. How to calculate the concentration curve (i.e., the C-curve) and residence time distribution curve (i.e., the E-curve) (Section 16.2).
- Characteristics of the RTD. How to calculate and use the cumulative RTD function, $F(t)$, the mean residence time, t_m , and the variance σ^2 (Section 16.3).
- The RTD in ideal reactors. How to evaluate $E(t)$, $F(t)$, t_m , and σ^2 for ideal PFRs, CSTRs, and laminar flow reactors (LFRs) so that we have a reference point as to how much our real (i.e., nonideal) reactor deviates from an ideal reactor (Section 16.4).
- How to diagnose problems with real reactors by comparing t_m , $E(t)$, and $F(t)$ with ideal reactors. This comparison will help to diagnose and troubleshoot bypassing and dead volume problems in real reactors (Section 16.5).

16.1 GENERAL CONSIDERATIONS

The reactors treated in the book thus far—the perfectly mixed batch, the plug-flow tubular, the packed bed, and the perfectly mixed continuous tank reactors—have been modeled as ideal reactors. Unfortunately, in the real world we often observe behavior very different from that expected from the exemplar; this behavior is true of students, engineers, college professors, and chemical reactors. Just as we must learn to work with people who are not perfect,[†] so the reactor analyst must learn to diagnose and handle chemical reactors whose performance deviates from the ideal. Nonideal reactors and the principles behind their analysis form the subject of this chapter and the next two chapters.

[†] See the AIChE webinar “Dealing with Difficult People”: www.aiche.org/academy/webinars/dealing-difficult-people.

We want to analyze and characterize nonideal reactor behavior.

Peter V. Danckwerts was an interesting character and a number of stories about him can be found in the biography by Peter Vary.[‡] The basic ideas that Danckwerts used in the distribution of residence times to characterize and model nonideal reactions are really few in number. The two major uses of the residence time distribution to characterize nonideal reactors are

[‡] P. Vary, *Life on the Edge*, London: PFV Publications, 2012.

1. To diagnose problems of reactors in operation.
2. To predict conversion or effluent concentrations in existing/available reactors when a new chemical reaction is used in the reactor.

The following two examples illustrate reactor problems one might find in a chemical plant.

Example 1

A packed-bed reactor is shown in Figure 16-1. When a reactor is packed with catalyst, the reacting fluid usually does not flow uniformly through the reactor. Rather, there may be sections in the packed bed that offer little resistance to flow (Path 1) and, as a result, a portion of the fluid may channel through this pathway. Therefore, the molecules following this pathway do not spend much time in the reactor. On the other hand, if there is internal circulation or a high resistance to flow, the molecules could spend a long time in the reactor (Path 2). Consequently, we see that there is a distribution of times that molecules spend in the reactor in contact with the catalyst.

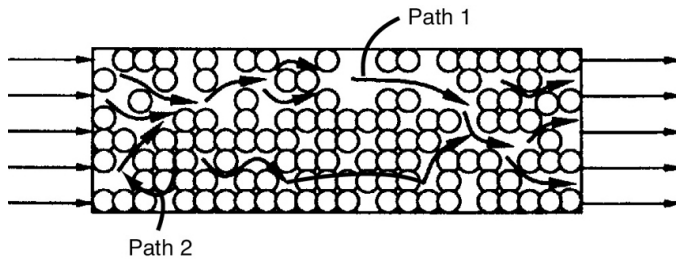


Figure 16-1 Packed-bed reactor.

Example 2

In many continuous-stirred tank reactors, the inlet and outlet pipes are somewhat close together (Figure 16-2). In one operation, it was desired to scale up pilot plant results to a much larger system. It was realized that some short-circuiting occurred, so the tanks were modeled as perfectly mixed CSTRs with a bypass stream. In addition to short-circuiting, stagnant regions (dead zones) are often encountered. In these regions, there is little or no exchange of material with the well-mixed regions and, consequently, virtually

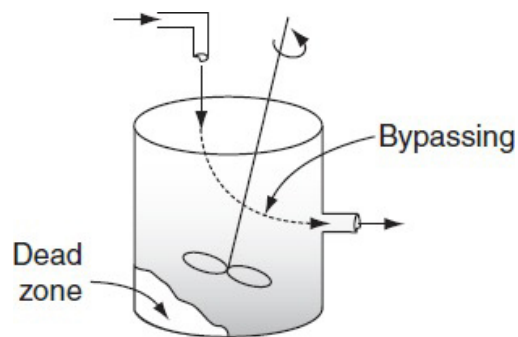


Figure 16-2 CSTR.

We want to find ways of determining the dead zone volume and the fraction of the volumetric flow rate bypassing the system.

no reaction occurs there. Experiments were carried out to determine the amount of the material effectively bypassed and the volume of the dead zone. A simple modification of an ideal reactor successfully modeled the essential physical characteristics of the system and the equations were readily solvable.

The three concepts

- RTD
- Mixing
- Model

Three concepts are used to describe nonideal reactors in these examples: *the distribution of residence times in the system (RTD)*, *the quality of mixing*, and *the model used to describe the system*. All three of these concepts are considered when describing deviations from the mixing patterns assumed in ideal reactors. The three concepts can be regarded as characteristics of the mixing in nonideal reactors.

One way to order our thinking on nonideal reactors is to consider modeling the flow patterns in our reactors as either ideal CSTRs or PFRs as a *first* approximation. In real reactors, however, nonideal flow patterns exist, resulting in ineffective contacting and lower conversions than in the case of ideal reactors. We must have a method of accounting for this nonideality, and to achieve this goal we use the next higher level of approximation, which involves the use of *macromixing* information (RTD) ([Sections 16.1–16.4](#)). The next level uses microscale (*micromixing*) information ([Chapter 17](#)) to make predictions about the conversion in nonideal reactors. After completing the first four sections, 16.1–16.4, the reader can proceed directly to [Chapter 17](#) to learn how to calculate the conversion and product distributions exiting real reactors. [Section 16.5](#) closes the chapter by discussing how to use the RTD to diagnose and troubleshoot reactors. Here, we focus on two common problems: reactors with bypassing and dead volumes. Once the dead volumes, V_D , and bypassing volumetric flow rates, v_b , are

determined, the strategies in Chapter 18 to model the real reactor with ideal reactors can be used to predict conversion.

Chance Card: **Do not pass go, proceed directly to Chapter 17.**



Reactor Monopoly

16.1.1 Residence Time Distribution (RTD) Function

The idea of using the distribution of residence times in the analysis of chemical reactor performance was apparently first proposed in a pioneering paper by MacMullin and Weber.¹ However, the concept did not appear to be used extensively until the early 1950s, when Prof. P. V. Danckwerts gave organizational structure to the subject of RTD by defining most of the distributions of interest.² The ever-increasing amount of literature on this topic since then has generally followed the nomenclature of Danckwerts, and this will be done here as well.

¹ R. B. MacMullin and M. Weber, Jr., *Trans. Am. Inst. Chem. Eng.*, 31, 409 (1935).

² P. V. Danckwerts, *Chem. Eng. Sci.*, 2, 1 (1953).

Residence time

In an ideal plug-flow reactor, all the atoms of material leaving the reactor have been inside it for *exactly* the same amount of time. Similarly, in an ideal batch reactor, all the atoms of

materials within the reactor have been inside the BR for an *identical* length of time. The time the atoms have spent in the reactor is called the **residence time** of the atoms in the reactor.

The "RTD": Some molecules leave quickly, others overstay their welcome.

The idealized plug-flow and batch reactors are the only two types of reactors in which all the atoms in the reactors have exactly the same residence time. In all other reactor types, the various atoms in the feed spend different times inside the reactor; that is, there is a distribution of residence times of the material within the reactor. For example, consider the CSTR; the feed introduced into a CSTR at any given time becomes completely mixed with the material already in the reactor. In other words, some of the atoms entering the CSTR leave it almost immediately because material is being continuously withdrawn from the reactor; other atoms remain in the reactor almost forever because all the material recirculates within the reactor and is virtually never removed from the reactor at one time. Many of the atoms, of course, leave the reactor after spending a period of time somewhere in the vicinity of the mean residence time. In any reactor, the distribution of residence times can significantly affect its performance in terms of conversion and product distribution.

We will use the RTD to characterize nonideal reactors.

The *residence time distribution* (RTD) of a reactor is a characteristic of the mixing that occurs in the chemical reactor. There is no axial mixing in a plug-flow reactor, and this omission is reflected in the RTD. The CSTR is thoroughly mixed and possesses a far different kind of RTD than the plug-flow reactor. As will be illustrated later (cf. Example 16-3), not all RTDs are unique to a particular reactor type; markedly different reactors and reactor sequencing can display identical

RTDs. Nevertheless, the RTD exhibited by a given reactor yields distinctive clues to the type of mixing occurring within it and is one of the most informative characterizations of the reactor.³

³ There are a number of mixing tutorials on the AIChE Webinar Web site and as an AIChE student member you have free access to all these webinars. See www.aiche.org/search/site/webinar.

16.2 MEASUREMENT OF THE RTD

The RTD is determined experimentally by injecting an inert chemical, molecule, or atom, called a *tracer*, into the reactor at some time $t = 0$ and then measuring the tracer concentration, C , in the effluent stream as a function of time, cf. Figure 16-3. In addition to being a nonreactive species that is easily detectable, the tracer should have physical properties similar to those of the reacting mixture and be completely soluble in the mixture. It also should not adsorb on the walls or other surfaces in the reactor. The latter requirements are needed to ensure that the tracer's behavior will reliably reflect that of the material flowing through the reactor. Colored and radioactive materials along with inert gases are the most common types of tracers. The two most used methods of injection are *pulse input* and *step input*.

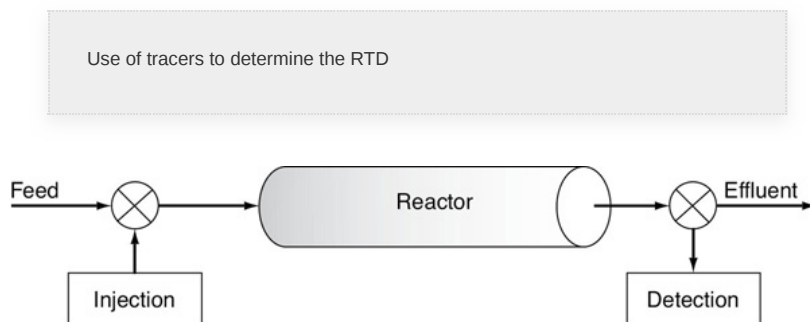


Figure 16-3 Experimental setup to determine $E(t)$.

16.2.1 Pulse Input Experiment

The C-curve

In a pulse input, an amount of tracer N_0 is suddenly injected in one shot into the feed stream entering the reactor in as short a time as is humanly possible. The outlet concentration is then measured as a function of time. Typical concentration–time curves at the inlet and outlet of an arbitrary reactor are shown in [Figure 16-4](#) on page 848. The effluent tracer concentration versus time curve is referred to as the C -curve in RTD analysis. We shall first analyze the injection of a tracer pulse for a single-input and single-output system in which *only flow* (i.e., no dispersion) carries the tracer material across system boundaries. Here, we choose an increment of time Δt sufficiently small that the concentration of tracer, $C(t)$, exiting between time t and time $(t + \Delta t)$ is essentially the same. The amount of tracer material, ΔN , leaving the reactor between time t and $t + \Delta t$ is then

$$\Delta N = C(t) v \Delta t \quad (16 - 1)$$

where v is the effluent volumetric flow rate. In other words, ΔN is the amount of material exiting the reactor that has spent an amount of time between t and $t + \Delta t$ in the reactor. If we now divide by the total amount of material that was injected into the reactor, N_0 , we obtain

$$\frac{\Delta N}{N_0} = \frac{vC(t)}{N_0} \Delta t \quad (16 - 2)$$

which represents *the fraction of material that has a residence time in the reactor between time t and $t + \Delta t$.*

For pulse injection we define

$$E(t) = \frac{vC(t)}{N_0} \quad (16 - 3)$$

so that

$$\frac{\Delta N}{N_0} = E(t) \Delta t \quad (16-4)$$

Interpretation of $E(t) dt$

The quantity $E(t)$ is called the **residence time distribution function**. It is the function that describes in a quantitative manner how much time different fluid elements have spent in the reactor. The quantity $E(t) dt$ is the fraction of fluid exiting the reactor that has spent between time t and $t + dt$ inside the reactor.

Figure 16-4 shows schematics of the inlet and outlet concentrations for both a pulse input and step input for the experimental setup in Figure 16-3.

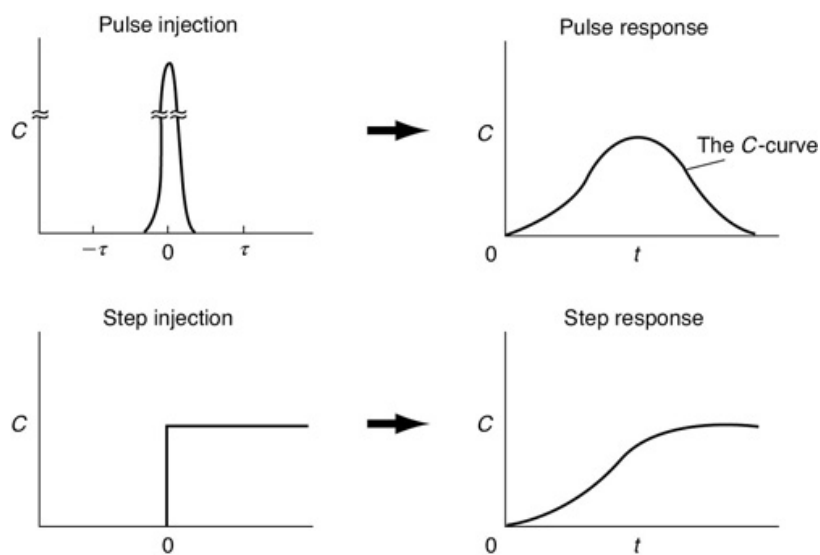
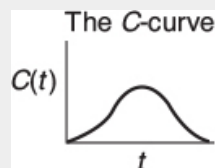


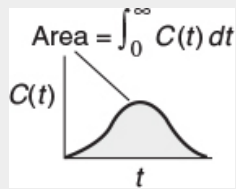
Figure 16-4 RTD measurements..



If N_0 is not known directly, it can be obtained from the outlet concentration measurements by summing up all the amounts of materials, ΔN , between time equal to zero and infinity.

Writing Equation (16-1) in differential form yields

$$dN = vC(t) dt \quad (16 - 5)$$

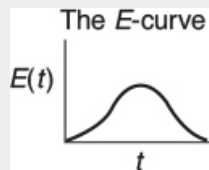


and then integrating, we obtain

$$N_0 = \int_0^{\infty} vC(t) dt \quad (16 - 6)$$

The volumetric flow rate is usually constant, so we can define $E(t)$ as

We find the RTD function, $E(t)$, from the tracer concentration $C(t)$



$$E(t) = \frac{C(t)}{\int_0^{\infty} C(t) dt} \quad (16 - 7)$$

The E-curve is just the C-curve divided by the area under the C-curve.

An alternative way of interpreting the residence time function is in its integral form:

$$\left[\begin{array}{l} \text{Fraction of material leaving the reactor} \\ \text{that has resided in the reactor} \\ \text{for a time between } t_1 \text{ and } t_2 \end{array} \right] = \int_{t_1}^{t_2} E(t) dt$$

We know that the fraction of all the material that has resided for a time t in the reactor between $t = 0$ and $t = \infty$ is 1; therefore

Eventually, all guests must leave.

$$\int_0^{\infty} E(t) dt = 1 \quad (16 - 8)$$

The following example will show how we can calculate and interpret $E(t)$ from the effluent concentrations from the response to a pulse tracer input to a real (i.e., nonideal) reactor.

Example 16–1 Constructing the $C(t)$ and $E(t)$ Curves

A sample of the tracer hytane at 320 K was injected as a pulse into a reactor, and the effluent concentration was measured as a function of time, resulting in the data shown in [Table E16-1.1](#).

Pulse input

TABLE E16-1.1 TRACER DATA

t (<i>min</i>)	0	0	1	2	3	4	5	6	7	8	9	1	1	1
		.										0	2	4
		5												
C (g / m^3)	0	0	1	5	8	1	8	6	4	3	2	1	0	0
		.	.			0					.	.	.	
		6	4								2	6	6	

The measurements represent the exact concentrations at the times listed and not average values between the various sampling tests.

1. Construct a figure showing the tracer concentration $C(t)$ as a function of time.
2. Construct a figure showing $E(t)$ as a function of time.

Solution

1. By plotting C as a function of time, using the data in [Table E16-1.1](#), the curve shown in [Figure E16-1.1](#) is obtained.

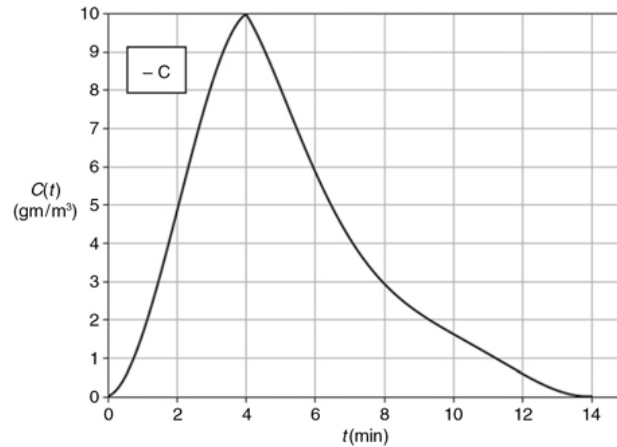


Figure E16-1.1 The C-curve.

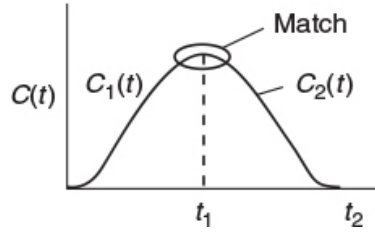
To convert the $C(t)$ curve in **Figure E16-1.1** to an $E(t)$ curve we use the area under the $C(t)$ curve. There are three ways we can determine the area using this data.

1. Brute force: calculate the area by measuring the area of the squares and partial squares under the curve, and then summing them up. *Who in the world do you think would use this method? Not sure I would.*
2. Use the integration formulas given in **Appendix A.4**. Possibly Method 2 Simpson's rule.
3. Fit the data to one or more polynomials using Polymath or some other software program. We will choose Polymath to fit the data. *Note:* A step-by-step tutorial to fit the data points using Polymath is given on the CRE Web site (www.umich.edu/~elements/6e/index.html) LEP 16-1. We will use two polynomials to fit the C -curve, one for the ascending portion, $C_1(t)$, and one for the descending portion, $C_2(t)$, both of which meet at t_1 . Like Nike. *Just do it.*

Using the Polymath polynomial fitting routine (see tutorial), the data in **Table E16-1.1** yields the following two polynomials:

$$\text{For } t \leq 4 \text{ min then } C_1(t) = 0.0039 + 0.274 t + 1.57 t^2 - 0.255 t^3 \quad (\text{E16-1.1})$$

$$\begin{aligned} \text{For } t \geq 4 \text{ min then } C_2(t) = & -33.4 + 37.2 t - 11.6 t^2 + 1.7 t^3 - 0.13 t^4 + 0.005 t^5 \\ & - 7.7 \times 10^{-5} t^5 \end{aligned} \quad (\text{E16-1.2})$$



We then use an *if statement* in our fitted curve.

If ($t \leq 4$ and $t > 0$) then C_1 else if ($t > 4$ and $t \leq 14$) then C_2 else 0

To find the area under the curve, A , we use the ODE solver.

Let A represent the area under the curve, then

$$\frac{dA}{dt} = C(t) \quad (\text{E16-1.3})$$

$$A = \int_0^{14} C(t) dt \quad (\text{E16-1.4})$$

2. Construct $E(t)$.

$$E(t) = \frac{C(t)}{\int_0^{\infty} C(t) dt} = \frac{C(t)}{A}$$

The Polymath program and results are shown in [Table E16-1.2](#) where we see $A = 51$.

TABLE E16-1.2 POLYMATH PROGRAM TO FIND AREA UNDER THE C -CURVE

Calculated values of DEQ variables			Differential equations
Variable	Initial value	Final value	
1 Area	0	51.06334	*1 d(Area)/d(t) = C
2 C	0.0038746	0.0148043	Explicit equations 1 C2 = -33.43818 + 37.18972*t - 11.58838*t^2 + 1.695303*t^3 - 0.1298667*t^4 + 0.005028*t^5 - 7.743*10^-5*t^6 2 C1 = 0.0038746 + 0.2739782*t + 1.574621*t^2 - 0.2550041*t^3 3 C = If(t<=4 and t>=0) then C1 else if(t>4 and t<=14) then C2 else 0
3 C1	0.0038746	-387.266	
4 C2	-33.43818	0.0148043	
5 t	0	14.	

Now that we have the area, A (i.e., $51 \text{ g}\cdot\text{min}/\text{m}^3$), under the C -curve, we can construct the $E(t)$ curves. We now calculate $E(t)$ by dividing each point on the $C(t)$ curve by $51.0 \text{ g}\cdot\text{min}/\text{m}^3$

$$E(t) = \frac{C(t)}{\int_0^{\infty} C(t) dt} = \frac{C(t)}{51 \text{ g}\cdot\text{min}/\text{m}^3} \quad (\text{E16-1.5})$$

with the following results:

TABLE E16-13 $C(t)$ AND $E(t)$

t (min)	0	1	2	3	4	5	6	7	8	9	10	11	12
$C(t)$ (g/m ³)	0	1	5	8	10	8	6	4	3	2	1	0	0
$E(t)$ (min ⁻¹)	0	0	0	0	0	0	0	0	0	0	0	0	0

Using Table E16-13 we can construct $E(t)$ as shown in Figure E16-1.2.

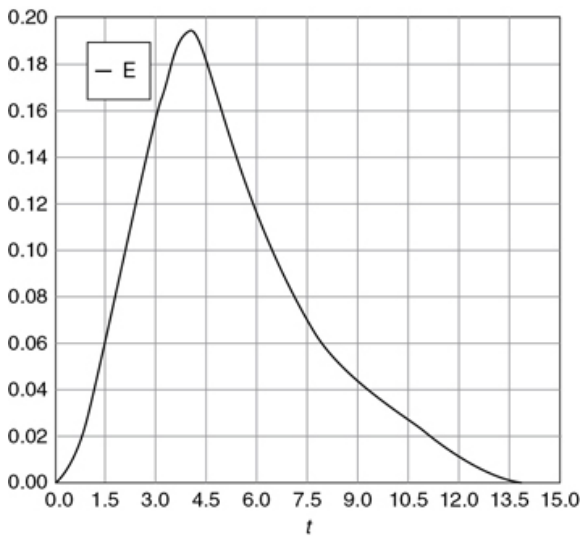


Figure E16-1.2 $E(t)$ -Curve.

The $E(t)$ Curve

Analysis: In this example, we fit the effluent concentration data $C(t)$ from an inert tracer pulse input to two polynomials and then used an *If statement* to model the complete curve. We then used the Polymath ODE solver to get the area under the curve that we then used to divide the $C(t)$ curve in order to obtain the $E(t)$. Once we have the $E(t)$ curve, we ask and easily answer such questions as “what fraction of the modules spend between 2 and 4 minutes in the reactor” or “what is the mean residence time t_m ?” We will address these questions in the following sections where we discuss characteristics of the residence time distribution (RTD).

The principal difficulties with the pulse technique lie in the problems connected with obtaining a reasonable pulse at a reactor’s entrance. The injection must take place over a period that is very short compared with residence times in various segments of the reactor or reactor system, and there must be a negligible amount of dispersion between the point of injection and the entrance to the reactor system. If these conditions can be fulfilled, this technique represents a simple and direct way of obtaining the RTD.

Drawbacks to the pulse injection to obtain the RTD

There could be problems in fitting $E(t)$ to a polynomial if the effluent concentration–time curve were to have a long tail because the analysis can be subject to large inaccuracies. This problem principally affects the denominator of the right-hand side of Equation (16-7), that is, the integration of the $C(t)$ curve. It is desirable to extrapolate the tail and analytically

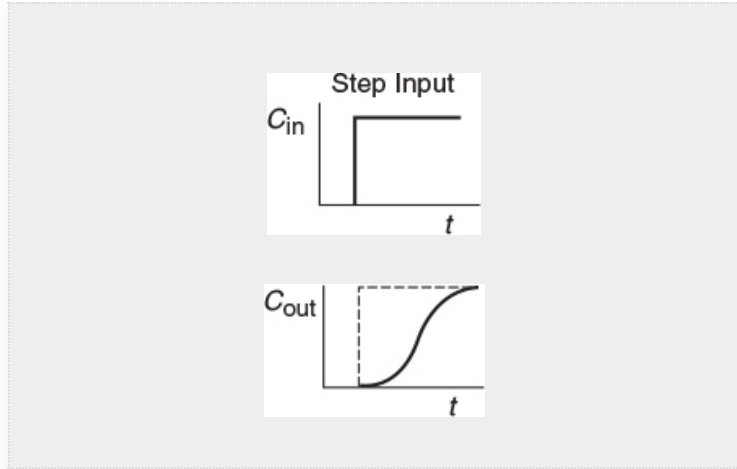
continue the calculation. The tail of the curve may sometimes be approximated as an exponential decay. The inaccuracies introduced by this assumption are very likely to be much less than those resulting from either truncation or numerical imprecision in this region. Methods of *Fitting the Tail* are described in the *Professional Reference Shelf R16.1*.



16.2.2 Step Tracer Experiment

Now that we have an understanding of the meaning of the RTD curve from a pulse input, we will formulate a relationship between a step tracer injection and the corresponding concentration in the effluent.

The inlet concentration most often takes the form of either a perfect *pulse input* (Dirac delta function), *imperfect pulse injection* (see [Figure 16-4](#)), or a *step input*. Just as the RTD function $E(t)$ can be determined directly from a pulse input, the cumulative distribution $F(t)$ can be determined directly from a step input. *The cumulative distribution gives the fraction of material $F(t)$ that has been in the reactor at time t or less.* We will now analyze a *step input* in the tracer concentration for a system with a constant volumetric flow rate. Consider a constant rate of tracer addition to a feed that is initiated at time $t = 0$. Before this time, no tracer was added to the feed. Stated symbolically, we have



$$C_{in}(t) = \begin{cases} 0 & t < 0 \\ C_0, \text{ constant} & t \geq 0 \end{cases} \quad (16-9)$$

The concentration of tracer in the feed to the reactor is kept at this level until the concentration in the effluent is indistinguishable from that in the feed; the test may then be discontinued. A typical outlet concentration curve for this type of input is shown in Figure 16-4.

Because the inlet concentration is a constant with time, C_0 , we can take it outside the integral sign; that is,

$$C_{out}(t) = C_0 \int_0^t E(t') dt'$$

Dividing by C_0 yields

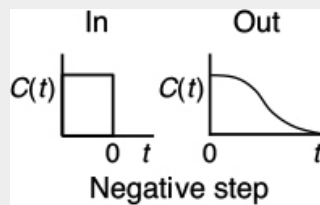
$$\begin{aligned} \left[\frac{C_{out}(t)}{C_0} \right]_{\text{step}} &= \int_0^t E(t') dt' = F(t) \\ F(t) &= \left[\frac{C_{out}(t)}{C_0} \right]_{\text{step}} \end{aligned} \quad (16-10)$$

We differentiate this expression to obtain the RTD function $E(t)$:

$$E(t) = \frac{dF}{dt} = \frac{d}{dt} \left[\frac{C_{out}(t)}{C_0} \right]_{\text{step}} \quad (16-11)$$

The positive step is usually easier to carry out experimentally than the pulse test, and it has the additional advantage that the total amount of tracer in the feed over the period of the test does not have to be known as it does in the pulse test. One possible drawback in this technique is that it is sometimes difficult to maintain a constant tracer concentration in the feed. Obtaining the RTD from this test also involves differentiation of the data and presents an additional and probably more serious drawback to the technique, because differentiation of data can, on occasion, lead to large errors. A third problem lies with the large amount of tracer required for this test. If the tracer is very expensive, a pulse test is almost always used to minimize the cost.

Advantages and drawbacks to the step injection



Other tracer techniques exist, such as negative step (i.e., elution), frequency-response methods, and methods that use inputs other than steps or pulses. These methods are usually much more difficult to carry out than the ones presented and are not encountered as often. For this reason, they will not be treated here, and the literature should be consulted for their virtues, defects, and the details of implementing them and analyzing the results. A good source for this type of information is Wen and Fan.³

³ C. Y. Wen and L. T. Fan, *Models for Flow Systems and Chemical Reactors*, New York: Marcel Dekker, 1975.

16.3 CHARACTERISTICS OF THE RTD

From $E(t)$ we can learn how long different molecules have been in the reactor.

Sometimes $E(t)$ is called the *exit-age distribution function*. If we regard the “age” of an atom as the time it has resided in the reaction environment, then $E(t)$ concerns the age distribution of the effluent stream. It is *the* most used of the distribution functions connected with reactor analysis because it characterizes the lengths of time various atoms spend at reaction conditions.

16.3.1 Integral Relationships

The fraction of the exit stream that has resided in the reactor for a period of time shorter than a given value t is equal to the sum over all times less than t of $E(t) \Delta t$, or expressed continuously, by integrating $E(t)$ between time $t = 0$ and time, t .

$$\int_0^t E(t) dt = F(t) = \left[\begin{array}{c} \text{Fraction of effluent} \\ \text{that has been in reactor} \\ \text{for less than time } t \end{array} \right] \quad (16-12)$$

Analogously, we have, by integrating between time t and time $t \Rightarrow \infty$

$$\int_t^\infty E(t) dt = 1 - F(t) = \left[\begin{array}{c} \text{Fraction of effluent} \\ \text{that has been in reactor} \\ \text{for longer than time } t \end{array} \right] \quad (16-13)$$

Because t appears in the integration limits of these two expressions, Equations (16-12) and (16-13) are both functions of time. Danckwerts defined Equation (16-12) as a *cumulative distribution function and called it $F(t)$* .⁴ We can calculate $F(t)$ at various times t from the area under the curve of a plot of $E(t)$ versus t , that is, the E -curve. A typical shape of the $F(t)$

curve is shown in Figure 16-5. One notes from this curve that 80% (i.e., $F(t) = 0.8$) of the molecules spend 8 minutes or less in the reactor, and 20% of the molecules [$1 = F(t)$] spend longer than 8 minutes in the reactor.

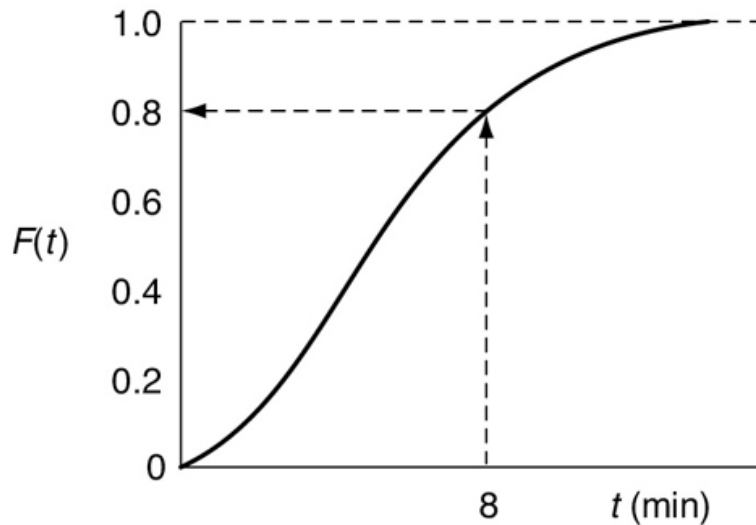


Figure 16-5 Cumulative distribution curve, $F(t)$.

⁴ P. V. Danckwerts, *Chem. Eng. Sci.*, 2, 1 (1953).

The F -curve is another function that has been defined as the normalized response to a particular input. Alternatively, Equation (16-12) has been used as a definition of $F(t)$, and it has been stated that as a result it can be obtained as the response to a positive step tracer test. Sometimes the F -curve is used in the same manner as the RTD in the modeling of chemical reactors. An excellent industrial example is the study of Wolf and White, who investigated the behavior of screw extruders in polymerization processes.⁵

⁵ D. Wolf and D. H. White, *AIChE J.*, 22, 122 (1976).

The F -curve

16.3.2 Mean Residence Time

In previous chapters treating ideal reactors, a parameter frequently used was the space time or average residence time, τ , which was defined as being equal to (V/v) . It will be shown that, in the absence of dispersion, and for constant volumetric flow ($v = v_0$) no matter what RTD exists for a particular reactor, ideal or nonideal, this nominal space time, τ , is equal to the *mean residence time*, t_m .

$$\tau = t_m$$

As is the case with other variables described by distribution functions, the mean value of the variable is equal to the first moment of the RTD function, $E(t)$. Thus the mean residence time is

The first moment gives the average time the effluent molecules spent in the reactor.

$$t_m = \frac{\int_0^\infty tE(t) dt}{\int_0^\infty E(t) dt} = \int_0^\infty tE(t) dt \quad (16 - 14)$$

We now wish to show how we can determine the total reactor volume using the cumulative distribution function.

In the Additional Material for Chapter 16 on the Web site (http://www.umich.edu/~elements/6e/16chap/expanded_ch16_exampleB.pdf), a proof is given that the mean residence time is equal to the space time, for the case of a constant volumetric flow rate, that is,

$$t_m = \tau \quad (16 - 15)$$

This result is true *only* for a *closed system* (i.e., no dispersion across boundaries; as is the case in Chapter 18). The exact reactor volume is determined from the equation

$$\boxed{V = vt_m} (16 - 16)$$

16.3.3 Other Moments of the RTD

It is very common to compare RTDs by using their moments instead of trying to compare their entire distributions (e.g., Wen and Fan).⁶ For this purpose, three moments are normally used. The first is the mean *residence time*, t_m . The second moment commonly used is taken about the mean and is called the *variance*, σ^2 , or square of the standard deviation. It is defined by

⁶ C. Y. Wen and L. T. Fan, *Models for Flow Systems and Chemical Reactors*, New York: Decker, 1975, Chap. 11.

The second moment about the mean is the variance.

$$\boxed{\sigma^2 = \int_0^\infty (t - t_m)^2 E(t) dt} (16 - 17)$$

The magnitude of this moment is an indication of the “spread” of the distribution; the greater the value of this moment is, the greater a distribution’s spread will be.

The third moment is also taken about the mean and is related to the *skewness*, s^3 . The skewness is defined by

The two parameters most commonly used to characterize the RTD are τ and σ^2 .

$$\boxed{S^3 = \frac{1}{\sigma^{3/2}} \int_0^\infty (t - t_m)^3 E(t) dt} (16 - 18)$$

The magnitude of the third moment measures the extent that a distribution is skewed in one direction or another in reference to the mean.

Rigorously, for a complete description of a distribution, all moments must be determined. Practically, these three are usually sufficient for a reasonable characterization of an RTD.

Example 16–2 Mean Residence Time and Variance Calculations

Using the data given in Table E16-1.3 in Example 16-1

- 1. Construct the $F(t)$ curve.
- 2. Calculate the mean residence time, t_m .
- 3. Calculate the variance about the mean, σ^2 .
- 4. Calculate the fraction of fluid that spends between 3 and 6 minutes in the reactor.
- 5. Calculate the fraction of fluid that spends 2 minutes or less in the reactor.
- 6. Calculate the fraction of the material that spends 3 minutes or longer in the reactor.

Solution

- 1. To construct the F -curve, we simply integrate the E -curve

$$E(t) = \frac{C(t)}{A} = \frac{C(t)}{51} \quad (\text{E16} - 1.5)$$

using an ODE solver such as Polymath shown in Table E16-2.1

$$\frac{dF}{dt} = E(t) \quad (16 - 11)$$

The Polymath program and results are shown in Table E16-2.1 and Figure E16-2.1(b), respectively.

TABLE E16-1.3 $C(t)$ AND $E(t)$

t (min)	0	1	2	3	4	5	6	7	8	9	1	1	1
											0	2	4
$C(t)$ (g/m ³)	0	1	5	8	1	8	6	4	3	2	1	0	0
		.			0					.	.	.	
		4								2	6	6	
$E(t)$ (min ⁻¹)	0	0	0	0	0	0	0	0	0	0	0	0	0
	
		0	1	1	2	1	1	0	0	0	0	0	
		2		6		6	2	8	6	4	3	1	
		7								3		2	

Calculating the mean residence time,
 $\tau = t_m = \int_0^\infty tE(t) dt$

2. We also show in Table E16-2.1 the Polymath program to calculate the mean residence time, t_m . By differentiating Equation (16-14), we can easily use Polymath to find t_m , that is,

$$\frac{dt_m}{dt} tE(t) \quad (\text{E16} - 2.1)$$

with $t = 0$ then $E = 0$ and $t = 14$ then $E = 0$. Equation (E16-2.1) and the calculated result is also shown in Table E16-2.1 where we find

$$t_m = 5.1 \text{ minutes}$$

TABLE E16-2.1 POLYMATH PROGRAM AND RESULTS
TO CONTRUCT THE E - AND F -CURVES

Calculated values of DEQ variables			Differential equations
Variable	Initial value	Final value	
1 Area	51.	51.	1 d(tm)/d(t) = t*E
2 C	0.0038746	0.0148043	2 d(F)/d(t) = E
3 C1	0.0038746	-387.266	Explicit equations
4 C2	-33.43818	0.0148043	1 C1 = 0.0038746 + 0.2739782*t + 1.574621*t^2 - 0.2550041*t^3
5 E	7.597E-05	0.0002903	2 Area = 51
6 F	0	1.00125	3 C2 = -33.43818 + 37.18972*t - 11.58838*t^2 + 1.695303*t^3 - 0.1298667*t^4 + 0.005028*t^5 - 7.743*10^-5*t^6
7 t	0	14.	4 C = If(t<=4 and t>=0) then C1 else If(t>4 and t<=14) then C2 else 0
8 tm	0	5.107247	5 E = C/Area

Using the Polymath plotting routines, we can construct Figures E16-2.1(a) and (b) after executing the program shown in the Polymath Table E16-2.1.

The $E(t)$ and $F(t)$ Curves

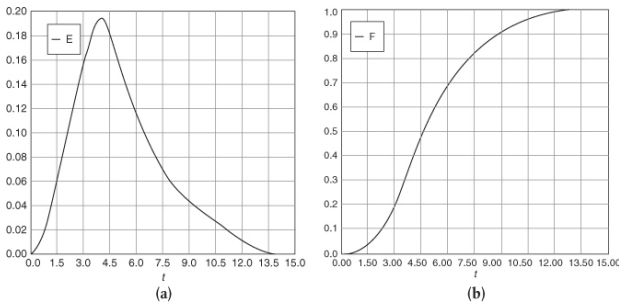


Figure E16-2.1 (a) E -Curve; (b) F -Curve.

3. Now that we have found the mean residence time t_m , we can calculate the variance σ^2 .

Calculating the variance

$$\sigma^2 = \int_0^\infty (t - t_m)^2 E(t) dt \quad (\text{E16 - 2.2})$$

We now differentiate Equation (E16-2.2) with respect to t

$$\frac{d\sigma^2}{dt}(t - t_m)^2 E(t) \quad (\text{E16 - 2.3})$$

and then use Polymath to integrate between $t = 0$ and $t = 14$, which is the last point on the E-curve.

The results of this integration are shown in Table E16-2.2 where we find $\sigma^2 = 6.2 \text{ minutes}^2$, so $\sigma = 2.49 \text{ minutes}$.

TABLE E16-2.2 POLYMATH PROGRAM AND RESULTS
TO CALCULATE THE MEAN RESIDENCE TIME, t_m ,
AND THE VARIANCE σ^2

Calculated values of DEQ variables			Differential equations	
Variable	Initial value	Final value	1	d(Sigma2)/d(t) = ((t-tmf)^2 * E
1 Area	51.	51.	Explicit equations	
2 C	0.0038746	0.0148043	1	C1 = 0.0038746 + 0.2739782*t + 1.574621*t^2 - 0.2550041*t^3
3 C1	0.0038746	-387.266	2	Area = 51
4 C2	-33.43818	0.0148043	3	C2 = -33.43818 + 37.18972*t - 11.58838*t^2 + 1.695303*t^3 - 0.1298667*t^4 + 0.005028*t^5 - 7.743*10^-5*t^6
5 E	7.597E-05	0.0002903	4	C = If((t<=4 and t>=0) then C1 else If(t>4 and t<=14) then C2 else 0
6 Sigma2	0	6.212473	5	E = C/Area
7 t	0	14.	6	tmf = 5.1
8 tmf	5.1	5.1		

4. To find the fraction of fluid that spends between 3 and 6 minutes, we simply integrate the E -curve between 3 and 6

$$F_{3-6} = \int_3^6 E(t) dt$$

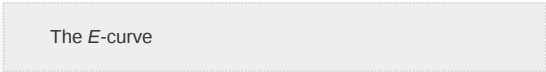
The Polymath program is shown in Table E16-2.3 along with the output.

TABLE E16-2.3 POLYMATH PROGRAM TO FIND THE
FRACTION OF FLUID THAT SPENDS BETWEEN 3
AND 6 MINUTES IN THE REACTOR

Calculated values of DEQ variables			Differential equations	
Variable	Initial value	Final value	1	d(F)/d(t) = E
1 C	8.112288	5.881819	Explicit equations	
2 C1	8.112288	3.253214	1	C1 = 0.0038746 + 0.2739782*t + 1.574621*t^2 - 0.2550041*t^3
3 C2	10.2549	5.881819	2	C2 = -33.43818 + 37.18972*t - 11.58838*t^2 + 1.695303*t^3 - 0.1298667*t^4 + 0.005028*t^5 - 7.743*10^-5*t^6
4 E	0.1590645	0.1153298	3	C = If((t<=4 and t>=0) then C1 else If(t>4 and t<=14) then C2 else 0
5 F	0	0.4952889	4	E = C/51
6 t	3.	6.		

We see that approximately 50% (i.e., 49.53%) of the material spends between 3 and 6 minutes in the reactor.

We can visualize this fraction with the use of plot of $E(t)$ versus (t) as shown in Figure E16-2.2. The shaded area in Figure E16-2.2 represents the fraction of material leaving the reactor that has resided in the reactor between 3 and 6 minutes. Evaluating this area, we find that 50% of the material leaving the reactor spends between 3 and 6 minutes in the reactor.



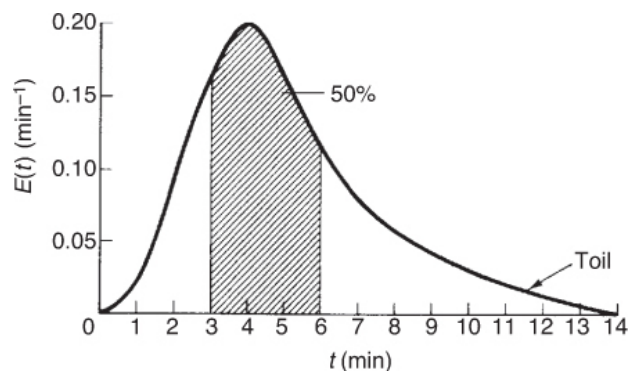


Figure E16-2.2 Fraction of material that spends between 3 and 6 minutes in the reactor.

5. We shall next consider the fraction of material that has been in the reactor for a time t or less; that is, the fraction that has spent between 0 and t minutes in the reactor, $F(t)$. This fraction is just the shaded area under the curve up to $t = t$ minutes. This area is shown in Figure E16-2.3 for $t = 3$ minutes. Calculating the area under the curve, we see that approximately 20% of the material has spent 3 minutes or less in the reactor.

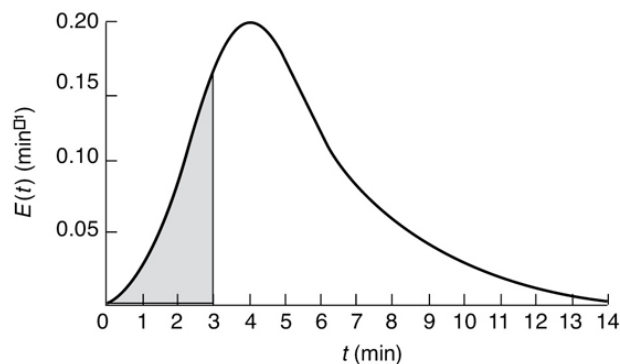


Figure E16-2.3 Fraction of material that spends 3 minutes or less in the reactor.

6. The fraction of fluid that spends a time $t = 3$ min or greater in the reactor is

$$\left[\begin{array}{c} \text{Greater} \\ \text{than time } t \end{array} \right] = 1 - F(t) = 1 - 0.2 = 0.8$$

therefore 80% of the fluid spends a time $t = 3$ min or greater in the reactor.

The standard deviation is $\sigma^2 = 6.19 \text{ min}^2$, so $\sigma = 2.49 \text{ min}$.

Analysis: In this example we calculated two important properties of the RTD, the mean time molecules spend in the reactors, t_m , and the variance about this mean, σ^2 . We will

calculate these properties from the RTD of other nonideal reactors and then show in Chapter 18 how to use them to formulate models of real reactors using combinations of ideal reactors. We will use these models along with reaction-rate data to predict the conversion in the nonideal reactor we obtained from the reactor storage shed.

16.3.4 Normalized RTD Function, $E(\Theta)$

Frequently, a normalized RTD is used instead of the function $E(t)$. If the parameter Θ is defined as

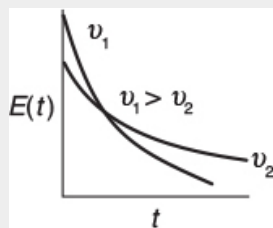
$$\Theta \equiv \frac{t}{\tau} \quad (16 - 19)$$

Why we use a normalized RTD

The quantity Θ represents the number of reactor volumes of fluid, based on entrance conditions, that have flowed through the reactor in time t . The dimensionless RTD function, $E(\Theta)$ is then defined as

$$E(\Theta) \equiv \tau E(t) \quad (16 - 20)$$

and plotted as a function of Θ , as shown in the margin.



The purpose of creating this normalized distribution function is that the flow performance inside reactors of different sizes can be compared directly. For example, if the normalized function $E(\Theta)$ is used, *all* perfectly mixed CSTRs have numerically the same RTD. If the simple function $E(t)$ is used,

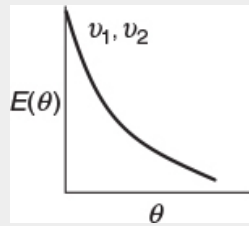
numerical values of $E(t)$ can differ substantially for CSTRs different volumes, V , and entering volumetric flow rates, v_0 . As will be shown later in Section 16.4.2, $E(t)$ for a perfectly mixed CSTR

$E(t)$ for an ideal CSTR

$$E(t) = \frac{1}{\tau} e^{-t/\tau} \quad (16-21)$$

and therefore

$$E(\Theta) = \tau E(t) = e^{-\Theta} \quad (16-22)$$



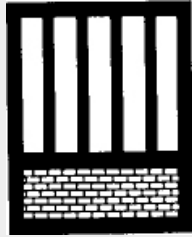
From these equations it can be seen that the value of $E(t)$ at identical times can be quite different for two different volumetric flow rates, say v_1 and v_2 . But for the same value of Θ , the value of $E(\Theta)$ is the same irrespective of the size or volumetric flow rate of a perfectly mixed CSTR.

It is a relatively easy exercise to show that

$$\int_0^{\infty} E(\Theta) d\Theta = 1 \quad (16-23)$$

and is recommended as a 93-s divertissement. (Jofostan University chemical engineers claim they can do it in 87 s.)

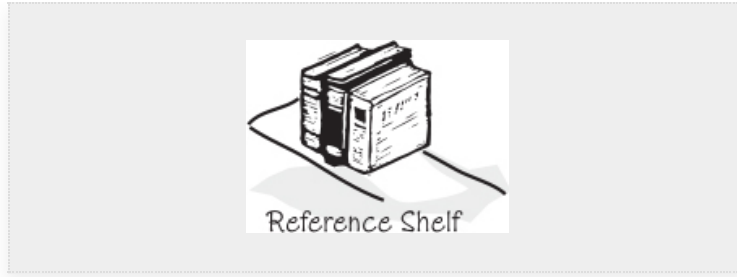
16.3.5 Internal-Age Distribution, $I(\alpha)$



Tombstone jail How long have you been here? $I(\alpha)\Delta\alpha$ When do you expect to get out?

Although this section is not a prerequisite to the remaining sections, the internal-age distribution is introduced here because of its close analogy to the external-age distribution. We shall let α represent the age of a molecule inside the reactor. The internal-age distribution function $I(\alpha)$ is a function such that $(I(\alpha)\Delta\alpha)$ is the fraction of material now *inside the reactor* that has been inside the reactor for a period of time between α and $(\alpha + \Delta\alpha)$. It may be contrasted with $E(\alpha)\Delta\alpha$, which is used to represent the material *leaving the reactor* that has spent a time between α and $(\alpha + \Delta\alpha)$ in the reaction zone; $I(\alpha)$ characterizes the time the material has been (and still is) in the reactor at a particular time. The function $E(\alpha)$ is viewed outside the reactor and $I(\alpha)$ is viewed inside the reactor. In unsteady-state problems, it can be important to know what the particular state of a reaction mixture is, and $I(\alpha)$ supplies this information. For example, in a catalytic reaction using a catalyst whose activity decays with time, the internal-age distribution of the catalyst activities in the reactor $I(\alpha)$ can be of use in determining the amount of catalyst decay, $a(\alpha)$ when modeling the reactor.

The internal-age distribution is discussed further on the *Professional Reference Shelf (R16.2)* where the following relationships between the cumulative internal-age distribution $I(\alpha)$ and the cumulative external-age distribution $F(\alpha)$



$$I(\alpha) = (1 - F(\alpha)) / \tau \quad (16 - 24)$$

and between $E(t)$ and $I(t)$

$$E(\alpha) = -\frac{d}{d\alpha} [\tau I(\alpha)] \quad (16 - 25)$$

are derived. For a CSTR, it is shown that the internal-age distribution function is

$$I(\alpha) = -\frac{1}{\tau} e^{-\alpha/\tau} \quad (16 - 26)$$

16.4 RTD IN IDEAL REACTORS

16.4.1 RTDs in Batch and Plug-Flow Reactors

The RTDs in plug-flow reactors and ideal batch reactors are the simplest to consider. All the atoms leaving such reactors have spent precisely the same amount of time within the reactors. The distribution function in such a case is a spike of infinite height and zero width, whose area is equal to 1; the spike occurs at $t = V/v = \tau$, or $\Theta = 1$, as shown in [Figure 16-6](#).

The $E(t)$ function is shown in [Figure 16-6\(a\)](#), and $F(t)$ is shown in [Figure 16-6\(b\)](#).

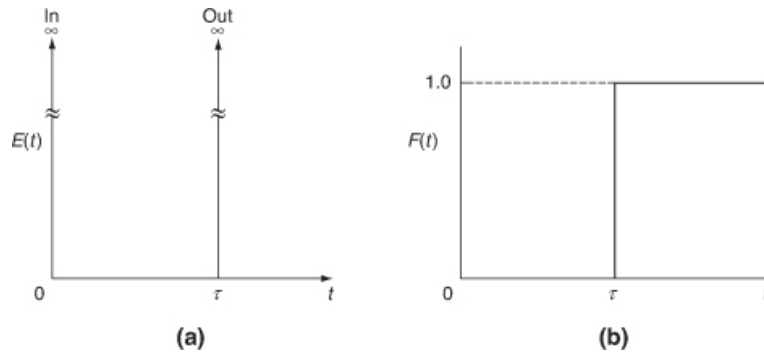


Figure 16-6 Ideal plug-flow response to a pulse tracer input.

Mathematically, this spike is represented by the Dirac delta function:

$E(t)$ for a plug-flow reactor

$$E(t) = \delta(t - \tau) \quad (16 - 27)$$

Properties of the Dirac delta function

The Dirac delta function has the following properties:

$$\delta(x) = \begin{cases} 0 & \text{when } x \neq 0 \\ \infty & \text{when } x = 0 \end{cases} \quad (16 - 28)$$

$$\int_{-\infty}^{\infty} \delta(x) dx = 1 \quad (16 - 29)$$

$$\int_{-\infty}^{\infty} g(x) \delta(x - \tau) dx = g(\tau) \quad (16 - 30)$$

To calculate τ the mean residence time, we set $g(x) = t$

$$t_m = \int_0^{\infty} t E(t) dt = \int_0^{\infty} t \delta(t - \tau) dt = \tau \quad (16 - 31)$$

But we already knew this result, as did all chemical reaction engineering students at the university in Riça, Jofostan. To calculate the variance, we set $g(t) = (t - \tau)^2$, and the variance, σ^2 , is

PFR RTD

Parameters

$$t_m = \tau \text{ and } \sigma^2 = 0$$

$$\sigma^2 = \int_0^\infty (t - \tau)^2 \delta(t - \tau) dt = 0$$

All material spends exactly a time τ in the reactor, so there is no variance [$\sigma^2 = 0$]!

The cumulative distribution function $F(t)$ is

$$F(t) = \int_0^t E(t) dt = \int_0^t \delta(t - \tau) dt \quad (16 - 32)$$

16.4.2 Single-CSTR RTD

From a tracer balance we can determine $E(t)$.

In an ideal CSTR, the concentration of any substance in the effluent stream is identical to the concentration throughout the reactor. Consequently, it is possible to obtain the RTD from conceptual considerations in a fairly straightforward manner. A material balance on an inert tracer that has been injected as a pulse at time $t = 0$ into a CSTR yields for $t > 0$

$$\underbrace{\text{In}}_0 - \underbrace{\text{Out}}_{\nu C} = \underbrace{\text{Accumulation}}_{V \frac{dC}{dt}} \quad (16 - 33)$$

Because the reactor is perfectly mixed, C in this equation is the concentration of the tracer both in the effluent and within the reactor. Separating the variables and integrating with $C = C_0$ at $t = 0$ yields

$$C(t) = C_0 e^{-t/\tau} \quad (16-34)$$

The C -curve for an ideal CSTR can be plotted from Equation (16-34), which is the concentration of tracer in the effluent at any time t .

To find $E(t)$ for an ideal CSTR, we first recall Equation (16-7) and then substitute for $C(t)$ using Equation (16-34). That is,

$$E(t) = \frac{C(t)}{\int_0^\infty C(t) dt} = \frac{C_0 e^{-t/\tau}}{\int_0^\infty C_0 e^{-t/\tau} dt} = \frac{e^{-t/\tau}}{\tau} \quad (16-35)$$

Evaluating the integral in the denominator completes the derivation of the RTD for an ideal CSTR and one notes they are the same as previously given by Equations (16-21) and (16-22)

$E(t)$ and $E(\Theta)$ for a CSTR

$$\begin{array}{l} E(t) = \frac{e^{-t/\tau}}{\tau} \quad (16-21) \\ E(\Theta) = e^{-\Theta} \quad (16-22) \end{array}$$

the cumulative distribution is

$$f(t) = \int_0^t E(t) dt = \int_0^t \frac{e^{-t/\tau}}{\tau} dt = 1 - e^{-t/\tau} \quad (16-32)$$

Recall that $\Theta = t/\tau$ and $E(\Theta) = \tau E(t)$.

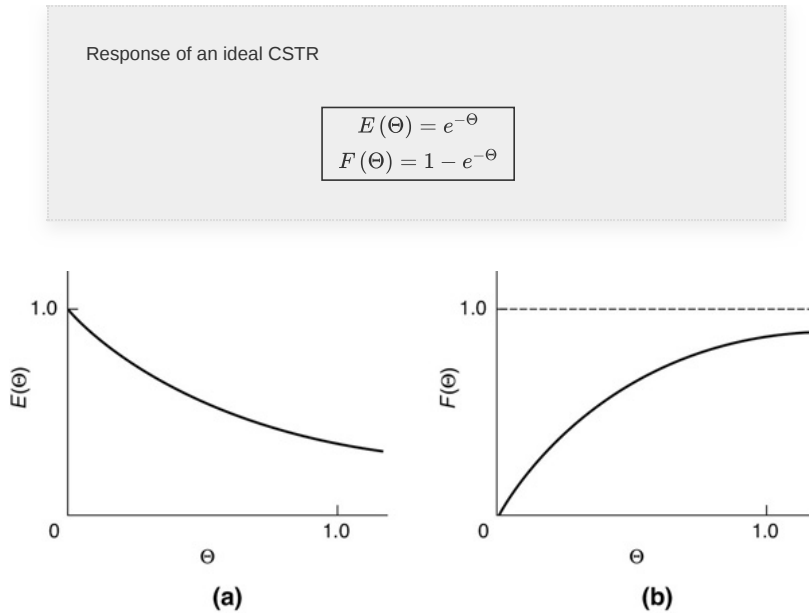


Figure 16-7 $E(\Theta)$ and $F(\Theta)$ for an Ideal CSTR.

The cumulative distribution $F(\Theta)$ is

$$F(\Theta) = \int_0^{\Theta} E(\Theta) d\Theta = 1 - e^{-\Theta} \quad (16 - 36)$$

The $E(\Theta)$ and $F(\Theta)$ functions for an ideal CSTR are shown in Figure 16-7(a) and (b), respectively.

Earlier it was shown that for a constant volumetric flow rate, the mean residence time in a reactor is equal to (V/v) , or τ . This relationship can be shown in a simpler fashion for the CSTR. Applying the definition of the mean residence time to the RTD for a CSTR, we obtain

$$t_m = \int_0^{\infty} t E(t) dt = \int_0^{\infty} \frac{t}{\tau} e^{-t/\tau} dt = \tau \quad (16 - 14)$$

Thus, the nominal holding time (space time) $\tau = (V/v)$ is also the mean residence time that the material spends in the reactor.

The second moment about the mean is the variance and is a measure of the spread of the distribution about the mean. The variance of residence times in a perfectly mixed tank reactor is (let $x = t/\tau$)

For a perfectly mixed CSTR: $t_m = \tau$

and $\sigma = \tau$.

$$\sigma^2 = \int_0^\infty \frac{(t-\tau)^2}{\tau} e^{-t/\tau} dt = \tau^2 \int_0^\infty (x-1)^2 e^{-x} dx = \tau^2 \quad (16-37)$$

Then, $\sigma = \tau$. The standard deviation is the square root of the variance. For a CSTR, the standard deviation of the residence time distribution is as large as the mean itself!!

16.4.3 Laminar-Flow Reactor (LFR)

Before proceeding to show how the RTD can be used to estimate conversion in a reactor, we shall derive $E(t)$ for a laminar-flow reactor. For laminar flow in a tubular (i.e., cylindrical) reactor, the velocity profile is parabolic, with the fluid in the center of the tube spending the shortest time in the reactor. A schematic diagram of the fluid movement after a time t is shown in Figure 16-8. The figure at the left shows how far down the reactor each concentric fluid element has traveled after a time t .

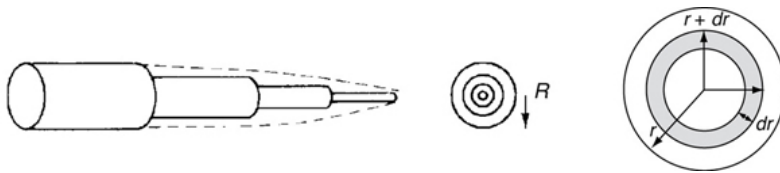
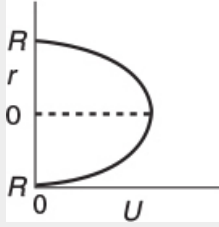


Figure 16-8 Schematic diagram of fluid elements in a laminar-flow reactor.

Molecules near the center spend a shorter time in the reactor than those close to the wall.

The velocity profile in a pipe of outer radius R is

$$U(r) = U_{\max} \left[1 - \left(\frac{r}{R} \right)^2 \right] = 2U_{\text{avg}} \left[1 - \left(\frac{r}{R} \right)^2 \right] = \frac{2v_0}{\pi R^2} \left[1 - \left(\frac{r}{R} \right)^2 \right] \quad (16-38)$$



Parabolic Velocity Profile

where U_{\max} is the centerline velocity and U_{avg} is the average velocity through the tube. U_{avg} is just the volumetric flow rate divided by the cross-sectional area.

The time of passage of an element of fluid at a radius r is

$$t(r) = \frac{L}{U(r)} = \frac{\pi R^2 L}{v_0} \frac{1}{2[1-(r/R)^2]} \quad (16-39)$$

$$= \frac{\tau}{2[1-(r/R)^2]} \quad (16-40)$$

The volumetric flow rate of fluid out of the reactor between r and $(r + dr)$, dv , is

$$dv = U(r) 2\pi r dr \quad (16-41)$$

We are just doing a few manipulations to arrive at $E(t)$ for an LFR

The fraction of total fluid passing out between r and $(r + dr)$ is dv/v_0 , that is,

$$\frac{dv}{v_0} = \frac{U(r) 2(\pi r dr)}{v_0} \quad (16-42)$$

The fraction of fluid between r and $(r + dr)$ that has a flow rate between v and $(v + dv)$ and spends a time between t and $(t + dt)$ in the reactor is

$$E(t) dt = \frac{dv}{v_0} \quad (16-43)$$

We now need to relate the fluid fraction, Equation (16-43), to the fraction of fluid spending between time t and $t = dt$ in the reactor. First we differentiate Equation (16-40)

$$dt = \frac{\tau}{2R^2} \frac{2r dr}{[1-(r/R)^2]^2} = \frac{4}{\tau R^2} \left\{ \frac{\tau/2}{[1-(r/R)^2]} \right\}^2 r dr \quad (16-44)$$

and then use Equation (16-40) to substitute t for the term in brackets to yield

$$dt = \frac{4t^2}{\tau R^2} r dr \quad (16-45)$$

Combining Equations (16-42) and (16-45), and then using Equation (16-40) that relates for $U(r)$ and $t(r)$, we now have the fraction of fluid spending between time t and $t = dt$ in the reactor

$$E(t) dt = \frac{dv}{v_0} = \frac{L}{t} \left(\frac{2\pi r dr}{v_0} \right) = \frac{L}{t} \left(\frac{2\pi}{v_0} \right) \frac{\tau R^2}{4t^2} dt = \frac{\tau^2}{2t^3} dt$$

$$E(t) = \frac{\tau^2}{2t^3} \quad (16-46)$$

The minimum time the fluid may spend in the reactor is

$$t = \frac{L}{U_{\max}} = \frac{L}{2U_{\text{avg}}} \left(\frac{\pi R^2}{\pi R^2} \right) = \frac{V}{2v_0} = \frac{\tau}{2}$$

Consequently, the complete RTD function for a laminar-flow reactor is

At last! $E(t)$ for a laminar-flow reactor

$$E(t) = \begin{cases} 0 & t < \frac{\tau}{2} \\ \frac{\tau^2}{2t^3} & t \geq \frac{\tau}{2} \end{cases} \quad (16-47)$$

The cumulative distribution function for $t \geq \tau/2$ is

$$F(t) = \int_0^t E(t) dt = 0 + \int_{\tau/2}^t E(t) dt = \int_{\tau/2}^t \frac{\tau^2}{2t^3} dt = \frac{\tau^2}{2} \int_{\tau/2}^t \frac{dt}{t^3} = 1 - \frac{\tau^2}{4t^3} \quad (16-48)$$

The mean residence time t_m is

For LFR $t_m = \tau$

$$\begin{aligned} t_m &= \int_{\tau/2}^{\infty} t E(t) dt = \frac{\tau^2}{2} \int_{\tau/2}^{\infty} \frac{dt}{t^2} \\ &= \frac{\tau^2}{2} \left[-\frac{1}{t} \right]_{\tau/2}^{\infty} = \tau \end{aligned}$$

This result was shown previously to be true for any reactor *without dispersion*. The mean residence time is just the space time τ .

The dimensionless form of the RTD function is

Normalized RTD function for a laminar-flow reactor

$$E(\Theta) = \begin{cases} 0 & \Theta < 0.5 \\ \frac{1}{2\Theta^3} & \Theta \geq 0.5 \end{cases} \quad (16-49)$$

and is plotted in Figure 16-9.

Comparing LFR, CSTR, and PFR

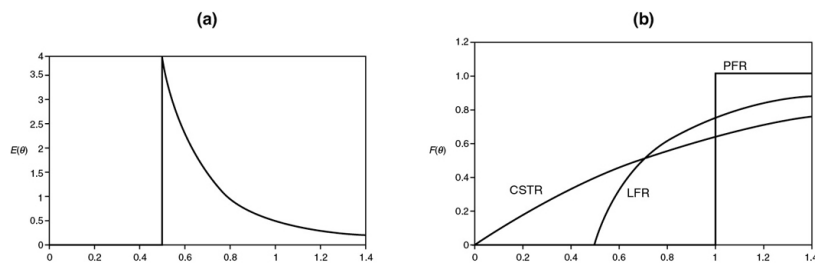


Figure 16-9 (a) $E(\Theta)$ for an LFR; (b) $F(\Theta)$ for a PFR, CSTR, and LFR.

The dimensionless cumulative distribution, $F(\Theta)$ for $\Theta \geq 1/2$, is

$$F(\Theta) = 0 + \int_{\frac{1}{2}}^{\Theta} E(\Theta) d\Theta = \int_{\frac{1}{2}}^{\Theta} \frac{d\Theta}{2\Theta^3} = \left(1 - \frac{1}{4\Theta^2}\right)$$

$$F(\Theta) = \begin{cases} 0 & \Theta < \frac{1}{2} \\ \left(1 - \frac{1}{4\Theta^2}\right) & \Theta \geq \frac{1}{2} \end{cases} \quad (16-50)$$

Figure 16-9(a) shows $E(\Theta)$ for a laminar-flow reactor (LFR), while Figure 16-9(b) compares $F(\Theta)$ for a PFR, CSTR, and LFR.

Experimentally injecting and measuring the tracer in a laminar-flow reactor can be a difficult task if not a nightmare. For example, if one uses as a tracer chemicals that are photoactivated as they enter the reactor, the analysis and interpretation of $E(t)$ from the data become much more involved.⁷

⁷ D. Levenspiel, *Chemical Reaction Engineering*, 3rd ed. New York: Wiley, 1999, p. 342.

16.5 PFR/CSTR SERIES RTD

Modeling the real reactor as a CSTR and a PFR in series

In some stirred tank reactors, there is a highly agitated zone in the vicinity of the impeller that can be modeled as a perfectly mixed CSTR. Depending on the location of the inlet and outlet pipes, the reacting mixture may follow a somewhat tortuous path either before entering or after leaving the perfectly mixed zone—or even both. This tortuous path may be modeled as a plug-flow reactor. Thus, this type of reactor may be modeled

as a CSTR in series with a plug-flow reactor, and the PFR may either precede or follow the CSTR. In this section, we develop the RTD for a series arrangement of a CSTR and a PFR.

First consider the CSTR followed by the PFR (Figure 16-10). The mean residence time in the CSTR will be denoted by τ_s and the mean residence time in the PFR by τ_p . If a pulse of tracer is injected into the entrance of the CSTR, the CSTR output concentration as a function of time will be

$$C = C_0 e^{-t/\tau_s}$$

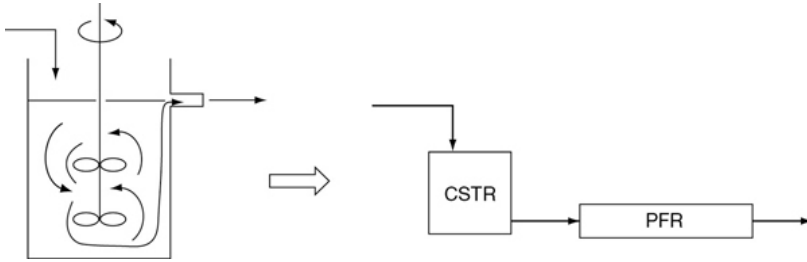


Figure 16-10 Real reactor modeled as a CSTR and PFR in series.

This output will be delayed by a time τ_p at the outlet of the plug-flow section of the reactor system. Thus, the RTD of the reactor system is

$$E(t) = \begin{cases} 0 & t < \tau_p \\ \frac{e^{-(t-\tau_p)/\tau_s}}{\tau_s} & t \geq \tau_p \end{cases} \quad (16-51)$$

See Figure 16-11.

The RTD is not unique to a particular reactor sequence.

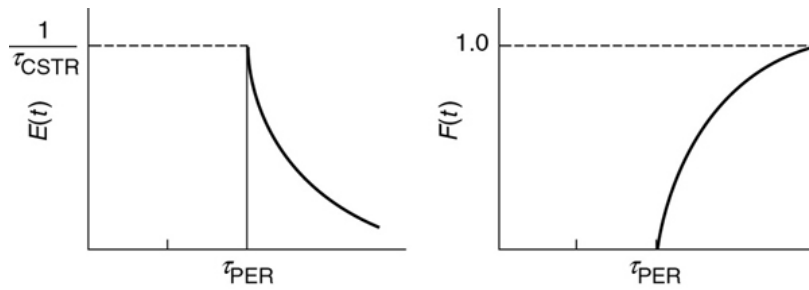


Figure 16-11 RTD curves $E(t)$ and $F(t)$ for a CSTR and a PFR in series.

Next, consider a reactor system in which the CSTR is preceded by the PFR. If the pulse of tracer is introduced into the entrance of the plug-flow section, then the same pulse will appear at the entrance of the perfectly mixed section τ_p seconds later, meaning that the RTD of the reactor system will again be

$E(t)$ is the same, no matter which reactor comes first.

$$E(t) = \begin{cases} 0 & t < \tau_p \\ \frac{e^{-(t-\tau_p)/\tau_s}}{\tau_s} & t \geq \tau_p \end{cases} \quad (16-51)$$

which is *exactly* the same as when the CSTR was followed by the PFR.

It turns out that no matter where the CSTR occurs within the PFR/CSTR reactor sequence, the same RTD results.

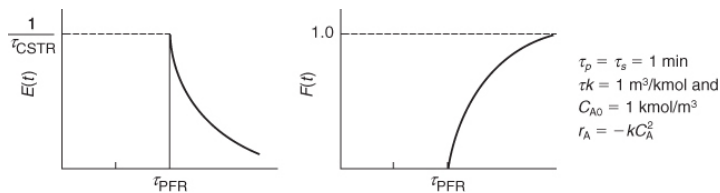
Nevertheless, this is not the entire story as we will see in Example 16-3.

Example 16-3 Comparing Early and Late Mixing for a Second-Order Reaction

Examples of early and late mixing for a given RTD

Consider a second-order reaction being carried out in a *real* CSTR that can be modeled as two different reactor systems: In the first system an ideal CSTR is followed by an ideal PFR (Figure E16-3.1); in the second system the PFR precedes the CSTR (Figure E16-3.2). To simplify the calculations, let τ_s and τ_p each equal 1 minute, let the reaction-rate constant equal $1.0 \text{ m}^3/\text{kmol}\cdot\text{min}$, and let the initial concentration of liquid reactant, C_{A0} , equal $1.0 \text{ kmol}/\text{m}^3$. Find the conversion in each system.

For the parameters given, we note that in these two arrangements (see Figures E16-3.1 and E16-3.2), the RTD function, $E(t)$, is the same



Solution

- Let's first consider the case of early mixing when the CSTR is followed by the plug-flow section (Figure E16-3.1).

Early Mixing

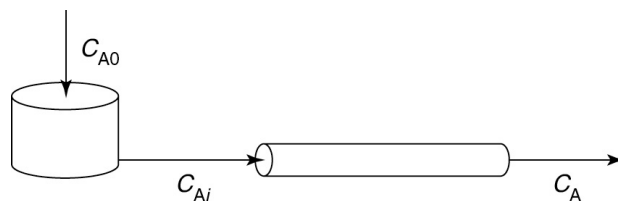


Figure E16-3.1 Early mixing scheme.

A mole balance on the CSTR section gives upon inserting the rate law

$$V = \frac{F_{A0} - F_{Ai}}{-r_{Ai}} = \frac{v_0(C_{A0} - C_{Ai})}{kC_{Ai}^2}$$

Rearranging

$$v_0(C_{A0} - C_{Ai}) = kC_{Ai}^2 V \quad (\text{E16-3.1})$$

Dividing by v_0 and rearranging, we have quadric equation to solve for the intermediate concentration C_{Ai}

$$\tau_s k C_{Ai}^2 + C_{Ai} - C_{A0} = 0$$

Substituting for τ_s and k

$$\tau_s k = 1 \text{ min} \cdot \frac{\text{m}^3}{\text{kmol} \cdot \text{min}} = \frac{1 \text{ m}^3}{\text{kmol}}$$

Solving for C_{Ai} gives

$$C_{Ai} = \frac{\sqrt{1+4\tau_s k C_{A0}} - 1}{2\tau_s k} = \frac{-1+\sqrt{1+4}}{2} = 0.618 \text{ kmol/m}^3 \quad (\text{E16-3.2})$$

This concentration will be fed into the PFR. The PFR mole balance is

$$\frac{dF_A}{dV} = v_0 \frac{dC_A}{dV} = \frac{dC_A}{d\tau_p} = r_A = -kC_A^2 \quad (\text{E16-3.3})$$

Integrating Equation (E16-3.3)

$$\frac{1}{C_A} - \frac{1}{C_{Ai}} = \tau_p k \quad (\text{E16-3.4})$$

Substituting $C_{Ai} = 0.618 \text{ kmol/m}^3$, $\tau_p = 1 \text{ min}$, $k = 1 \text{ m}^3/\text{kmol} \cdot \text{min}$, and $\tau_p k = 1 \text{ m}^3/\text{kmol}$ in Equation (E16-3.4) yields

$$\begin{aligned} \text{Early Mixing CSTR} \rightarrow \text{PFR} \\ X = 0.618 \end{aligned}$$

$$C_A = 0.382 \text{ kmol/m}^3$$

as the concentration of reactant in the effluent from the reaction system. The conversion is

$$X = \left(\frac{C_{A0} - C_A}{C_{A0}} \right)$$

$$X = \left(\frac{1 - 0.382}{1} \right) = 0.618 = 61.8\%$$

2. Now, let's consider the case of late mixing.

When the perfectly mixed section is preceded by the plug-flow section (Figure E16-3.2), the outlet of the PFR is the inlet to the CSTR, C_{Ai} . Again, solving Equation (E16-3.3)

$$\frac{1}{C_{Ai}} - \frac{1}{C_{A0}} = \tau_p k$$

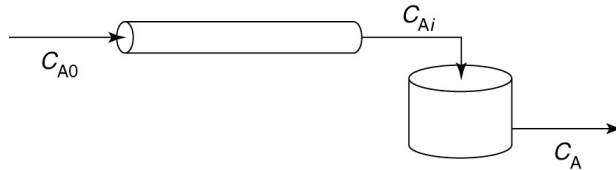


Figure E16-3.2 Late mixing scheme.

Solving for intermediate concentration, C_{Ai} , given $\tau_p k = 1 \text{ m}^3/\text{mol}$ and a $C_{A0} = 1 \text{ mol/m}^3$

$$C_{Ai} = 0.5 \text{ kmol/m}^3$$

Next, solve for C_A exiting the CSTR.

A material balance on the perfectly mixed section (CSTR) gives

$$\tau_s k C_A^2 + C_A - C_{Ai} = 0 \quad (\text{E16} - 3.5)$$

$$C_A = \frac{\sqrt{1+4\tau_s k C_{Ai}} - 1}{2\tau_s k} = \frac{-1 + \sqrt{1+2}}{2} = 0.366 \text{ kmol/m}^3 \quad (\text{E16-3.6})$$

Late Mixing
PFR → CSTR
 $X = 0.634$

Early mixing
 $X = 0.618$
Late mixing
 $X = 0.634$

as the concentration of reactant in the effluent from the reaction system. The corresponding conversion is 63.4%; that is,

$$X = 1 - (C_A/C_{A0}) = 1 - \frac{0.366}{1.0} = 63.4\%$$

Analysis: The RTD curves are identical for both configurations. However, the conversion was not the same. In the first configuration, a conversion of 61.8%

was obtained; in the second configuration, 63.4%. While the difference in the conversions is small for the parameter values chosen, **the point is that there is a difference.** Let me say that again, *the point is that there is a difference* and we **must** explore it further in Chapters 17 and 18.

While $E(t)$ was the same for both reaction systems, the conversion was

Chance Card: **Do not pass go, proceed directly to Chapter 17.**

The conclusion from this example is of extreme importance in reactor analysis: **The RTD is not a complete description of structure for a particular reactor or system of reactors.**

The RTD is unique for a particular or given reactor. However, as we just saw, the reactor or reaction system is not unique for a particular RTD. When analyzing nonideal reactors, the RTD alone is not sufficient to determine its performance, and more information is needed. It will be shown in Chapter 17 that in addition to the RTD, an adequate model of the nonideal reactor flow pattern and knowledge of the quality of mixing or “degree of segregation” are both required to characterize a reactor properly.



Reactor Monopoly

At this point, the reader has the necessary background to go directly to Chapter 17 where we use the RTD to calculate the

mean conversion in a real reactor using different models of ideal chemical reactors.

16.6 DIAGNOSTICS AND TROUBLESHOOTING

16.6.1 General Comments

As discussed in [Section 16.1](#), the RTD can be used to diagnose problems in existing reactors. As we will see in further detail in [Chapter 18](#), the RTD functions $E(t)$ and $F(t)$ can be used to model the real reactor as combinations of ideal reactors.

[Figure 16-12](#) illustrates typical RTDs resulting from different nonideal reactor situations. [Figures 16-12\(a\) and \(b\)](#) correspond to “nearly” ideal PFRs and CSTRs, respectively. The RTD for the nonideal reactor in [Figure 16-12\(c\)](#) modeled as a PBR with channeling and dead zones is shown in [Figure 16-12\(d\)](#). In [Figure 16-12\(d\)](#), one observes that a principal peak occurs at a time smaller than the space time ($\tau = V/v_0$) (i.e., early exit of fluid) and also that some fluid exits at a time greater than space-time τ . This curve is consistent with the RTD for a packed-bed reactor with channeling (i.e., bypassing) and stagnant zones (i.e., not mixed with bulk flow) as discussed earlier in [Figure 16-1](#). [Figure 16-12\(f\)](#) shows the RTD for the nonideal CSTR in [Figure 16-12\(e\)](#), which has dead zones *and* bypassing. The dead zone serves not only to reduce the effective reactor volume, so the active reactor volume is smaller than expected, but also results in longer residence times for the tracer molecules to diffuse in and out of these “dead or stagnant” zones.

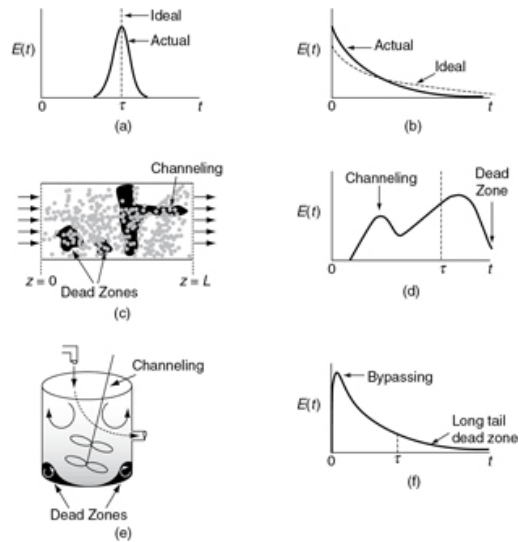


Figure 16-12 (a) RTD for *near* plug-flow reactor; (b) RTD for *near* perfectly mixed CSTR; (c) packed-bed reactor with dead zones and channeling; (d) RTD for packed-bed reactor in (c); (e) tank reactor with short-circuiting flow (bypass); (f) RTD for tank reactor with channeling (bypassing or short-circuiting) and a dead zone in which the tracer slowly diffuses in and out.

RTDs that are commonly observed

What's wrong with my reactor?

16.6.2 Simple Diagnostics and Troubleshooting Using the RTD for Ideal Reactors

16.6.2A The CSTR

We now consider three CSTRs: (a) one that operates normally, (b) one with bypassing, and (c) one with a dead volume. For a well-mixed CSTR, as we saw in [Section 16.4.2](#), the response to a pulse tracer is

CSTR RTD Functions

Concentration:

$$C(t) = C_0 e^{-t/\tau} \quad (16-34)$$

RTD function:

$$E(t) = \frac{1}{\tau} e^{-t/\tau} \quad (16-35)$$

Cumulative function:

$$F(t) = 1 - e^{-t/\tau} \quad (16-36)$$

$$\tau = \frac{V}{v_0}$$

where τ is the space time—the case of perfect operation.

1. Perfect Operation (P) Model

Here, we will measure our reactor with a yardstick to find V and our flow rate with a flow meter to find v_0 in order to calculate $\tau = V/v_0$. We can then compare the curves for imperfect operation (cf. [Figures 16-14](#) and [16-15](#)) with the curves shown below in [Figure 16-13](#) for perfect (i.e., ideal) CSTR operation

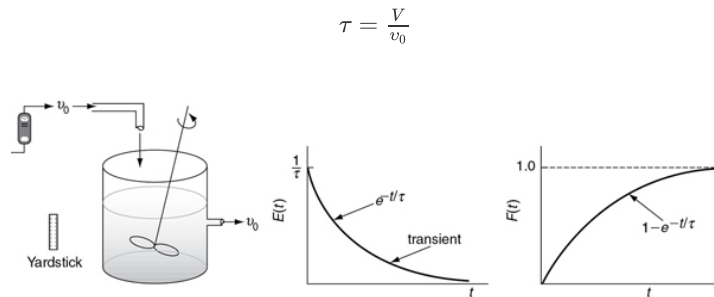


Figure 16-13 Perfect operation of a CSTR.

If τ is large, there will be a slow decay of the output transient, $C(t)$, and $E(t)$ for a pulse input. If τ is small, there will be rapid decay of the transient, $C(t)$, and $E(t)$ for a pulse input.

2. Bypassing (BP) Model

In [Figure 16-14](#), the real reactor on the left is modeled by an ideal reactor with bypassing, as shown on the right.

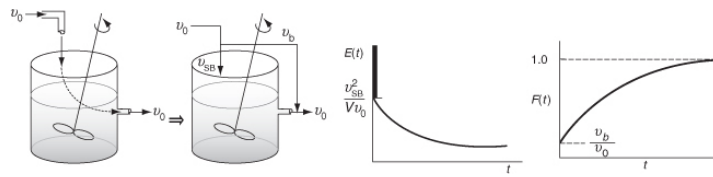


Figure 16-14 Ideal CSTR with bypass.

The entering volumetric flow rate is divided into a volumetric flow rate that enters the reacting system, v_{SB} , and a volumetric flow rate that bypasses the reacting mixture system completely v_b . Where $v_0 = v_{SB} = v_b$. The subscript SB denotes a model of a reactor system with bypassing. The reactor system volume V_S is the well-mixed portion of the reactor.

The analysis of a bypass to the CSTR may be elucidated by observing the output to a *step tracer* input to the real reactor. The CSTR with bypassing will have RTD curves similar to those in Figure 16-15.

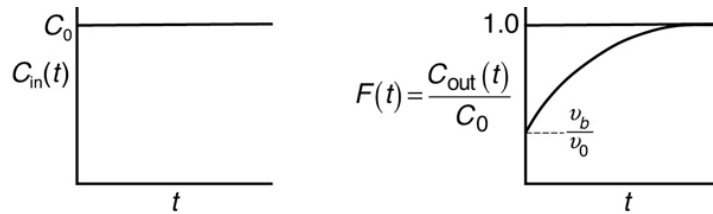


Figure 16-15 Inlet (a) and outlet (b) concentration curves correspond to Figure 16-14.

We see the concentration output in the form $C(t)/C_0$ for a step input will be the F -curve and the initial jump will be equal to the fraction bypassed. The corresponding equation for the F -curve is

$$F(t) = \frac{v_b}{v_0} + \frac{v_{SB}}{v_0} \left[1 - e^{-\left(\frac{v_{SB}t}{V}\right)} \right]$$

differentiating the F -Curve we obtain the E -curve

$$E(t) = \frac{v_b}{v_0} \delta(t - 0) + \frac{v_{SB}^2}{V v_0} e^{-\left(\frac{v_{SB}t}{V}\right)}$$

Here, a fraction of the tracer (v_b/v_0) will exit immediately while the rest of the tracer will mix and become diluted with volume V and exponentially increase up to $C_{out}(t)$, where $F(t) = 1.0$.

Because some of the fluid bypasses, the flow passing through the system will be less than the total volumetric rate, $v_{SB} < v_0$; consequently, $\tau_{SB} > \tau$. For example, let's say the volumetric flow rate, which bypasses the reactor, v_b , is 25% of the total (e.g., $v_b = 0.25 v_0$). The volumetric flow rate entering the reactor system, v_{SB} , is 75% of the total ($v_{SB} = 0.75 v_0$) and the corresponding true space time (τ_{SB}) for the system volume with bypassing is

$$\tau_{SB} = \frac{V}{v_{SB}} = \frac{V}{0.75v_0} = 1.33\tau$$

The space time, τ_{SB} , will be greater than it would be if there were no bypassing. Because τ_{SB} is greater than τ , there will be a slower decay of the transients $C(t)$ and $E(t)$ than there would be with perfect operation.

3. Dead Volume (DV) Model

Consider the CSTR in Figure 16-16 without bypassing but instead with a stagnant or dead volume.

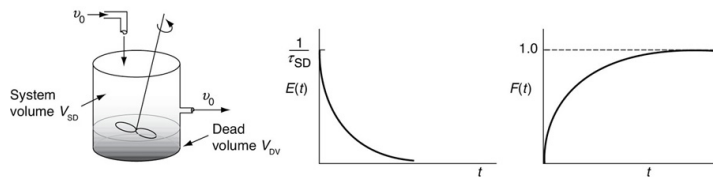


Figure 16-16 Ideal CSTR with dead volume.

The total volume, V , is the same as that for perfect operation, $V = V_{DV} + V_{SD}$. The subscript DV in V_{DV} represents the dead volume in the model, and the subscript SD in V_{SD} is the reacting system volume in the model. Here, the dead volume where **absolutely no** reaction takes place, V_{DV} , acts like a fictitious brick at the bottom taking up precious reactor volume. The system volume where the reaction can take place, that is, V_{SD} , is reduced because of this dead volume and therefore less conversion can be expected.

We see that because there is a dead volume that the fluid does not enter, there is less system volume, V_{SD} , available for reaction than in the case of perfect operation, that is, $V_{SD} < V$. Consequently, the fluid will pass through the reactor with the dead volume more quickly than that of perfect operation, that is, $\tau_{SD} < \tau$.

If

$$V_{DV} = 0.2V, V_{SD} = 0.8V, \text{ then } \tau_{SD} = \frac{0.8V}{v_0} = 0.8\tau$$

Also as a result, the transients $C(t)$ and $E(t)$ will decay more rapidly than that for perfect operation because there is a smaller system volume.

Summary

A summary for ideal CSTR mixing volume is shown in Figure 16-17.

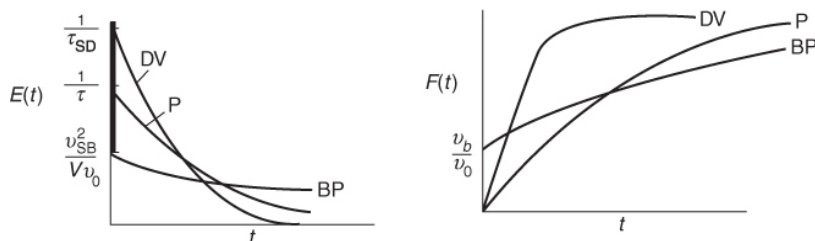


Figure 16-17 Comparison of $E(t)$ and $F(t)$ for CSTR under perfect operation, bypassing, and dead volume. (**BP** = bypassing model, **P** = perfect operation model, and **DV** = dead volume model).

Knowing the volume V measured with a yardstick and the flow rate v_0 entering the reactor measured with a flow meter, one can calculate and plot $E(t)$ and $F(t)$ for the ideal case (P) and then compare with the measured RTD $E(t)$ to see whether the RTD suggests either bypassing (BP) or dead zones (DV).

16.6.2B Tubular Reactor

A similar analysis to that for a CSTR can be carried out on a tubular reactor.

1. Perfect Operation of PFR (P) Model

We again measure the volume V with a yardstick and v_0 with a flow meter. The $E(t)$ and $F(t)$ curves are shown in Figure 16-18. The triangles drawn in Figures 16-18 and 16-19 should really be Dirac delta functions with zero width at the base. The space time for a perfect PFR is

$$\tau = V/v_0$$

2. PFR with Channeling (Bypassing, BP) Model

Let's consider channeling (bypassing), as shown in Figure 16-19, similar to that shown in Figures 16-2 and 16-12(d). The space time for the reactor system with bypassing (channeling) τ_{SB} is

$$\tau_{SB} = \frac{V}{v_{SB}}$$

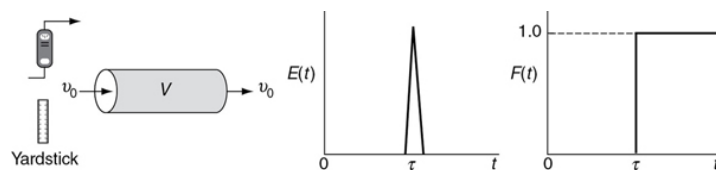


Figure 16-18 Perfect operation of a PFR.

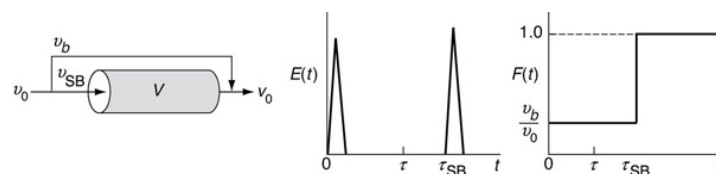


Figure 16-19 PFR with bypassing similar to the CSTR.

Because $v_{SB} < v_0$, the space time for the case of bypassing is greater when compared to perfect operation, that is,

$$\tau_{SB} > \tau$$

If 25% is bypassing (i.e., $v_b = 0.25 v_0$) and only 75% is entering the reactor system (i.e., $v_{SB} = 0.75 v_0$), then $\tau_{SB} = V/(0.75v_0) = 1.33\tau$. The fluid that *does* enter the reactor system flows in a plug flow. Here, we have two spikes in the $E(t)$ curve: one spike at the origin and one spike at τ_{SB} that comes after τ for perfect operation. Because the volumetric flow rate is reduced, the time of the second spike will be greater than τ for perfect operation.

3. PFR with Dead Volume (DV) Model

The dead volume, V_{DV} , could be manifested by internal circulation at the entrance to the reactor as shown in Figure 16-20.

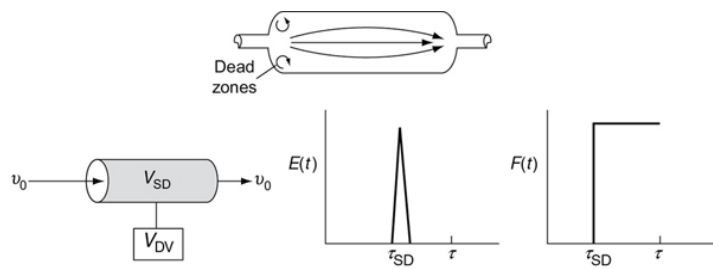


Figure 16-20 PFR with dead volume.

The system volume, V_{SD} , is where the reaction takes place and the total reactor volume is ($V = V_{SD} + V_{DV}$). The space time, τ_{SD} , for the reactor system with only dead volume is

$$\tau_{SD} = \frac{V_{SD}}{v_0}$$

Compared to perfect operation, the space time τ_{SD} is smaller and the tracer spike will occur before τ for perfect operation.

$$\tau_{SD} < \tau$$

Here again, the dead volume takes up space that is not accessible. As a result, the tracer will exit early because the system volume, V_{SD} , through which it must pass is smaller than the perfect operation case.

Summary

Figure 16-21 is a summary of these three cases.

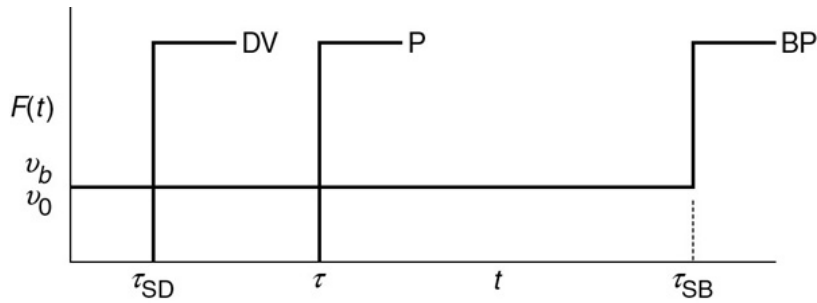


Figure 16-21 Comparison of PFR under perfect operation, bypassing, and dead volume (**DV** = dead volume model, **P** = perfect PFR model, **BP** = bypassing model).

In addition to its use in diagnosis, the RTD can be used to predict conversion in existing reactors when a new reaction is tried in an old reactor. However, as we saw in [Section 16.5](#), the RTD is not unique for a given system, and we need to develop models for the RTD to predict conversion. Examples of these models will be discussed in [Chapter 18](#).

There are many situations where the fluid in a reactor is *neither* well mixed *nor* approximates plug flow. The idea is this: We have seen that the RTD can be used to diagnose or interpret the type of mixing, bypassing, and so on, that occurs in an existing reactor that is currently on stream and is not yielding the conversion predicted by the ideal reactor models. Now let's envision another use of the RTD. Suppose we have a nonideal reactor either on line or sitting in storage. We have characterized this reactor and obtained the RTD function. What will be the conversion of a reaction with a known rate law that is carried out in a reactor with a known RTD?

The question

How can we use the RTD to predict conversion in a real reactor?

In Chapter 17 we show how this question can be answered in a number of ways.

16.7 AND NOW... A WORD FROM OUR SPONSOR—SAFETY 16 (AWFOS—S16 CRITICAL THINKING ACTIONS)

In addition to critical thinking questions discussed in Table 15-3, Chapter 15, we also have Rubenfeld and Scheffer[†] seven Critical Thinking Actions (CTAs) shown in Table 16-1. We will use Example 13-2 on the explosion that occurred after the charge to the reactor was tripled in order to hypothesize the CTAs for each of type of action.*

[†] M. G. Rubenfeld and B. Scheffer, *Critical Thinking TACTICS for Nurses: Achieving the IOM Competencies*, 2nd ed. Sudbury, MA: Jones & Bartlett Publishers, 2010.

* H. S. Fogler, *Elements of Chemical Reaction Engineering*, 6th ed. Boston MA: Pearson, 2020.

TABLE 16-1 TYPES OF CRITICAL THINKING ACTIONS (CTAs) AND EXAMPLES MONSANTO EXPLOSION (EXAMPLE 13-2)**

Types of CTA	Example Phrases of CTA	CTA Safety Examples
1. Predicting : envisionin g a plan and its consequen ces	• I co ul d i m ag in	I knew that if the cooling system were to fail for more than 9 minutes (cf. Example 13-2), the reaction would run away.

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2. Analyzing : separating or breaking a whole into parts to discover their nature, function, and relationshi ps	<ul style="list-style-type: none">• I di ss ec te d th e sit ua ti on ...• I tri ed to re du ce th in gs to m an	I dissected the energy balance to find the parameters that were the most sensitive to down time and temperature increases and would cause the reaction to run away.

		ag ea bl e un its ...	
		<ul style="list-style-type: none">• I de tai le d a sc he m ati c pi ct ur e of ...	
		<ul style="list-style-type: none">• I so rt ed th in gs ou t by ...	
		<ul style="list-style-type: none">• I lo ok ed fo r th	

	<div>e pa rts th at ...</div> <div><ul style="list-style-type: none">I lo ok ed at ea ch pi ec e in di vi du all y ...</div>	
<div>3. Information seeking: searching for evidence, facts, or knowledge by identifying relevant sources and gathering objective, subjective, historical, and current data from</div>	<div><ul style="list-style-type: none">I m ad e su re I ha d all th e pi ec es of th e</div>	<div>I looked up the heat of reaction to calculate the heat generated Q_g in the reactor at the start of the reaction to see whether it would be greater than the heat removed, Q_r.</div>

those sources	pi ct ur e ... • I kn e w I ne ed ed to lo ok up , or st ud y ... • I w on de re d ho w I co ul d fi nd ou t ... • I as
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	<p>ence ce of ...</p> <ul style="list-style-type: none">• I ne ed ed to ha ve all th e fa ct s ...	
<p>4. Applying standards: judging according to establishe d personal, profession al, or social rules or criteria</p>	<ul style="list-style-type: none">• I ju dg ed th at ac co rd in g to ...• I co m pa re d th is	<p>I measured the corrosion inside the reactor tubes and determined the tube wall thickness was insufficient to withstand 1,000 psi according to established standards for the pipe material.</p>

		sit ua ti on to w ha t I kn e w to be th e ru le ...	
		<ul style="list-style-type: none">• I th ou gh t of /st ud ie d th e po lic y fo r ...	
		<ul style="list-style-type: none">• I kn e w I ha d	

		to ...	
		<ul style="list-style-type: none">• The re ar e ce rt ai n th in gs yo u ju st ha ve to ac co un t fo r ...	
		<ul style="list-style-type: none">• I th ou gh t of th e bo tt o m li ne th at	

		<p>is al w ay s ...</p> <ul style="list-style-type: none">• I kn e w it w as un et hi ca l to ...	
<p>5. Discriminating: recognizing differences and similarities among things or situations and distinguishing carefully as to category or rank</p>	<ul style="list-style-type: none">• I gr ou pe d th in gs to ge th er ...• I pu t th in gs	<p>I made a list of all the things that could go wrong when we restarted the cooling system.</p> <p>The reaction runaway occurred after cooling water failure for 10 minutes as the situation was different, that is, reactor was charged three times more than normal charge rate.</p>	

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	<ul style="list-style-type: none">• This situation was different from the same as ...	
6. Transforming knowledge: changing or converting the condition, nature, form, or function of concepts among contexts	<ul style="list-style-type: none">• I wonder if that would fit in this situation	<p>I was puzzled at first because I did not understand why the reactor took so long to explode after the cooling system failed (cf. <u>Example 13-2</u>). Then I calculated and determined that the rate of temperature increase (dT/dt) was so small that it took a long time, 2 hours, to reach a point where the Arrhenius dependence dominated the heat-generated term.</p>

		ti on ...	
		<ul style="list-style-type: none">• I to ok w ha t I kn e w an d as ke d m ys el f if it w ou ld w or k ...	
		<ul style="list-style-type: none">• I i m pr ov ed on th e ba si cs by ad	

		di ng ...	
		<ul style="list-style-type: none">• At fir st I w as pu zz le d; th en I sa w th at th er e w er e si m ila rit ie s to ...	
		<ul style="list-style-type: none">• I fi gu re d if th is w er	

	e tr ue , th en th at w ou ld al so be tr ue .	
7. Logical reasoning: drawing inferences or conclusions that are supported in or justified by evidence	<ul style="list-style-type: none">• I deduced from them information that ...• I could tr	<p>I justified my conclusion that the reaction would not have run away for the increased feed charge by carrying out a number of computer simulations to show that the heat generated, Q_g, was less than the heat removed, Q_r, for a downtime less than 5 minutes.</p>

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	<ul style="list-style-type: none"> • M y ra ti on al e fo r th e co nc lu si on w as ... 	
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--- See page 58–59, H. S. Fogler, S. E. LeBlanc, and B. R. Rizzo, *Strategies for Creative Problem Solving*, 3rd ed. Boston, MA: Prentice Hall, 2014.

HSF favorite actions (1) I envisioned the outcome would be ... (2) I dissected the situation ... (3) I know I had to look up or study ... (4) I judged that according to ... (5) I grouped things together ... (6) At first I was puzzled; then I saw that there were similarities to ... (7) I justified my conclusion with the evidence that ...

Closure. After completing this chapter, the reader will be able to use the tracer concentration–time data to calculate the external-age distribution function $E(t)$, the cumulative distribution function $F(t)$, the mean residence time, t_m , and the variance, σ^2 . The reader will be able to sketch $E(t)$ for ideal reactors, and by comparing $E(t)$ from the experiment with $E(t)$ for ideal reactors (PFR, PBR, CSTR, laminar-flow reactor (LFR)), be able to diagnose problems in real reactors. The reader will be able to use the RTD curves to identify the nonideal reactor problems of dead volume and bypassing.

SUMMARY

1. The quantity $E(t) dt$ is the fraction of material exiting the reactor that has spent between time t and $(t + dt)$ in the reactor.

2. The mean residence time

$$t_m = \int_0^\infty t E(t) dt = \tau \quad (\text{S16-1})$$

is equal to the space time τ for constant volumetric flow, $v = v_0$.

3. The variance about the mean residence time is

$$\sigma^2 = \int_0^\infty (t - t_m)^2 E(t) dt \quad (\text{S16-2})$$

4. The cumulative distribution function $F(t)$

$$\begin{aligned} F(t) &= \int_0^t E(t) dt && \text{The cumulative distribution function } F(t) \text{ gives} \\ &&& \text{the fraction of effluent material that has been} \\ &&& \text{in the reactor for a time } t \text{ or less} \\ 1 - F(t) &= \int_0^\infty E(t) dt && \text{Fraction of effluent material that has been in} \\ &&& \text{the reactor for a time } t \text{ or longer} \end{aligned} \quad (\text{S16-3})$$

5. The RTD functions for an ideal reactor are

PFR:

$$E(t) = \delta(t - \tau) \quad (\text{S16-4})$$

CSTR:

$$E(t) = \frac{e^{-t/\tau}}{\tau} \quad (\text{S16-5})$$

LFR:

$$E(t) = 0 \quad t < \frac{\tau}{2} \quad (\text{S16-6})$$

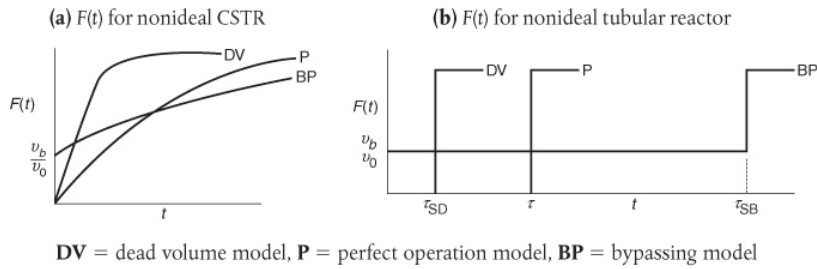
$$E(t) = \frac{\tau^2}{2t^3} \quad t \geq \frac{\tau}{2} \quad (\text{S16-7})$$

6. The dimensionless residence time is

$$\Theta = \frac{t}{\tau} \quad (\text{S16-8})$$

$$E(\Theta) = \tau E(t) \quad (\text{S16-9})$$

7. Diagnosing nonideal reactors with dead volume and bypassing



CRE WEB SITE MATERIALS

- **Expanded Material on the Web Site**

1. [*Web Example 16-1 Gas-Liquid Reactor*](#)
2. [*Proof That in the Absence of Dispersion, the Mean Residence Time, \$t_m\$, is Equal to Space Time, that is, \$t_m = \tau\$*](#)
3. [*Side Note on the Medical Uses of RTD*](#)
4. [*Solved Problems WP16-14_C and WP16-15_D*](#)

- **Learning Resources**

1. [*Summary Notes*](#)
2. [*Web Material Links*](#)

The Attainable Region Analysis

<http://www.umich.edu/~elements/6e/16chap/learn-attainableregions.html>

<http://hermes.wits.ac.za/attainableregions/>

- **Living Example Problems**

1. [*Living Example 16-1 Determining \$E\(t\)\$*](#)
2. [*Living Example 16-2T: Tutorial to Find \$E\(t\)\$ from \$C\(t\)\$*](#)
3. [*Living Example 16-2 \(a\) and \(b\) Finding \$t_m\$ and \$\sigma^2\$*](#)

- **Professional Reference Shelf**

R16.1. *Fitting the Tail*

Whenever there are dead zones into which the material diffuses in and out, the C - and E -curves may exhibit long tails. This section shows how to analytically describe fitting these tails to the curves.

$$E(t) = ae^{-bt}$$

b = slope of $\ln E$ vs. t

$$a = be^{bt_1} [1 - F(t_1)]$$

R16.2. Internal-Age Distribution

The internal-age distribution currently in the reactor is given by the distribution of ages with respect to how long the molecules have been in the reactor.

The equation for the internal-age distribution is derived and an example is given showing how it is applied to catalyst deactivation in a “fluidized CSTR.”

(<http://www.umich.edu/~elements/6e/16chap/obj.html#/>)

Useful Links

Living
Example
Problems

Extra Help

Additional
Materials

Professional
Reference
Shelf

Computer
Simulation
Problem
Statements

Evaluation

Self Tests

i>Clicker
Questions

QUESTIONS, SIMULATIONS, AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$\mathbf{A} = \bullet \mathbf{B} = \blacksquare \mathbf{C} = \blacklozenge \mathbf{D} = \blacklozenge\blacklozenge$$

Questions

Q16-1_A QBR (*Question Before Reading*). What concept does RTD add to our CRE algorithm and where does it fit in the algorithm (1) Mole Balance, (2) Stoichiometry, and so on?

Q16-2_A Read over the problems of this chapter. Discuss with a classmate ideas for making up an original problem that uses the concepts presented in this chapter. The guidelines are given in Question Q5-3_A, page 217.

RTDs from real reactors can be found in *Ind. Eng. Chem.*, 49, 1000 (1957); *Ind. Eng. Chem. Process Des. Dev.*, 3, 381 (1964); *Can. J. Chem. Eng.*, 37, 107 (1959); *Ind. Eng. Chem.*, 44, 218 (1952); *Chem. Eng. Sci.*, 3, 26 (1954); and *Ind. Eng. Chem.*, 53, 381 (1961).

Q16-3_B

1. **Example 16-1.** What fraction of the fluid spends 9 minutes or longer in the reactor? What fraction spends 2 minutes or less?
2. **Example 16-3.** How would the $E(t)$ change if the PFR space time, τ_p , was reduced by 50% and τ_s was increased by 50%? What fraction spends 2 minutes or less in the reactor?

Q16-4 Go to the LearnChemE screencast link for **Chapter 16** (<http://www.learncheme.com/screencasts/kinetics-reactor-design>). View one or more of the screencast 5- to 6-minute videos and write a two-sentence evaluation.

Q16-5 AWFOS–S16

1. List additional QTAs that could have been taken in addition to the ones listed for each CTA in the table.
2. Apply the seven types of actions of CTA to **Example 13-2** and write an action that should have been taken for each type.

Computer Simulations and Experiments

P16-1_A Living Example 16-3 Wolfram and Python

1. Vary and find the combination of parameters for which the exit conversion is virtually the same for both early mixing and late mixing.
2. Find the combination of parameters for which there is a maximum difference between early mixing and late mixing.
3. Explain your findings for (i) and (ii) and then write a set of conclusions.

Problems

P16-2_B (a) (*Excellent Exam Problem*) Suggest a diagnosis (e.g., bypassing, dead volume, multiple mixing zones, internal circulation) for each of the following real reactors in **Figure P16-2_B** (a) (1–10 curves) that had

the following RTD $[E(t), E(\Theta), F(t), F(\Theta)]$ or $(1 - F(\Theta))$ curves:

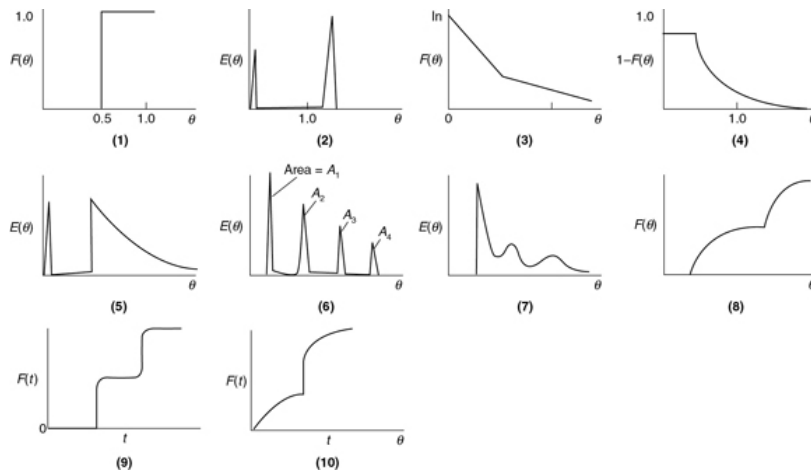


Figure P16-2B (a) RTD curves.

P16-2B (b) Suggest a model (e.g., combinations of ideal reactors, bypassing) for each RTD function shown in **Figure P16-2B(a)** (1–10) that would give the RTD function. For example, for the real tubular reactor, whose $E(\Theta)$ curve is shown in **Figure P16-2B (a)** (5) above, the model is shown in **Figure P16-2B (b)** below. The real reactor is modeled as having bypassing, a back mix zone, and a PFR zone that mimics the real CSTR.

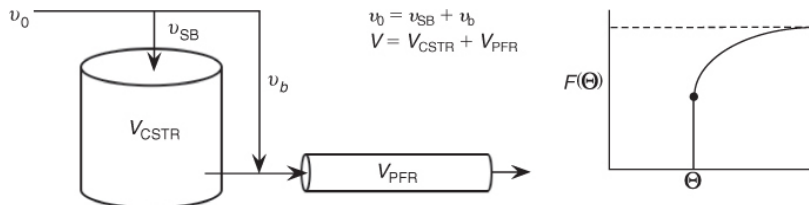
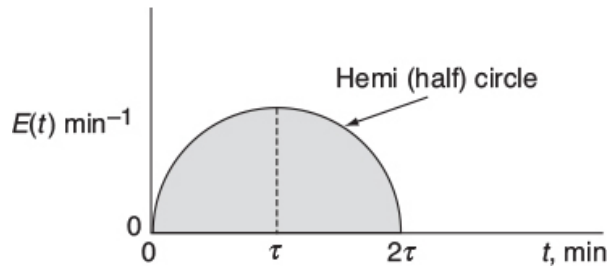


Figure P16-2B (b) Real reactor modeled as CSTR and PFR with bypass.

P16-3C OEQ (Old Exam Question)—Graduate Course.

Consider the $E(t)$ curve below.



Mathematically this hemi circle is described by these equations:

For $2\tau \geq t \geq 0$, then $E(t) = \sqrt{\tau^2 - (t - \tau)^2} \text{ min}^{-1}$ (hemi circle)

For $t > 2\tau$, then $E(t) = 0$

1. What is the mean residence time?
2. What is the variance? (Ans: $\sigma^2 = 0.159 \text{ min}^2$)

P16-4B A step tracer input was used on a real reactor with the following results:

For $t \leq 10 \text{ min}$, then $C_T = 0$

For $10 \leq t \leq 30 \text{ min}$, then $C_T = 10 \text{ g/dm}^3$

For $t \geq 30 \text{ min}$, then $C_T = 40 \text{ g/dm}^3$

1. What is the mean residence time t_m ?
2. What is the variance σ^2 ?

P16-5B OEQ (Old Exam Question). The following $E(t)$ curves were obtained from a tracer test on two tubular reactors in which dispersion is believed to occur.

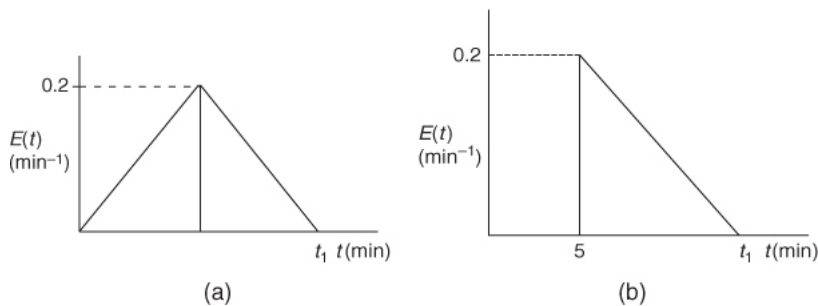


Figure P16-5B (a) RTD Reactor A; (b) RTD Reactor B

1. What is the final time t_1 (in minutes) for the reactor shown in Figure P16-5B (a)?
How about in Figure P16-5B (b)?
2. What is the mean residence time, t_m , and variance, σ^2 , for the reactor shown in Figure P16-5B (a)?
How about in Figure P16-5B (b)?
3. What is the fraction of the fluid that spends 7 minutes or longer in Figure P16-5B (a)?
How about in Figure P16-5B (b)?

P16-6B An RTD experiment was carried out in a nonideal reactor that gave the following results:

$E(t) = 0$	for	$t < 1 \text{ min}$
$E(t) = 1.0 \text{ min}^{-1}$	for	$1 \leq t \leq 2 \text{ min}$
$E(t) = 0$	for	$t > 2 \text{ min}$

1. What are the mean residence time, t_m , and variance σ^2 ?
2. What is the fraction of the fluid that spends a time 1.5 minutes or longer in the reactor?
3. What fraction of fluid spends 2 minutes or less in the reactor?
4. What fraction of fluid spends between 1.5 and 2 minutes in the reactor?
(Ans: Fraction = 0.5)

P16-7 Derive $E(t)$, $F(t)$, t_m , and σ^2 for a turbulent flow reactor with $1/7$ the power law, that is,

$$U = U_{\max} \left(1 - \frac{r}{R} \right)^{1/7}$$

P16-8 OEQ (Old Exam Question)—Graduate Course.

Consider the RTD function

$$E(t) = \begin{cases} A - B(t_0 - t)^3 & \text{for } 0 \leq t < 2t_0 \\ 0 & \text{for } t > 2t_0 \end{cases}$$

1. Sketch $E(t)$ and $F(t)$.
2. Calculate t_m and σ^2 .

3. What are the restrictions (if any) on A, B, and t_0 ? *Hint:*

$$\int_0^\infty E(t) dt = 1.$$

P16-9_A Evaluate the first moment about the mean

$$m_1 = \int_0^\infty (t - \tau) E(t) dt$$

for an ideal PFR, a CSTR, and a laminar-flow reactor.

P16-10_B Gasoline shortages in the United States have produced long lines of motorists at service stations. The table below shows a distribution of the times required to obtain gasoline at 23 Center County service stations.

- What is the average time required?
- If you were to ask randomly among those people waiting in line, “How long have you been waiting?” what would be the average of their answers?

<i>Total Waiting Time (min)</i>	0	3	6	9	1	1	1	2
					2	5	8	1
<i>Number of Stations Having That Total Waiting Time</i>	0	4	3	5	8	2	1	0

- Can you generalize your results to predict how long you would have to wait to enter a five-story parking garage that has a 4-hour time limit?
(Thanks to R. L. Kabel, Pennsylvania State University)

P16-11_B OEQ (Old Exam Question). The volumetric flow rate through a reactor is $10 \text{ dm}^3/\text{min}$. A pulse test gave the following concentration measurements at the outlet:

$t \text{ (min)}$	$c \times 10^5$
0	0
0.4	329

1.0	622
2	812
3	831
4	785
5	720
6	650
8	523
10	418
15	238
20	136
25	77
30	44
35	25
40	14
45	8

50	5
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60	1
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1. Plot the external-age distribution $E(t)$ as a function of time.
2. Plot the external-age cumulative distribution $F(t)$ as a function of time.
3. What are the mean residence time t_m and the variance, σ^2 ?
4. What fraction of the material spends between 2 and 4 minutes in the reactor? (**Ans:** Fraction = 0.16)
5. What fraction of the material spends longer than 6 minutes in the reactor?
6. What fraction of the material spends less than 3 minutes in the reactor? (**Ans:** Fraction = 0.192)
7. Plot the normalized distributions $E(\Theta)$ and $F(\Theta)$ as a function of Θ .
8. What is the reactor volume?
9. Plot the internal-age distribution $I(t)$ as a function of time.
10. What is the mean internal age α_m ?
11. This problem is continued in Problems **P17-14C** and **P18-12C**.

P16-12B An RTD analysis was carried out on a liquid-phase reactor (*Chem. Eng. J.* 1, 76 (1970)). Analyze the following data:

$t(s)$	0	150	175	200	225	240	250
$C \times 10^3 \text{ (g/m}^3\text{)}$	0	0	1	3	7.4	9.4	9.7
$t(s)$	275	300	325	350	375	400	450

$C \times 10^3 \text{ (g/m}^3\text{)}$	8.2	5.0	2.5	1.2	0.5	0.2	0	

1. Plot the $E(t)$ curve for these data.
2. What fraction of the material spends between 230 and 270 seconds in the reactor?
3. Plot the $F(t)$ curve for these data.
4. What fraction of the material spends less than 250 seconds in the reactor?
5. What is the mean residence time?
6. What is the variance σ^2 ?
7. Plot $E(\Theta)$ and $F(\Theta)$ as a function of Θ .

P16-13_C (*Distributions in a stirred tank*) Using a negative step tracer input, Cholette and Cloutier (*Can. J. Chem. Eng.*, 37, 107 (1959)) studied the RTD in a tank for different stirring speeds. Their tank had a 30-in. diameter and a fluid depth of 30 in. inside the tank. The inlet and exit flow rates were 1.15 gal/min. Here are some of their tracer results for the relative concentration, C/C_0 (courtesy of the Canadian Society for Chemical Engineering):

NEGATIVE STEPS TRACER TEST

Impeller Speed (rpm)		
Time (min)	170	10
10	0.761	0.653
15	0.695	0.566
20	0.639	0.513

25	0.592	0.454
----	-------	-------

30	0.543	0.409
----	-------	-------

35	0.502	0.369
----	-------	-------

40	0.472	0.333
----	-------	-------

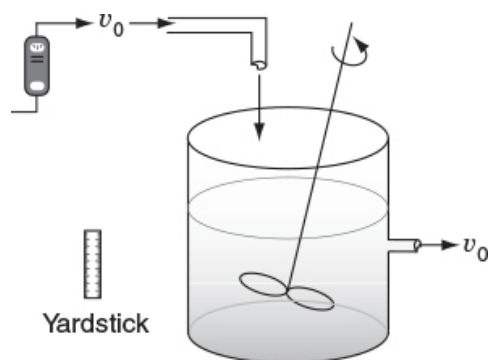
45	0.436	0.307
----	-------	-------

50	0.407	0.276
----	-------	-------

55	0.376	0.248
----	-------	-------

60	0.350	0.226
----	-------	-------

65	0.329	0.205
----	-------	-------



Calculate and plot the cumulative exit-age distribution, the intensity function, and the internal-age distributions as a function of time for this stirred tank at the two impeller

speeds. Can you tell anything about the dead zones and bypassing at the different stirrer rates?

SUPPLEMENTARY READING

1. Discussions of the measurement and analysis of residence time distribution can be found in

R. L. CURL and M. L. MCMILLIN, "Accuracies in residence time measurements," *AIChE J.*, 12, 819–822 (1966).

JOFO JACKSON, "Analysis of 'RID' Data from the Nut Cracker Reactor at the Riça Plant," *Jofostan J. Ind. Data*, 28, 243 (1982).

O. LEVENSPIEL, *Chemical Reaction Engineering*, 3rd ed. New York: Wiley, 1999, Chaps. 11–16.

2. An excellent discussion of segregation can be found in

J. M. DOUGLAS, "The effect of mixing on reactor design," *AIChE Symp. Ser.*, 48, vol. 60, p. 1 (1964).

3. Also see

M. DUDUKOVIC and R. FELDER, in *CHEMI Modules on Chemical Reaction Engineering*, vol. 4, ed. B. Crynes and H. S. Fogler. New York: AIChE, 1985.

E. B. NAUMAN, "Residence time distributions and micromixing," *Chem. Eng. Commun.*, 8, 53 (1981).

E. B. NAUMAN and B. A. BUFFHAM, *Mixing in Continuous Flow Systems*. New York: Wiley, 1983.

B. A. ROBINSON and J. W. TESTER, *Chem. Eng. Sci.*, 41(3), 469–483 (1986).

J. VILLERMAUX, "Mixing in chemical reactors," in *Chemical Reaction Engineering—Plenary Lectures*, ACS Symposium Series 226. Washington, DC: American Chemical Society, 1982.

17. Predicting Conversion Directly from the Residence Time Distribution

If you think you can, you can.

If you think you can't, you can't.

You are right either way.

—Steve LeBlanc

Overview. Chapter 16 showed how to determine the residence time distribution (RTD) functions $E(t)$ and $F(t)$ along with the mean residence time, t_m and the variance, σ^2 , from concentration–time data. We then used the RTD to characterize and diagnose ideal reactors. Because the residence time distribution is not unique for a given reaction system, we must use models if we want to predict the conversion in our nonideal reactor. In this chapter, we will use the RTD function, that is, $E(t)$, to predict the conversion, X , and the product distribution.

After completing this chapter you will be able to

- Describe the five most common models to predict conversion using RTD data (Section 17.1).
- Calculate conversion for single reactions directly from RTD data using the zero adjustable parameter models (a) segregation, (b) maximum mixedness, and (c) laminar-flow reactor (Section 17.2).
- Use software packages to calculate conversion in the extremes of micromixing (a) segregation and (b) maximum mixedness (Section 17.3).
- Calculate the conversion predicted by the one adjustable parameter tanks-in-series (T-I-S) model (Section 17.4).
- Apply the segregation and maximum mixedness models to nonideal reactors to predict the product distribution in reactors where multiple reactions are occurring (Section 17.5).

17.1 MODELING NONIDEAL REACTORS USING THE RTD

17.1.1 Modeling and Mixing Overview

Now that we have characterized our reactor and have gone to the lab to take data to determine the reaction kinetic rate-law parameters, we need to choose a model to predict conversion in our real reactor.

The answer

$$\text{RTD} + \text{MODEL} + \text{KINETIC DATA} \Rightarrow \left\{ \begin{array}{l} \text{EXIT CONVERSION and} \\ \text{EXIT CONCENTRATIONS} \end{array} \right\}$$

We now present the five models shown in Table 17-1. We shall classify each model according to the number of adjustable parameters. In this chapter, we will discuss the *zero adjustable parameter models and the tanks-in-series (T-I-S) model*. In Chapter 18, we will discuss the *dispersion model and models with two adjustable parameters* that will be used to predict conversion.

Ways we use the RTD data to predict conversion in nonideal reactors

TABLE 17-1 MODELS FOR PREDICTING CONVERSION FROM RTD DATA

1.	Zero adjustable parameters
1.	Segregation model
2.	Maximum mixedness model
2.	One adjustable parameter
1.	Tanks-in-series model
2.	Dispersion model
3.	Two adjustable parameters
Real reactors modeled as combinations of ideal reactors	

For the *zero adjustable parameter models*, we do not need to make any intermediate calculations; we use the *E*- and *F*-curves directly to predict the conversion given the rate law and kinetic parameters. For the *one-parameter models*, we use the RTD to calculate mean residence time, t_m , and variance, σ^2 , which we can then use (1) to find the number of tanks in series necessary to accurately model a nonideal CSTR and (2) calculate the Peclet number, Pe , to find the conversion in a tubular flow reactor using the dispersion model.

For the *two-parameter models*, we will show in [Chapter 18](#) how to create combinations of ideal reactors to model the nonideal reactor. We then use the RTD to calculate the model parameters such as fraction bypassed, fraction dead volume, exchange volume, and ratios of reactor volumes that then can be used along with the reaction kinetics to predict conversion.

17.1.2 Mixing

The RTD tells us how long the various fluid elements have been in the reactor, but it does not tell us anything about the exchange of matter between the fluid elements (i.e., *the mixing*). The mixing of reacting species is one of the major factors controlling the behavior of chemical reactors.

Fortunately for first-order reactions, mixing is not important, and knowledge of the length of time each molecule spends in the reactor is all that is needed to predict conversion. For first-order reactions, the conversion is independent of concentration (recall [Table 5-1](#), page 162 and Equation (E13-1.4) in Example E13-1)

$$\frac{dX}{dt} = k(1 - X) \quad (\text{E13-1.4})$$

A model is needed for reactions other than first order.

Consequently, mixing with the surrounding molecules is *not* important. Therefore, once the RTD is determined, we can predict the conversion that will be achieved in the real reactor provided that the specific reaction rate for the first-order reaction is known. However, for reactions other than first order, knowledge of the RTD is not sufficient to predict conversion. For reactions other than first order, the *degree of*

mixing of molecules must be known in addition to how long each molecule spends in the reactor. Consequently, we must develop models that account for the mixing of molecules inside the reactor.

The more complex models of nonideal reactors necessary to describe reactions other than first order must contain information about *micromixing* in addition to that of *macromixing*. To facilitate our discussion on micromixing, we define the *age* of a molecule as the time a molecule has been inside the reactor. **Macromixing** produces a distribution of residence times *without*, specifying how molecules of different ages encounter one another in the reactor. **Micromixing**, on the other hand, describes how molecules of different ages encounter one another in the reactor. There are two extremes of *micromixing*:

1. All molecules of the same age group remain together as they travel through the reactor and are not mixed with any other age until they exit the reactor (i.e., complete segregation).
2. Molecules of different age groups are completely mixed at the molecular level as soon as they enter the reactor (complete micromixing).

For a given state of macromixing (i.e., a given RTD), these two extremes of micromixing will give the upper and lower limits on conversion in a nonideal reactor.

Late Mixing

Segregation

Early Mixing

Maximum Mixedness

We shall define a *globule*¹ as a fluid particle containing millions of molecules all of the same age. A fluid in which the globules of a given age do not mix with other globules is called a macrofluid. A *macrofluid* could be visualized as noncoalescent globules where all the molecules in a given globule have the same age. A fluid in which molecules are not constrained to remain in the globule and are free to move everywhere is called a *microfluid*.² There are two extremes of mixing of the *macrofluid* globules—early mixing and late

mixing. These two extremes of late and early mixing are shown in Figure 17-1(a) and (b), respectively. The extremes of late and early mixing are referred to as *complete segregation* and *maximum mixedness*, respectively. For single reactions with orders greater than one or less than zero, the segregation model will predict the highest conversion. For reaction orders between zero and one, the maximum mixedness model will predict the highest conversion. This concept is discussed further in Section 17.3.1.

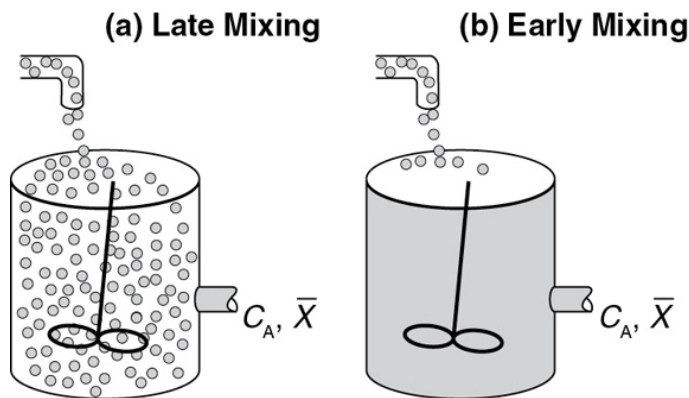


Figure 17-1 (a) Macrofluid and (b) microfluid mixing on the molecular level.

¹ Pronounced gläbyööl *not* Go Blue.

² J. Villermaux, *Chemical Reactor Design and Technology*. Boston: Martinus Nijhoff, 1986.

Here \bar{X} represents the mean conversion in the exit stream.

17.2 ZERO ADJUSTABLE PARAMETER MODELS

17.2.1 Segregation Model

In a “*perfectly mixed*” CSTR, the entering fluid is assumed to be distributed immediately and evenly throughout the reacting mixture. This mixing is assumed to take place even on the microscale, and elements of different ages mix together thoroughly to form a *completely micromixed* fluid (see Figure 17-1(b)). However, if fluid elements of different ages do not mix together at all, the elements remain segregated from each other, and the fluid is termed *completely segregated* (see Figure 17-1(a)). The extremes of complete micromixing and complete segregation are the limits of the micromixing of a reacting mixture.

The extremes of micromixing

In developing the segregated mixing model, we first consider a CSTR because the application of the concepts of mixing quality are most easily illustrated using this reactor type. In the segregated flow model, we visualize the flow through the reactor to consist of a continuous series of globules (Figure 17-2).

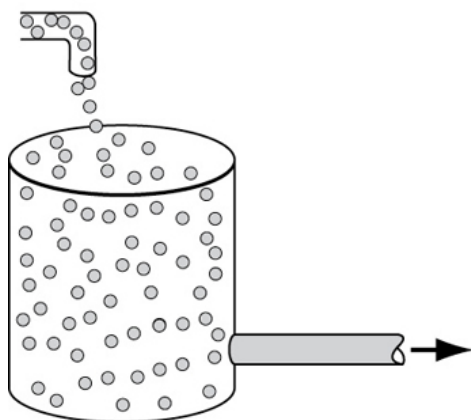


Figure 17-2 Little batch reactors (globules) inside a CSTR.

In the segregation model, globules behave as batch reactors operated for different times.

These globules retain their identity; that is, they do not interchange material with other globules in the fluid during their period of residence in the reaction environment. In other words, they remain segregated until they exit the reactor and mix immediately. In addition, each globule spends a different amount of time in the reactor. In essence, what we are doing is lumping all the molecules that have exactly the same residence time in the reactor into the same globule. The principles of reactor performance in the presence of completely segregated mixing were first described by Danckwerts and Zwietering.^{3,4}

³ P. V. Danckwerts, *Chem. Eng. Sci.*, 8, 93 (1958).

⁴ T. N. Zwietering, *Chem. Eng. Sci.*, 11, 1 (1959).

The segregation model has mixing at the latest possible point.

Another way of looking at the segregation model for a continuous-flow system is the PFR shown in Figures 17-3(a) and (b). Because the fluid flows down the reactor in plug flow, each exit stream corresponds to a specific residence time in the reactor. Batches of molecules are removed from the reactor at different locations along the reactor in such a manner as to duplicate the RTD function, $E(t)$. The molecules removed near the entrance to the reactor correspond to those molecules having short residence times in the reactor. Physically, this effluent would correspond to the molecules that channel rapidly through the reactor. The farther the molecules travel along the reactor before being removed, the longer their residence time. The points at which the various groups or batches of molecules are removed correspond to the RTD function for the reactor.

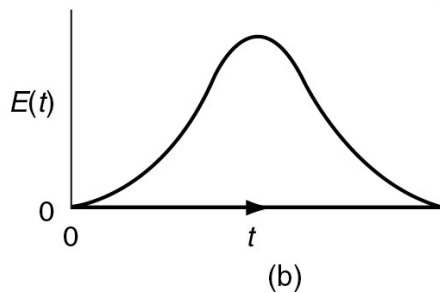
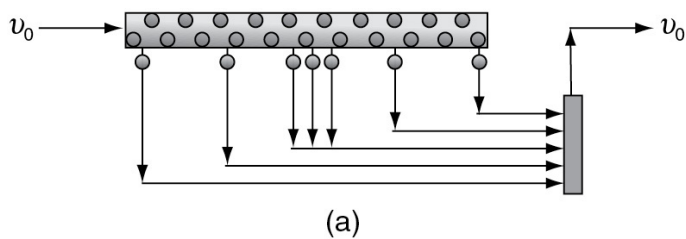


Figure 17-3 Mixing at the latest possible point.



Little batch reactors

$E(t)$ matches the removal of the batch reactors.

Because there is no molecular interchange between globules, each globule acts essentially as its own batch reactor. The reaction time in any one of these tiny batch reactors is equal to the time that the particular globule has spent in the reaction environment and determined by their time of exit. The distribution of residence times among the globules is given by the RTD of the particular reactor.

$$\text{RTD} + \text{MODEL} + \text{KINETIC DATA} \Rightarrow \left\{ \begin{array}{l} \text{EXIT CONVERSION and} \\ \text{EXIT CONCENTRATIONS} \end{array} \right\}$$

Now that we have the reactor's RTD, we will choose a model, apply the rate law and rate-law parameters to predict conversion as shown in the box earlier. We will start with the segregation model.

To determine the mean conversion in the effluent stream, we must average the conversions of all of the various globules in the exit stream:

$$\begin{aligned} \left[\begin{array}{c} \text{Mean} \\ \text{Conversion} \\ \text{of those globules} \\ \text{spending between} \\ \text{time } t \text{ and } t + dt \\ \text{in the reactor} \end{array} \right] &= \left[\begin{array}{c} \text{Conversion} \\ \text{achieved in a globule} \\ \text{after spending a time } t \\ \text{in the reactor} \end{array} \right] \times \left[\begin{array}{c} \text{Fraction} \\ \text{of globules that} \\ \text{spend between } t \\ \text{and } t + dt \text{ in the} \\ \text{reactor} \end{array} \right] \\ d\bar{X} &= X(t) \times E(t)dt \end{aligned}$$

then

$$d\bar{X} = X(t) \times E(t)dt$$

Dividing by dt

$$\frac{d\bar{X}}{dt} = X(t) E(t) \quad (17-1)$$

Summing over all globules of all different ages, the mean conversion is

$$\bar{X} = \int_0^{\infty} X(t)E(t) dt \quad (17-2)$$

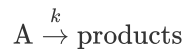
Mean conversion for the segregation model

Consequently, if we have the batch reactor equation for $X(t)$ and measure the RTD experimentally, we can find the mean conversion in the exit stream. *Thus, if we have the RTD, the reaction-rate law and parameters, then for a segregated flow situation (i.e., model), we have sufficient information to calculate the conversion.* An example that may help give additional physical insight to the segregation model is given on the CRE Web site (<http://www.umich.edu/~elements/6e/17chap/prof-compare.html> and <http://www.umich.edu/~elements/6e/17chap/summary.html-top1a1>).



Segregation Model for a First-Order Reaction

Consider the following first-order reaction:



We treat the globules that spend different amounts of time in the real reactor as little batch reactors. For a batch reactor we have

$$-\frac{dN_A}{dt} = -r_A V$$

For constant volume and with $N_A = N_{A0}(1 - X)$

$$N_{A0} \frac{dX}{dt} = r_A V = k C_A V = k N_A = k N_{A0} (1 - X)$$

$$\frac{dX}{dt} = k (1 - X) \quad (17-3)$$

Solving for $X(t)$, we have for any globule that spends a time t in the real reactor

$$X(t) = 1 - e^{-kt}$$

Because different globules spend different times, we have to add up the conversions from all the globules of all different ages.

Mean conversion for a first-order reaction

$$\bar{X} = \int_0^\infty X(t)E(t)dt = \int_0^\infty (1 - e^{-kt})E(t)dt = \int_0^\infty E(t)dt - \int_0^\infty e^{-kt}E(t)dt \quad (17-4)$$

$$\boxed{\bar{X} = 1 - \int_0^\infty e^{-kt}E(t)dt} \quad (17-5)$$

We will now determine the mean conversion predicted by the segregation model for an ideal PFR, a CSTR, and an LFR.

**Example 17-1 Mean Conversion in an Ideal PFR,
an Ideal CSTR, and a Laminar-Flow Reactor**

Derive the equation for conversion for a first-order reaction using the segregation model when the RTD is equivalent to **(a) an ideal PFR, (b) an ideal CSTR,** and **(c) a laminar-flow reactor (LFR).** Compare these conversions with those obtained from the design equation.

Solution

(a) For the PFR, the RTD function was given by Equation (16-27)

$$E(t) = \delta(t - \tau) \quad (16-27)$$

Recalling Equation (17-5)

$$\bar{X} = \int_0^\infty X(t) E(t) dt = 1 - \int_0^\infty e^{-kt} E(t) dt \quad (17-5)$$

Substituting Equation (16-27) for the RTD function for a PFR gives

$$\bar{X} = 1 - \int_0^\infty (e^{-kt}) \delta(t - \tau) dt \quad (\text{E17-1.1})$$

Using the integral properties of the Dirac delta function, Equation (16-30), we obtain

$$\boxed{\bar{X} = 1 - e^{-k\tau} = 1 - e^{-Da_1}} \quad (\text{E17-1.2})$$

where for a first-order reaction the Damköhler number is $Da_1 = \tau k$.

Using our PFR algorithm and combining the mole balance, rate law, and stoichiometric relationships (cf. Chapter 5), we had

$$\frac{dX}{d\tau} = k(1 - X) \quad (\text{E17-1.3})$$

Integrating yields

$$\boxed{X = 1 - e^{-k\tau} = 1 - e^{-Da_1}} \quad (\text{E17-1.4})$$

Twins!

which is identical to the conversion predicted by the segregation model \bar{X} .

(b) For the CSTR, the RTD function was given in Equation (16-21) as

$$E(t) = \frac{1}{\tau} e^{-t/\tau} \quad (\text{E17-1.5})$$

Recalling Equation (17-5), the mean conversion for a first-order reaction is

$$\bar{X} = 1 - \int_0^\infty e^{-kt} E(t) dt \quad (17-6)$$

$$\bar{X} = 1 - \int_0^\infty \frac{e^{-(1/\tau+k)t}}{\tau} dt$$

$$\bar{X} = 1 + \frac{1}{k+1/\tau} \frac{1}{\tau} e^{-(k+1/\tau)t} \Big|_0^\infty$$

The conversion predicted from the segregation model is

$$\boxed{\bar{X} = \frac{\tau k}{1+\tau k} = \frac{Da_1}{1+Da_1}} \quad (\text{E17-1.6})$$

As expected, using the $E(t)$ for an ideal PFR and CSTR with the segregation model gives a mean conversion \bar{X} identical to that obtained by using the algorithm in Chapter 5.

Using our algorithm in Chapter 5, we showed that combining the CSTR mole balance, the rate law, and stoichiometry, we have

$$F_{A0}X = -r_A V$$

$$v_0 C_{A0} X = k C_{A0} (1-X) V$$

Solving for X , we see the conversion predicted from our Chapter 5 algorithm is the same as that for the segregation model

$$\boxed{X = \frac{\tau k}{1+\tau k}} \quad (\text{E17-1.7})$$

Another set of twins!!

$Da_1 = \tau k$	$X_{\text{LFR Exact}}$	$X_{\text{LFR Approx.}}$	X_{PFR}	X_{CSTR}
0.1	0.0895	0.093	0.0952	0.091
1	0.557	0.56	0.632	0.501
2	0.781	0.782	0.865	0.667
4	0.940	0.937	0.982	0.80
10	0.9982	0.9981	0.9999	0.91

We see in Table E17-1.1 $X_{\text{LFR Exact}}$ = Exact solution to Equation (E17-1.10) and the approximate solution $X_{\text{LFR Approx.}}$ = Equation (E17-1.11). We note that in all cases, the Approximate and Exact solutions are in close agreement.

For large values of the Damköhler number then, there is complete conversion along the streamlines off the center streamline so that the conversion is determined along the pipe axis such that

$$\bar{X} = 1 - \int_{0.5}^{\infty} 4e^{-\tau k \Theta} d\Theta = 1 - 4e^{-0.5\tau k} / \tau k \quad (\text{E17-1.12})$$

Figure E17-1.1 shows a comparison of the mean conversion in an LFR, PFR, and CSTR as a function of the Damköhler number for a first-order reaction.

Comparing the conversion profiles for a PFR, a CSTR, and an LFR

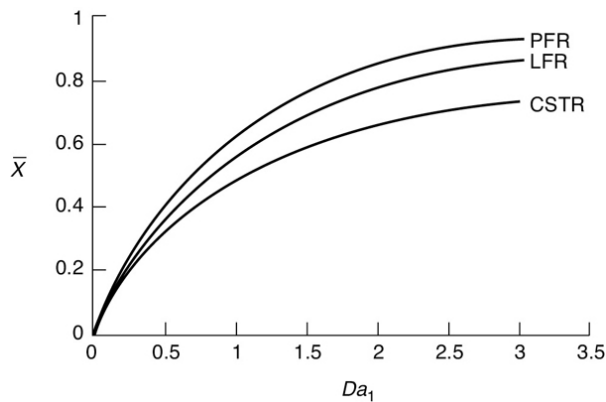


Figure E17-1.1 Conversion in a PFR, LFR, and CSTR as a function of the Damköhler number (Da_1) for a first-order reaction ($Da_1 = \tau k$).

Analysis: One of the first things we observe is that the plug-flow reactor (PFR) and laminar-flow reactor (LFR) conversion profiles as a function of the Damköhler number are quite close for first-order reactions. Secondly, for small Da ($Da < 0.5$) the mean exit conversion for all the models (PFR, LFR and CSTR) is virtually identical. Finally, we see that the mean conversion for the three models diverges with increasing Da .

Important Point:

For a first-order reaction, knowledge of $E(t)$ is sufficient.

We have just shown for a *first-order* reaction that whether you assume complete micromixing (Equation (E17-1.7)) or complete segregation (Equation (E17-1.6)) in a CSTR, the same conversion results. This phenomenon occurs because the rate of change of conversion for a first-order reaction does *not* depend on the concentration of the reacting molecules (Equation (17-3)); it does not matter what kind of molecule is next to it or colliding with it. Thus, the extent of micromixing does not affect a first-order reaction, so the segregated flow model can be used to calculate the conversion. As a result, *only the RTD is necessary to calculate the conversion for a first-order reaction in any type of reactor* (see Problem P17-3c). Knowledge of neither the degree of micromixing nor the

reactor flow pattern is necessary. We now proceed to calculate conversion in a real reactor using RTD data.

*Example 17-2 Mean Conversion, X_{seg} Calculations
in a Real Reactor*

Calculate the mean conversion in the reactor we have characterized by RTD measurements in [Examples 16-1](#) and [16-2](#) for a first-order, liquid-phase, irreversible reaction in a completely segregated fluid:



The specific reaction rate is 0.1 min^{-1} at 320 K. See [Examples 16-1](#) and [16-2](#).

Solution

Because each globule acts as a **batch reactor** of constant volume, we use the batch reactor design algorithm to arrive at the equation giving conversion as a function of time

$$X = 1 - e^{-kt} = 1 - e^{-0.1t} \quad (\text{E17-2.1})$$

To calculate the mean conversion, we need to evaluate the integral

$$\bar{X}_{\text{seg}} = \int_0^{\infty} X(t)E(t)dt \quad (17-2)$$

These calculations are easily carried out with the aid of a spreadsheet such as Excel or Polymath.

The RTD function for this reactor was determined previously and given in data from [Examples 16-1](#) and [16-2](#) and are repeated here in [Table E17-2.1](#), that is, $E(t) = C(t)/\text{Area}$.

Polymath Solution

$$\frac{d(X_{\text{seg}})}{dt} = X(t)E(t) \quad (\text{E17-2.2})$$

$$\frac{dX}{dt} = k(1 - X) \quad (\text{E17-2.3})$$

We saw in [Example 16-1.1](#) that $C(t)$ was first fit to a polynomial from which we calculated $\int_0^t C(t)dt = 51$. We then use this value to calculate the E -curve.

$$E(t) = \frac{C(t)}{51} \quad (\text{E17-2.4})$$

We now combine Equations (E17-2.2), (E17-2.3), and (E17-2.4). The Polymath program and results are given in Table E17-2.1.

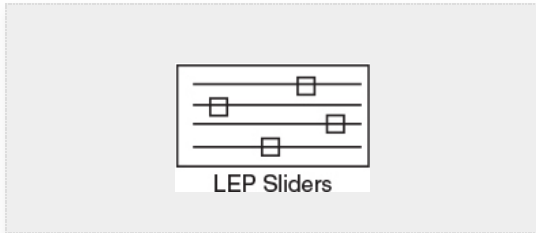


TABLE E17-2.1 SEGREGATION MODEL

Calculated values of DEQ variables			Differential equations
Variable	Initial value	Final value	
1 Area	51	51	1 $d(X)/dt = k(1-X)$
2 C	0.0038746	0.0148043	2 $d(X_{\text{seg}})/dt = X^*E$
3 C1	0.0038746	-387.266	3 $d(m)/dt = 1E$
4 C2	-33.43818	0.0148043	4 $d(F)/dt = E$
5 E	7.597E-05	0.0002903	Explicit equations
6 F	0	1.00125	
7 k	0.1	0.1	1 $C1 = 0.0038746 + 0.2739782t + 1.574621t^2 - 0.2550041t^3$
8 t	0	14	2 Area = 51
9 tm	0	5.10722	3 $k = 1$
10 X	0	0.753403	4 $C2 = -33.43818 + 37.18972t - 11.588838t^2 + 1.695303t^3 - 0.1298667t^4 + 0.005028t^5 - 7.743 \times 10^{-5}t^6$
11 Xseg	0	0.3822834	5 $C = 1$ if $t \leq 4$ and $b=0$ then C1 else if $(t=4 \text{ and } t \leq 14)$ then C2 else 0
			6 $E = C/\text{Area}$

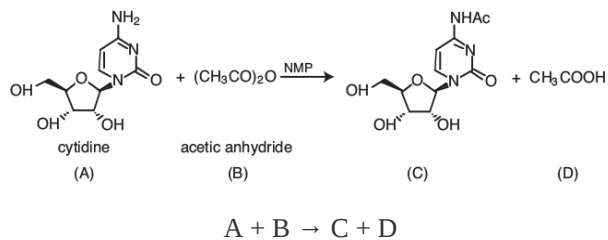
The conversion would be 75.3% if all the globules spent the same time as the last tracer molecule to exit the reactor (i.e., 14 minutes). However, not all globules spend the same time in the reactor. Instead we have a distribution of times the globules spend in the reactor. Consequently, we use the segregation model to find that the mean conversion for all the globules is 38.2%.

Analysis: We were given the conversion as a function of time for a batch reactor $X(t)$ and the RTD E -curve from Example 16-1. Using the segregation model and a polynomial fit for the E -curve, we were able to calculate the mean conversion using the segregation model, X_{seg} , in this nonideal reactor. We note there were **no** model-fitting parameters in making this calculation, just $E(t)$ from the data and $X(t)$.

As discussed previously, because the reaction is *first order*, the conversion calculated in Example 17-2 would be valid for a reactor with complete mixing, complete segregation, or any degree of mixing between the two. Although early or late mixing does not affect a first-order reaction, micromixing or complete segregation can give significantly different results for a second-order reaction system. We now analyze a second-order reaction using the segregation model.

Example 17-3 Mean Conversion for a Second-Order Reaction in a Laminar-Flow Reactor

The liquid-phase reaction between cytidine and acetic anhydride is carried out isothermally in an inert solution of *N*-methyl-2-pyrrolidone (NMP) with $\Theta_{\text{NMP}} = 28.9$. The reaction follows an elementary rate law. The feed is equal molar in A and B with $C_{A0} = 0.75 \text{ mol/dm}^3$, a volumetric flow rate of $0.1 \text{ dm}^3/\text{s}$, and a reactor volume of 100 dm^3 . Calculate the conversion in (a) an ideal PFR, (b) a BR, and (c) an LFR.

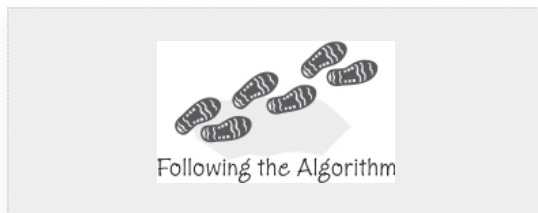


Additional information:⁶

⁶ J. J. Shatynski and D. Hanesian, *Ind. Eng. Chem. Res.*, 32, 594.

$k = 4.93 \times 10^{-3} \text{ dm}^3/\text{mol} \cdot \text{s}$ at 50°C with $E = 13.3 \text{ kcal/mol}$, $\Delta H_{\text{RX}} = -10.5 \text{ kcal/mol}$

Heat of mixing for $\Theta_{\text{NMP}} = \frac{F_{\text{NMP}}}{F_{A0}} = 28.9$, $\Delta H_{\text{mix}} = -0.44 \text{ kcal/mol}$



Solution

The reaction will be carried out isothermally at 50°C . The space time is

$$\tau = \frac{V}{v_0} = \frac{100 \text{ dm}^3}{0.1 \text{ dm}^3/\text{s}} = 1000 \text{ s}$$

(a) For an ideal PFR

Mole Balance

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} \quad (\text{E17-3.1})$$

Rate Law

$$-r_A = kC_A C_B \quad (\text{E17-3.2})$$

$$\text{Stoichiometry, } \Theta_B = 1$$

$$C_A = C_{A0}(1 - X) \quad (\text{E17-3.3})$$

$$C_B = C_A \quad (\text{E17-3.4})$$

Combining

$$\frac{dX}{dV} = \frac{kC_{A0}(1-X)^2}{v_0} \quad (\text{E17-3.5})$$

PFR calculation

Evaluating

Integrating and solving with $\tau = V/v_0$ and $X = 0$ for $V = 0$ gives

$$X = \frac{\tau k C_{A0}}{1 + \tau k C_{A0}} = \frac{Da_2}{1 + Da_2} \quad (\text{E17-3.6})$$

where Da_2 is the Damköhler number for a second-order reaction.

$$\begin{aligned} Da_2 = \tau k C_{A0} &= (1000 \text{ s}) \left(4.9 \times 10^{-3} \text{ dm}^3/\text{s} \cdot \text{mol} \right) \left(0.75 \text{ mol/dm}^3 \right) \\ &= 3.7 \end{aligned}$$

$$X = \frac{3.7}{4.7}$$

$$X = 0.787$$

(b) Batch reactor

$$\frac{dX}{dt} = \frac{-r_A}{C_{A0}} \quad (\text{E17-3.7})$$

$$\frac{dX}{dt} = kC_{A0}(1 - X)^2 \quad (\text{E17-3.8})$$

$$X(t) = \frac{kC_{A0}t}{1 + kC_{A0}t} \quad (\text{E17-3.9})$$

Batch calculation

If the batch reaction time is the same time as the space time, that is, $t = \tau$, the batch conversion is the same as the PFR conversion, $X = 0.787$.

(c) Laminar-flow reactor

The differential form for the mean conversion is obtained from Equation (17-1)

$$\frac{d\bar{X}}{dt} = X(t)E(t) \quad (17-1)$$

We use Equation (E17-3.9) to substitute for $X(t)$ in Equation (17-1). Because $E(t)$ for the LFR consists of two parts, we need to incorporate the IF statement in our ODE solver program. For the laminar-flow reaction, we write

$$E_1 = 0 \text{ for } t < \tau/2 \quad (\text{E17-3.10})$$

$$E_2 = \frac{\tau^2}{2t^3} \text{ for } t \geq \tau/2 \quad (\text{E17-3.11})$$

Let $t_1 = \tau/2$ so that the IF statement now becomes

$$E = \text{If}(t < t_1) \text{ then}(E_1) \text{ else}(E_2) \quad (\text{E17-3.12})$$

LFR calculation

One other thing to remember is that the ODE solver will recognize that $E_2 = \infty$ at $t = 0$ and refuse to run, so we must add a very small number to the denominator such as (0.001); for example,

$$E_2 = \frac{\tau^2}{(2t^3 + 0.001)} \quad (\text{E17-3.13})$$

You won't be able to carry out the integration of Equation (17-2) with the limit $t = \infty$ unless you are an honorary resident of Jofostan. However, you can use Poly-math, but the numerical integration time limit, t_f should be 10 or more times the reactor space time, $\tau = 20 \tau = 20000$ s. The Polymath program for this example is shown in Table E17-3.1.

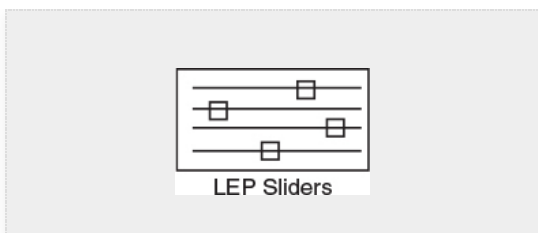


TABLE E17-3.1 LFR SEGREGATION MODEL

Calculated values of DEQ variables				Differential equations	
Variable	Initial value	Final value		1	$d(\bar{X})/dt = X^*E$
1 Cao	0.75	0.75		2	Explicit equations
2 E	0	6.25E-08		1	$k = .00493$
3 E2	5.0E+10	6.25E-08		2	$Cao = .75$
4 k	0.00493	0.00493		3	$X = k^*Cao^*t/(1+k^*Cao^*t)$
5 t	0	2.0E+04		4	$\tau = 1000$
6 t1	500.	500.		5	$t1 = \tau/2$
7 tau	1000.	1000.		6	$E2 = \tau^2/2/(t^3 + .00001)$
8 X	0	0.9866578		7	$E = \text{if } (t < t1) \text{ then } (0) \text{ else } (E2)$
9 Xbar	0	0.7413022			

We see that the mean conversion \bar{X} for the LFR is 74.1%.

In summary,

$$X_{\text{PER}} = 0.787$$

$$X_{\text{LFR}} = 0.741$$

Compare this result with the exact analytical formula for the laminar-flow reactor with a second-order reaction⁷

⁷ K. G. Denbigh, *J. Appl. Chem.*, 1, 227 (1951).

$$\bar{X} = Da_2 \left[1 - \left(\frac{Da_2}{2} \right) \ln \left(1 + \frac{2}{Da_2} \right) \right]$$

Analytical solution

where $Da_2 = kC_{A0}\tau$. For $Da_2 = 3.70$ we get

$$\bar{X} = 0.742$$

In many cases, we can approximate the conversion for an LFR with that calculated from the PFR models.

Analysis: In this example involving a *second-order* reaction, we applied the segregation model to the *E*-curve for two ideal reactors: the plug-flow reactor (PFR) and the laminar-flow reactor (LFR). We found that the difference between the predicted conversion in the PFR and the LFR reactor was 4.6%. We also learned that the analytical solution for a second-order reaction taking place in an LFR was virtually the same as that for the segregation model.

17.2.2 Maximum Mixedness Model

In the segregation model, mixing occurs at the latest possible point.

In a reactor modeled as a segregated fluid, mixing between particles of fluid does not occur until the fluid leaves the reactor. The reactor exit is, of course, the *latest* possible point where mixing can occur, and any effect of mixing is postponed until after all reaction has taken place, as shown in [Figure 17-3](#). We can also think of a completely segregated flow as being in a state of *minimum mixedness*. We now want to consider *the other extreme, that of maximum mixedness* consistent with a given residence time distribution.

In the maximum mixedness model, mixing occurs at the earliest possible point.

We return again to the plug-flow reactor with side entrances, only this time the fluid enters the reactor along its length ([Figure 17-4](#)). As soon as the fluid enters the reactor, it is completely mixed radially (but not longitudinally) with the other fluid already in the reactor. The entering fluid is fed into the reactor through the side entrances in such a manner that the RTD of the plug-flow reactor with side entrances is identical to the RTD of the real reactor.

λ = life expectancy

The globules at the far left of Figure 17-4(a) correspond to the molecules that spend a long time in the reactor, while those at the far right correspond to the molecules that channel through the reactor and spend a very short time in the reactor. In this reactor with side entrances, mixing occurs at the *earliest* possible moment consistent with the RTD. This situation is termed the condition of *maximum mixedness*.⁸ The approach for calculating conversion for a reactor in a condition of maximum mixedness will now be developed. In a reactor with side entrances, let λ = life expectancy be the time it takes for the fluid to move from a particular point to the end of the reactor. In other words, λ is the life expectancy of the fluid in the reactor at that point (Figure 17-5).

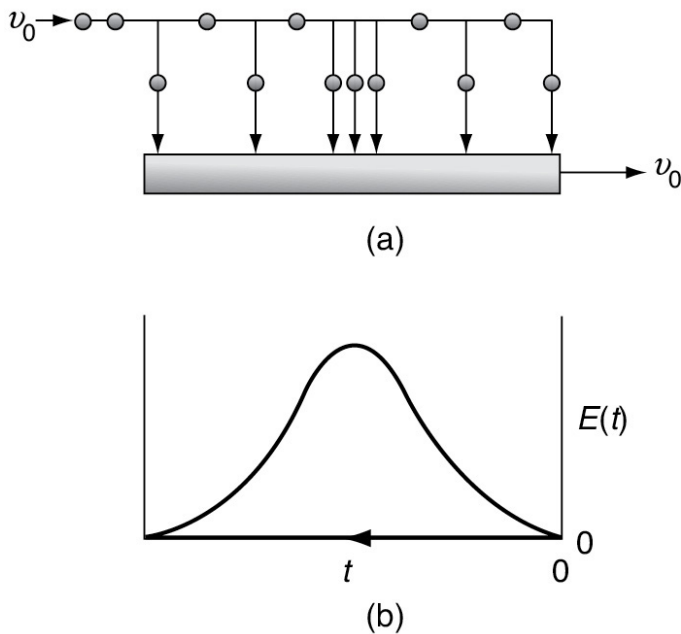


Figure 17-4 Mixing at the earliest possible point.

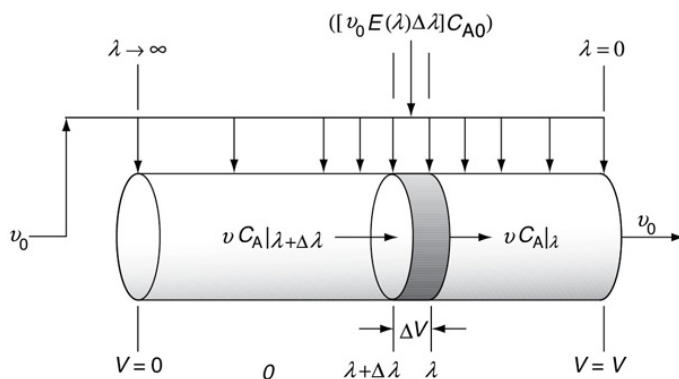


Figure 17-5 Modeling maximum mixedness by a plug-flow reactor with side entrances.

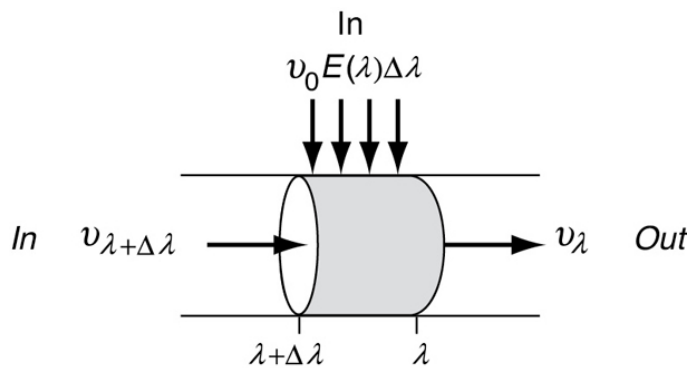
⁸ T. N. Zwietering, *Chem. Eng. Sci.*, 11, 1 (1959).

Maximum mixedness: mixing occurs at the earliest possible point.

Moving down the reactor from left to right, the life expectancy, λ , decreases and becomes zero at the exit. At the left end of the reactor (i.e., the entrance), λ approaches infinity or the maximum residence time if it is other than infinite.

Consider the fluid that enters the reactor through the sides of volume ΔV in Figure 17-5. The fluid that enters here will have a life expectancy between λ and $\lambda + \Delta\lambda$. The fraction of fluid that will have this life expectancy between λ and $\lambda + \Delta\lambda$ is $E(\lambda)\Delta\lambda$. The corresponding volumetric flow rate IN through the sides is $[v_0 E(\lambda)\Delta\lambda]$.

Fluid balance on $\Delta\lambda$ In + In = Out



The volumetric flow rate at λ , v_{λ} , is the flow rate that entered at $\lambda + \Delta\lambda$, that is, $v_{\lambda+\Delta\lambda}$, plus what entered through the sides $v_0 E(\lambda)\Delta\lambda$, that is,

$$v_{\lambda} = v_{\lambda+\Delta\lambda} + v_0 E(\lambda) \Delta\lambda$$

Rearranging and taking the limit as $\Delta\lambda \rightarrow 0$

$$\frac{dv_{\lambda}}{d\lambda} = -v_0 E(\lambda) \quad (17-7)$$

The volumetric flow rate v at the entrance to the reactor ($V = 0$, $\lambda = \infty$, and $X = 0$) is zero (i.e., $v_{\lambda} = 0$) because the fluid only

enters through the sides along the length.

Integrating Equation (17-7) with limits $v_\lambda = 0$ at $\lambda = \infty$ and $v_\lambda = v_\lambda$ at $\lambda = \lambda$, and then using Equation (16-13) we obtain

$$v_\lambda = v_0 \int_\lambda^\infty E(\lambda) d\lambda = v_0 [1 - F(\lambda)] \quad (17-8)$$

The volume of fluid in the reactor, ΔV , with a life expectancy between λ and $\lambda + \Delta\lambda$ is

$$\Delta V = v_\lambda \Delta\lambda = v_0 [1 - F(\lambda)] \Delta\lambda \quad (17-9)$$

The rate of generation of the substance A in this volume is

$$r_A \Delta V = r_A v_0 [1 - F(\lambda)] \Delta\lambda \quad (17-10)$$

We can now carry out a mole balance on substance A between λ and $\lambda + \Delta\lambda$

Mole balance

$$\begin{aligned} \left[\begin{array}{c} \text{In} \\ \text{at } \lambda + \Delta\lambda \end{array} \right] + \left[\begin{array}{c} \text{In} \\ \text{through sides} \end{array} \right] - \left[\begin{array}{c} \text{Out} \\ \text{at } \lambda \end{array} \right] + \left[\begin{array}{c} \text{Generation} \\ \text{by reaction} \end{array} \right] &= 0 \\ [v_\lambda + \Delta\lambda C_A]_{\lambda+\Delta\lambda} + [v_0 C_{A0} E(\lambda) \Delta\lambda] - [v_\lambda C_A]_\lambda + [r_A \Delta V] &= 0 \end{aligned}$$

Substituting for $v_{\lambda + \Delta\lambda}$, v_λ and ΔV

$$v_0 [1 - F(\lambda)] C_A|_{\lambda+\Delta\lambda} + v_0 C_{A0} E(\lambda) \Delta\lambda - v_0 [1 - F(\lambda)] C_A|_\lambda + r_A v_0 [1 - F(\lambda)] \Delta\lambda = 0 \quad (17-11)$$

Dividing Equation (17-11) by $v_0 \Delta\lambda$ and taking the limit as $\Delta\lambda \rightarrow 0$ gives

$$E(\lambda) C_{A0} + \frac{d\{[1-F(\lambda)]C_A(\lambda)\}}{d\lambda} + r_A [1 - F(\lambda)] = 0$$

Taking the derivative of the term in brackets

$$C_{A0} E(\lambda) + [1 - F(\lambda)] \frac{dC_A}{d\lambda} = C_A E(\lambda) + r_A [1 - F(\lambda)] = 0$$

Rearranging

$$\frac{dC_A}{d\lambda} = -r_A + \left(C_A - C_{A0} \right) \frac{E(\lambda)}{1-F(\lambda)} \quad (17-12)$$

We can also rewrite Equation (17-12) in terms of conversion as

$$-C_{A0} \frac{dX}{d\lambda} = -r_A - C_{A0} X \frac{E(\lambda)}{1-F(\lambda)} \quad (17-13)$$

or

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{A0}} + \frac{E(\lambda)}{1-F(\lambda)} X \quad (17-14)$$

Maximum mixedness gives the lower bound on X .

The boundary condition is as $\lambda \rightarrow \infty$, then $C_A = C_{A0}$ for Equation (17-12) (or $X = 0$ for Equation (17-13)). To obtain a solution, the equation is integrated backward numerically, starting at a very large value of λ and ending with the final conversion at $\lambda = 0$. For a given RTD and reaction orders greater than one or less than zero, the maximum mixedness model gives the lower bound on conversion as shown in Tables 17-1 and 17-2, pages 888, 909.

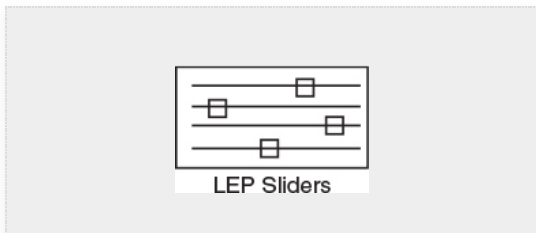
Example 17-4 Conversion Bounds for a Nonideal Reactor

The liquid-phase, second-order dimerization



for which $k = 0.01 \text{ dm}^3/\text{mol}\cdot\text{min}$ is carried out at a reaction temperature of 320 K. The feed is pure A with $C_{A0} = 8 \text{ mol/dm}^3$. The reactor is nonideal. The reactor volume is 1000 dm^3 , and the feed rate for our dimerization is going to be $25 \text{ dm}^3/\text{min}$.

We wish to know the bounds on the conversion for different possible degrees of micromixing for the RTD of this reactor. What are these bounds?



The Jofostan students carried out a tracer test by throwing 100 g of tracer ($N_0 = 100 \text{ g}$) into the reactor that had an entering volumetric flow rate of $25 \text{ dm}^3/\text{min}$ ($v_0 = 25 \text{ dm}^3/\text{min}$) and then measured the exit concentration ($C(t)$ as a function of time t) and the results are shown in columns 1 and 2 of [Table E17-4.1](#). The exit concentration, that is, the C -curve, was then fit to a polynomial. A tutorial on how to fit the tracer data points to a polynomial, for example,

$$C(t) = a_0 + a_1t + a_2t^2 + a_3t^3 + a_4t^4$$

is given in the *Living Example Problem* on the CRE Web site in both [Chapters 7](#) and [16](#). After finding a_0 , a_1 , and so on, we integrate the C_t -curve to find the total amount of tracer, N_0 , injected

$$N_0 = \int_0^\infty C(t)dt = \int_0^{14} C(t)dt$$

The E -curve

and then divide each concentration by N_0 , the total tracer concentration to construct the E -curve which is given in column 3, the corresponding polynomial fit for the E -curve is

E2 = -2.64e-9*t^3+1.3618e-6*t^2-.00024069*t+.015011

E1 = 4.44658e-10*t^4-1.1802e-7*t^3+1.35358e-5*t^2-.000865652*t+.028004

E = if (t<=70) then (E1) else (E2)

Solution

The bounds on the conversion are found by calculating conversions under conditions of (a) complete segregation and (b) maximum mixedness.

(a) Conversion if fluid is completely segregated. Using the CRE algorithm we find the batch reactor conversion for a second-order reaction is

X(t) = (kC_A0t) / (1+kC_A0t) (E17-4.1)

TABLE E17-4.1 RAW AND PROCESSED DATA

t (min)	C (mg/dm ³)	E(t) (min ⁻¹)	X (t)	X(t)E(t) (min ⁻¹)	X(t)E(t) Δt	λ(min)
0	112	0.0280	0	0	0	0
5	95.8	0.0240	0.286	0.00686	0.0172†	5
10	82.2	0.0206	0.444	0.00916	0.0400	10
15	70.6	0.0177	0.545	0.00965	0.0470	15

20	60.9	0.0152	0.61 5	0.00935	0.0475	20
30	45.6	0.0114	0.70 6	0.00805	0.0870	30
40	34.5	0.00863	0.76 2	0.00658	0.0732	40
50	26.3	0.00658	0.80 0	0.00526	0.0592	50
70	15.7	0.00393	0.84 8	0.00333	0.0859	70
10 0	7.6 7	0.00192	0.88 9	0.00171	0.0756	10 0
15 0	2.5 5	0.00063 8	0.92 3	0.00058 9	0.0575	15 0
20 0	0.9 0	0.00022 5	0.94 1	0.00021 2	<u>0.0200</u>	20 0
0.610						
1	2	3	4	5	6	7

[†]For the first point, we have $X(t)E(t)\Delta t = (0 + 0.00686) (5/2) = 0.0172$.

Spreadsheets work quite well here.

The conversion for a completely segregated fluid in a reactor is

$$X_{\text{seg}} = \int_0^\infty X(t)E(t) \, dt \quad (\text{E17-4.2})$$

differentiating

$$\frac{dX_{seg}}{dt} = X(t)E(t) \quad (E17-4.3)$$

Combining the mole balance, rate law, and stoichiometry for a “little” batch reactor, we obtain the differential equation of $X(t)$.

$$\frac{dX}{dt} = kC_{A0}(1 - X)^2 \quad (E17-4.4)$$

We now use Polymath to solve Equations (E17-4.3) and (E17-4.4) simultaneously to find X_{seg} .

The Polymath program and results are given in Table E17-4.2.

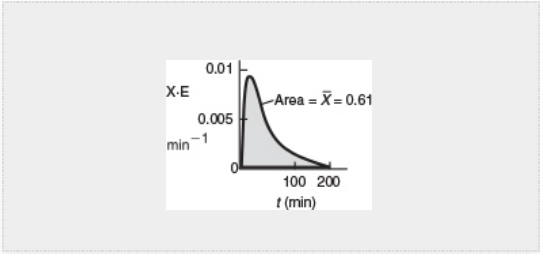


TABLE E17-4.2 SEGREGATION MODEL

POLYMATH Report			Differential equations	
Ordinary Differential Equations			1	$d(X_{seg})/d(t) = X \cdot E$
Calculated values of DEQ variables			2	$d(X)/d(t) = -ra/C_{ao}$
Variable	Initial value	Final value	Explicit equations	
1 Ca	8.	0.4705882	1	$C_{ao} = 8$
2 Cao	8.	8.	2	$Ca = Cao \cdot (1 - X)$
3 E	0.028004	0.000225	3	$k = .01$
4 E1	0.028004	0.1635984	4	$E2 = -2.64e-9 \cdot t^3 + 1.3618e-6 \cdot t^2 - .00024069 \cdot t + .015011$
5 E2	0.015011	0.000225	#	
6 k	0.01	0.01	5	$E1 = 4.44658e-10 \cdot t^4 - 1.1802e-7 \cdot t^3 + 1.35358e-5 \cdot t^2$
7 ra	-0.64	-0.0022145		$- .000865652 \cdot t + .028004$
8 t	0	200.	6	$E = \text{if } (t \leq 70) \text{ then } (E1) \text{ else } (E2)$
9 X	0	0.9411765	7	$ra = -k \cdot Ca^2$
10 Xseg	0	0.6054227		

The predicted conversion for a completely segregated flow is 0.605 or 61%.

$$X_{seg} = 0.61$$

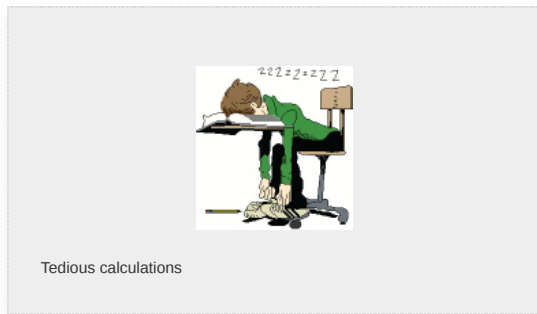
(b) Conversion for maximum mixedness model

Hand Calculation: In practice, we would never carry out step-by-step calculations to predict the conversion from the maximum mixedness model. It is presented

here in the hopes that it will give a clearer understanding of maximum mixedness. As we will see in [Example 17-5](#), the Polymath ODE solver is more proficient and unbelievably fast.

Conversion for maximum mixedness. The Euler method will be used for numerical integration

$$X_{i+1} = X_i + (\Delta\lambda) \left[\frac{E(\lambda_i)}{1-F(\lambda_i)} X_i - kC_{A0}(1 - X_i)^2 \right]$$



Integrating this equation presents some interesting results. If the equation is integrated from the exit side of the reactor, starting with $\lambda = 0$, the solution is unstable and soon approaches large negative or positive values, depending on what the starting value of X is. We want to find the conversion at the exit to the reactor, $\lambda = 0$. Consequently, we need to integrate backward.

$$X_{i+1} = X_i - \Delta\lambda \left[\frac{E(\lambda_i)X_i}{1-F(\lambda_i)} - kC_{A0}(1 - X_i)^2 \right]$$

If integrated from the point where $\lambda \rightarrow \infty$, oscillations may occur but are soon damped out, and the equation approaches the same final value no matter what initial value of X between 0 and 1 is used. We shall start the integration at $\lambda = 200$ and let $X = 0$ at this point. If we set $\Delta\lambda$ too large, the solution will blow up, so we will start out with $\Delta\lambda = 25$ and use the average of the measured values of $E(t)/[1 - F(t)]$ where necessary. We will now use the data in column 7 of [Table E17-4.1](#) to carry out the integration.

This calculation (b) is only given to provide insight to maximum mixedness.

At $\lambda = 200$, $X = 0$

$\lambda = 175$:

$$X(\lambda = 175) = X(\lambda = 200) - \Delta\lambda \left[\frac{E(200)X(200)}{1-F(200)} - kC_{A0}(1 - X(200))^2 \right]$$

$$X = 0 - (25) [(0.075)(0) - (0.01)(8)(1)^2] = 2$$

$\lambda = 150$:

$$X(\lambda = 150) = X(\lambda = 175) - \Delta\lambda \left[\frac{E(175)X(175)}{1-F(175)} - kC_{A0}(1 - X(175))^2 \right]$$

We need to take an average of $E / (1 - F)$ between $\lambda = 200$ and $\lambda = 150$.

$$X(\lambda = 150) = 2 - (25) \left[\left(\frac{0.075+0.0266}{2} \right) (2) - (0.01)(8)(1-2)^2 \right] = 1.46$$

$\lambda = 125$:

$$X(\lambda = 125) = 1.46 - (25) [(0.0266)(1.46) - (0.01)(8)(1 - 1.46)^2] = 0.912$$

$\lambda = 100$:

$$X(\lambda = 100) = 0.912 - (25) \left[\left(\frac{0.0266+0.0221}{2} \right) (0.912) - (0.01)(8)(1 - 0.912)^2 \right]$$

$$= 0.372$$

$\lambda = 70$:

$$X = 0.372 - (30) [(0.0221)(0.372) - (0.01)(8)(1 - 0.372)^2] = 1.071$$

$\lambda = 50$:

$$X = 1.071 - (20) [(0.0226)(1.071) - (0.01)(8)(1 - 1.071)^2] = 0.595$$

$\lambda = 40$:

$$X = 0.595 - (10) [(0.0237)(0.595) - (0.01)(8)(1 - 0.595)^2] = 0.585$$

Note: Oscillations in X are beginning to be damped out.

Running down the values of X along the right-hand side of the preceding equation shows that the oscillations have now damped out. Carrying out the remaining calculations down to the end of the reactor completes Table E17-4.3. The conversion for a condition of maximum mixedness in this reactor is 0.56 or 56%. It is interesting to note that there is little difference in the conversions for the two conditions of complete segregation (61%) and maximum mixedness (56%). With bounds this narrow, one may question the point in using additional models for the reactor to improve the predictability of conversion.

Calculate backward to reactor exit.

TABLE E17-4.3 MAXIMUM MIXEDNESS MODEL

$\lambda \text{ (min)}X$	
200	0.0
175	2.0
150	1.460
125	0.912
100	0.372
70	1.071
50	0.595
40	0.585
30	0.580

20	0.581
10	0.576
5	0.567
0	0.564

Summary	
PFR	76%
Segregation	61%
CSTR	58%
Max. mix	56%

Analysis: For comparison, it is left for the reader to show that the conversion for a PFR of this size would be 0.76, and the conversion in a perfectly mixed CSTR with complete micromixing would be 0.58. As mentioned in this example, you probably will never use this kind of *hand* calculation method to determine the maximum mixedness conversion. It is only presented to help give an intuitive understanding as one integrates the maximum mixedness model backward to the reactor entrance. Instead, an ODE solver such as Polymath is preferred. In Section 17.3, we will show how to solve maximum mixedness problems numerically using Polymath software.

17.3 USING SOFTWARE PACKAGES SUCH AS POLYMATH TO FIND MAXIMUM MIXEDNESS CONVERSION

The first thing we do when using a software package to solve the ODEs to find either the conversion or the exit concentrations in a *nonideal reactor* is to fit the tracer concentration measurements to a polynomial $C(t) = a_0 + a_1t + a_2t^2 + a_3t^3 + a_4t^4$ to obtain $C(t)$ from the data, such as Polymath. A tutorial on how to obtain an analytical expression is given in the *Living Example Problem* in both Chapters 7 and 16 on the CRE Web site, http://www.umich.edu/~elements/6e/07chap/Polynomial_Regression_Tutorial.pdf.

Maximum Mixedness Model Computer Calculations

Because software packages won't integrate backward, we need to change the variable such that the integration proceeds forward as λ decreases from some large value to zero. We do this by forming a new variable, z , which is the difference between the longest time measured in the $E(t)$ curve, \bar{T} , and λ , that is, $(\bar{T} - \lambda)$. In the case of Example 17-4, the longest time at which the tracer concentration was measured was 200 minutes (Table E17-4.1). Therefore, we will set $\bar{T} = 200$.

$$\begin{aligned} z &= \bar{T} - \lambda = 200 - \lambda \\ \lambda &= \bar{T} - z = 200 - z \quad (17-15) \end{aligned}$$

Realizing

$$\frac{dX}{d\lambda} = -\frac{dX}{dz} \quad (17-16)$$

Substituting for λ in Equation (17-14)

$$\boxed{\frac{dX}{d\lambda} = \frac{r_A}{C_{A0}} + \frac{E(\lambda)}{1-F(\lambda)}(X)} \quad (17-14)$$

changing variables and rearranging

$$\boxed{\frac{dX}{dz} = -\frac{r_A}{C_{A0}} - \frac{E(\bar{T}-z)}{1-F(\bar{T}-z)}X} \quad (17-17)$$

One now integrates between the limits $z = 0$ and $z = 200$ to find the exit conversion at $z = 200$, which corresponds to $\lambda = 0$.

Two concerns!!

In fitting $E(t)$ to a polynomial, one very important concern is to make sure that the polynomial does not become negative at large times. Another concern in the maximum mixedness calculations is that the term $(1 - F(\lambda))$ does not go to zero. Setting the maximum value of $F(t)$ at 0.999 rather than 1.0 will eliminate this problem. It can also be circumvented by integrating the polynomial for $E(t)$ to get $F(t)$ and then setting the maximum value of $F(t)$ at 0.999. If $F(t)$ is ever greater than 1.0 when fitting a polynomial, the solution will blow up when integrating Equation (17-17) numerically.

Example 17-5 Using Software to Make Maximum Mixedness Model Calculations

Use an ODE solver to determine the conversion predicted by the **maximum mixedness model** for the $E(t)$ curve given in Example E17-4.

Solution

Because of the shape of the $E(t)$ curve, it is necessary to use two polynomials, a third order and a fourth order, each for a different part of the curve to express the RTD, $E(t)$, as a function of time.

For values of λ less than 70, we use the polynomial

$$E_1(\lambda) = 4.447 \times 10^{-10} \lambda^4 - 1.18 \times 10^{-7} \lambda^3 + 1.353 \times 10^{-5} \lambda^2 - 8.657 \times 10^{-4} \lambda + 0.028 \quad (\text{E17-5.1})$$

For values of λ greater than 70, we use the polynomial

$$E_2(\lambda) = -2.640 \times 10^{-9} \lambda^3 + 1.3618 \times 10^{-6} \lambda^2 - 2.407 \times 10^{-4} \lambda + 0.015 \quad (\text{E17-5.2})$$

The resulting $E(t)$ curve is shown in [Figure E17-5.1](#).

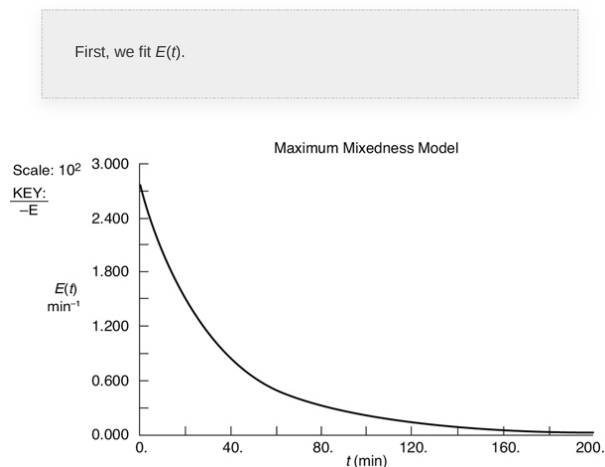


Figure E17-5.1 Polynomial fit of $E(t)$.

To use Polymath to carry out the integration, we change our variable from λ to z using the largest time measurement that was taken from $E(t)$ in [Table E17-4.1](#), which is 200 min:

$$z = 200 - \lambda$$

The equations to be solved are

Maximum Mixedness Model

$$\lambda = 200 - z \quad (\text{E17-5.3})$$

$$\frac{dX}{dz} = -\frac{r_A}{C_{A0}} - \frac{E(200-z)}{1-F(200-z)}X \quad (\text{E17-5.4})$$

$$\frac{dF}{d\lambda} = E(\lambda) \quad (\text{E17-5.5})$$

with $z = 0$ ($\lambda = 200$), $X = 0$, and $F = 1$ [i.e., $F(\lambda) = 0.999$]. **Caution:** Because $[1 - F(\lambda)]^{-1}$ tends to infinity at $F = 1$, ($z = 0$), we set the maximum value of F at 0.999 at $z = 0$.



LEP Sliders

Polynomials used to fit $E(t)$ and $F(t)$

TABLE E17-5.1 POLYMATH PROGRAM FOR MAXIMUM MIXEDNESS MODEL

Differential equations		Calculated values of DEQ variables		
1 d(x)/d(z) = -(ra/Cao+E/(1-F)*x)		Variable	Initial value	Final value
Explicit equations		1 Cao	8.	3.493809
1 Cao = 8		2 Cao	8.	8.
2 k = .01		3 E	0.000225	0.028004
3 lam = 200-z		4 E1	0.1635984	0.028004
4 Ca = Cao*(1-x)		5 E2	0.000225	0.015011
5 E1 = 4.44658e-10*lam^4-1.1802e-7*lam^3+1.35358e-5*lam^2-.000865652*lam+.028004		6 EF	0.075005	0.028004
6 E2 = -2.64e-9*lam^3+1.3618e-6*lam^2-.00024069*lam+.015011		7 F	0.9970002	0
7 F1 = 4.44658e-10/5*lam^5-1.1802e-7/4*lam^4+1.35358e-5/3*lam^3-.000865652/2*lam^2+.028004*lam		8 F1	5.633339	0
8 F2 = -(9.30769e-8*lam^3+5.02846e-5*lam^2-.00941*lam+.618231-1)		9 F2	0.9970002	0.381769
9 ra = -k*ca^2		10 k	0.01	0.01
10 E = if (lam<=70) then (E1) else (E2)		11 lam	200.	0
11 F = if (lam<=70) then (F1) else (F2)		12 ra	-0.64	-0.122067
12 EF = E/(1-F)		13 x	0	0.5632738
		14 z	0	200.

The Polymath equations are shown in [Table E17-5.1](#).
The solution is

$$\text{at } z = 200 \quad X = 0.563$$

The conversion predicted by the maximum mixedness model is 56.3%, $X_{\text{mm}} = 0.56$ while the conversion predicted from complete segregation was $X_{\text{seg}} = 0.61$.

Summary

$$X_{\text{PFR}} = 0.76$$

$$X_{\text{seg}} = 0.61$$

$$X_{\text{CSTR}} = 0.58$$

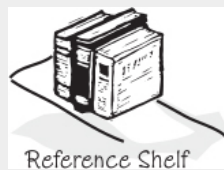
$$X_{\text{mm}} = 0.56$$

Analysis: As expected, the conversion X_{mm} calculated using Polymath or another software package is virtually the same as the hand calculation, but somewhat easier. The most difficult part of the calculation is to fit the E -curve and the F -curve to the polynomials and then to make sure that

$$\int_0^{\infty} E(t) dt = 1$$

for the polynomial parameters chosen.

17.3.1 Comparing Segregation and Maximum Mixedness Predictions



In the previous example, we saw that the conversion predicted by the segregation model, X_{seg} , was greater than that by the maximum mixedness model X_{mm} . Will this always be the case? *No!* To learn the answer is no, we take the second derivative of the rate law as shown in [Table 17-2](#).

Comparing X_{seg} and X_{mm}

TABLE 17-2 CRITERIA FOR HIGHEST CONVERSION X_{SEG} OR X_{MM}

If $\frac{\partial^2(-r_A)}{\partial C_A^2} > 0$	then $X_{\text{seg}} > X_{\text{mm}}$	(17-18)
If $\frac{\partial^2(-r_A)}{\partial C_A^2} < 0$	then $X_{\text{mm}} > X_{\text{seg}}$	(17-19)
If $\frac{\partial^2(-r_A)}{\partial C_A^2} = 0$	then $X_{\text{mm}} = X_{\text{seg}}$	(17-20)

We now apply Table 17-2 to power-law rate laws, for an n th order reaction we have

$$\begin{aligned}
 -r_A &= kC_A^n \\
 \frac{\partial(-r_A)}{\partial C_A} &= nkC_A^{n-1} \\
 \frac{\partial^2(-r_A)}{\partial C_A^2} &= n(n-1)kC_A^{n-2}
 \end{aligned}$$

From the product $[(n)(n-1)]$, we see

TABLE 17-3 COMPARING X_{SEG} OR X_{MM} FOR POWER-LAW MODELS

If $n > 1$,	then $\frac{\partial^2(-r_A)}{\partial C_A^2} > 0$	and $X_{\text{seg}} > X_{\text{mm}}$
If $n < 0$,	then $\frac{\partial^2(-r_A)}{\partial C_A^2} > 0$	and $X_{\text{seg}} > X_{\text{mm}}$
If $0 < n < 1$,	then $\frac{\partial^2(-r_A)}{\partial C_A^2} < 0$	and $X_{\text{mm}} > X_{\text{seg}}$

Important point

We note that in some cases X_{seg} is not too different from X_{mm} . However, when one is considering the destruction of toxic waste where $X > 0.99$ is desired, then even a small difference is significant!!

In this section, we have addressed the case where all we have is the RTD and no other knowledge about the flow pattern exists. Perhaps the flow pattern cannot be assumed because of a lack of information or other possible causes. Perhaps we

wish to know the extent of possible error from assuming an incorrect flow pattern. We have shown how to obtain the conversion, using only the RTD, for two limiting mixing situations: the earliest possible mixing consistent with the RTD, or *maximum mixedness*, and mixing only at the reactor exit, or *complete segregation*. Calculating conversions for these two cases gives bounds on the conversions that might be expected for different flow paths consistent with the observed RTD.

17.4 TANKS-IN-SERIES ONE PARAMETER MODEL, N

In the previous sections, we showed how to calculate conversion in nonideal reactors using no (*zero*) adjustable parameters. We now will show two ways to use one adjustable parameter to model the real reactor: (1) *the T-I-S model*, [Section 17.4](#), (2) *the dispersion model*, [Section 18.2](#). In this section, we show how to use the tanks-in-series (T-I-S) model to describe nonideal reactors and calculate conversion. The one parameter in T-I-S model is n , the number of tanks. We will use the RTD data to determine the number of ideal tanks, n , in series that will give approximately the same RTD as the nonideal reactor. Next, we will apply the reaction engineering algorithm developed in [Chapters 1–5](#) to calculate the conversion.

We are first going to develop the RTD equation for three tanks in series ([Figure 17-6](#)) and then generalize to n reactors in series to derive an equation that gives the number of tanks, n , in series that best fits the RTD data.

17.4.1 Find the Number of T-I-S to Model the Real Reactor

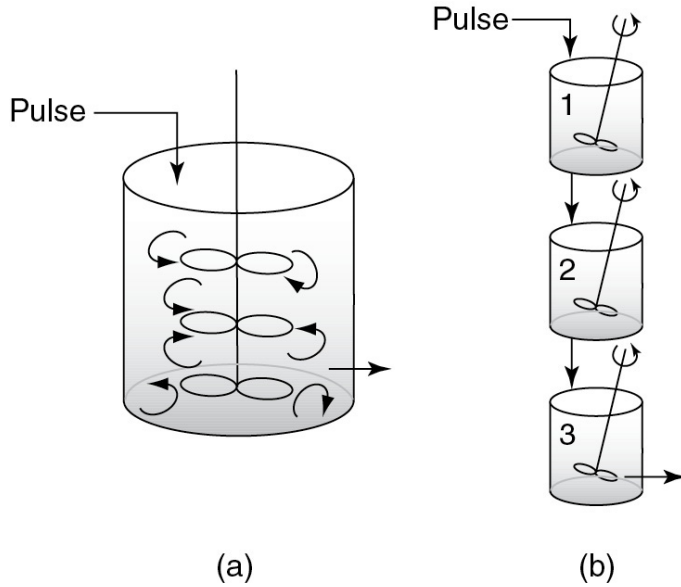


Figure 17-6 Tanks in series: (a) real system; (b) model system.

Figure 17-6 shows a one large CSTR that is modeled as three CSTRs in series. By carrying out sequential mole balances on each reactor in series as shown in the *Additional Material on the Web site for Chapter 17*, the concentration of tracer exiting the third CSTR is

$$C_3 = \frac{C_0 t^2}{2\tau_i^2} e^{-t/\tau_i} \quad (17-21)$$

with

$$\tau_i = \frac{V_i}{v_0} = \frac{V}{v_0} = \frac{\tau}{n} \quad (17-22)$$

where V is the total reactor volume and v_0 is the volumetric flow rate through all three reactors. Extrapolating the exiting conversion from the last of three reactors, Equation (17-21) to n reactors

$$C_n = C_0 \frac{t^{n-1}}{(n-1)\tau_i^{n-1}} e^{-t/\tau_i} \quad (17-23)$$

Substituting for C_n in Equation 16-7, the RTD function is

$$E(t) = \frac{C_n(t)}{\int_0^\infty C_n(t) dt} = \frac{t^{n-1}}{(n-1)!\tau_i^n} e^{-t/\tau_i} \quad (17-24)$$

Using the RTD data to find τ and σ^2 , the number of tanks-in-series, n , necessary to model the real reactor derived on the

Chapter 17 CRE Web site

(http://www.umich.edu/~elements/6e/17chap/Fogler_Ch17_Web_17.4_Tanks-in-Series.pdf) and is shown in Equation (17-25)

Number of T-I-S to match RTD

$$n = \frac{\tau^2}{\sigma^2} \quad (17-24)$$

with τ and σ given by

$$\begin{aligned} \tau &= \int_0^\infty tE(t)dt \\ \sigma^2 &= \int_0^\infty (t - \tau)^2 E(t)dt \end{aligned}$$

17.4.2 Calculating Conversion for the T-I-S Model

If the reaction is first order, we can use Equation (5-15) to calculate the conversion

$$X = 1 - \frac{1}{(1 + \tau_i k)^n} \quad (5-15)$$

It is acceptable (and usual) for the value of n calculated from Equation (18-11) to be a noninteger in Equation (5-15) to calculate the conversion. For reactions other than first order, an integer number of reactors must be used and sequential mole balances on each reactor must be carried out. If, for example, $n = 2.53$, then one could calculate the conversion for two tanks and also for three tanks to bound the conversion. The conversion and effluent concentrations would be solved sequentially using the algorithm developed in Chapter 5; that is, after solving for the effluent from the first tank, it would be used as the input to the second tank, and so on, as shown on the CRE Web site for Chapter 17 Additional Materials.

17.4.3 Tanks-in-Series versus Segregation for a First-Order Reaction

We have already stated that the segregation and maximum mixedness models are equivalent for a first-order reaction. The proof of this statement was left as an exercise in Problem P17-3C. We can extend this equivalency for a first-order reaction to the tanks-in-series (T-I-S) model

$$X_{\text{T-I-S}} = X_{\text{seg}} = X_{\text{mm}} \quad (\text{E17-26})$$

For a first-order reaction, the predicted conversions are the same.

The proof of Equation (17-26) is given in the *Additional Materials* on the CRE Web site for [Chapter 17](#).

17.5 RTD AND MULTIPLE REACTIONS

As discussed in [Chapter 8](#), when multiple reactions occur in reacting systems, it is best to work in concentrations, moles, or molar flow rates rather than conversion.

17.5.1 Segregation Model

In the **segregation model**, we consider each of the globules in the reactor to have different concentrations of reactants, C_A , and of products, C_P . These globules are mixed together immediately upon exiting to yield the exit concentration of A, \overline{C}_A , which is the average of all the globules exiting

$$\overline{C}_A = \int_0^\infty C_A(t)E(t)dt \quad (17-27)$$

$$\overline{C}_B = \int_0^\infty C_B(t)E(t)dt \quad (17-28)$$

The concentrations of the individual species, $C_A(t)$ and $C_B(t)$, in the different globules are determined from batch reactor calculations. For a constant-volume batch reactor, where q reactions are taking place, the coupled mole balance equations are

$$\frac{dC_A}{dt} = r_A = \sum_{i=1}^{i=q} r_{iA} \quad (17-29)$$

$$\frac{dC_B}{dt} = r_B = \sum_{i=1}^{i=q} r_{iB} \quad (17-30)$$

Solving for the exit concentrations using the segregation model for multiple reactions

These equations are solved simultaneously with to give the exit concentration. The RTDs, $E(t)$, in Equations (17-31) and (17-32) are determined from experimental measurements and then fit to a polynomial.

$$\frac{d\overline{C}_A}{dt} = C_A(t)E(t) \quad (17-31)$$

$$\frac{d\bar{C}_B}{dt} = C_B(t)E(t) \quad (17-32)$$

17.5.2 Maximum Mixedness

For the **maximum mixedness model**, we write Equation (17-12) for each species and replace r_A by the net rate of formation

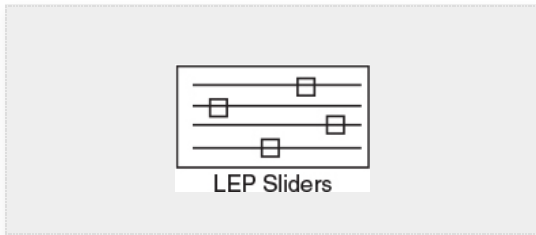
$$\frac{dC_A}{d\lambda} = -\sum r_{iA} + \left(C_A - C_{A0}\right) \frac{E(\lambda)}{1-F(\lambda)} \quad (17-33)$$

$$\frac{dC_B}{d\lambda} = -\sum r_{iB} + \left(C_B - C_{B0}\right) \frac{E(\lambda)}{1-F(\lambda)} \quad (17-34)$$

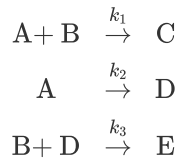
After substitution for the rate laws for each reaction (e.g., $r_{1A} = k_1 C_A$), these equations are solved numerically by starting at a very large value of λ say $\bar{T} = 200$, and integrating backward to $\lambda = 0$ to yield the exit concentrations C_A , C_B ,

We will now show how different RTDs with the *same* mean residence time can produce different product distributions for multiple reactions.

Example 17-6 RTD and Complex Reactions



Consider the following set of liquid-phase reactions



which are occurring in two different reactors with the same mean residence time, $t_m = 1.26$ minutes. However, the RTD is very different for each of the reactors, as can be seen in Figures E17-6.1 and E17-6.2.

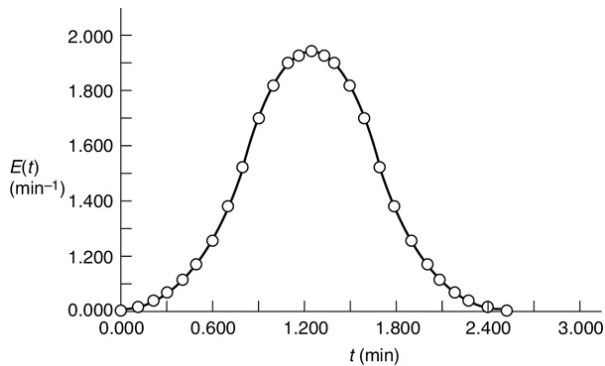


Figure E17-6.1 $E_1(t)$: asymmetric distribution.

Two different reactors with different RTDs, but the same mean residence time t_m

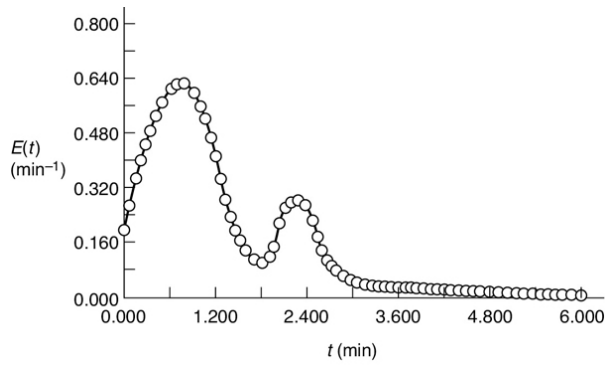


Figure E17-6.2 $E_2(t)$: bimodal distribution.

1. Fit polynomials to the RTDs for each reactor.
2. Determine the product distribution and selectivities (e.g., $\hat{S}_{C/D}$, $\hat{S}_{D/E}$) for
 1. The segregation model.
 2. The maximum mixedness model.

Before carrying out any calculations, what do you think the exit concentrations and conversion will be for these two very different RTDs with the same mean residence time?

Additional information:

$k_1 = k_2 = k_3 = 1$ in appropriate units at 350 K.

Solution

Segregation Model

Combining the mole balance and rate laws for a constant-volume batch reactor (i.e., globules), we have

$$\frac{dC_A}{dt} = r_A = r_{1A} + r_{2A} = -k_1 C_A C_B - k_2 C_A \quad (\text{E17-6.1})$$

$$\frac{dC_B}{dt} = r_B = r_{1B} + r_{3B} = -k_1 C_A C_B - k_3 C_B C_D \quad (\text{E17-6.2})$$

$$\frac{dC_C}{dt} = r_C = r_{1C} = k_1 C_A C_B \quad (\text{E17-6.3})$$

$$\frac{dC_D}{dt} = r_D = r_{2D} + r_{3D} = k_2 C_A - k_3 C_B C_D \quad (\text{E17-6.4})$$

$$\frac{dC_E}{dt} = r_E = r_{3E} = k_3 C_B C_D \quad (\text{E17-6.5})$$

and the concentration for each species exiting the reactor is found by integrating the equation

$$\frac{d\bar{C}_i}{dt} = C_i E(t) \quad (\text{E17-6.6})$$

over the life of the $E(t)$ curve. The *life* of the $E(t)$ curve is from $t = 0$ to the time at the last data point. For this example, the life of the $E_1(t)$ is 2.52 minutes ([Figure E17-6.1](#)), and the life of $E_2(t)$ is 6 minutes ([Figure E17-6.2](#)).

The initial conditions are $t = 0$, $C_A = C_B = 1$, and $C_C = C_D = C_E = 0$.

The Polymath program used to solve these equations is shown in [Table E17-6.1](#) for the asymmetric RTD, $E(t)$.

With the *exception* of the polynomial for $E(t)$, the Polymath programs for the bimodal RTD and asymmetric are identical for the segregation model. The Polymath program for the segregation model for the asymmetric distribution is shown in [Table E17-6.1](#) and the program for the maximum mixedness model for the bimodal distribution is shown in [Table E17-6.3](#). A comparison of the exit concentrations and selectivities of the two RTD curves is shown in [Table E17-6.2](#).

TABLE E17-6.1 POLYMATH PROGRAM FOR
SEGREGATION MODEL WITH ASYMMETRIC RTD
(MULTIPLE REACTIONS)

ODE Report (RK45)**Differential equations as entered by the user**

- ```
[1] d(ca)/d(t) = ra
[2] d(cb)/d(t) = rb
[3] d(cc)/d(t) = rc
[4] d(cabar)/d(t) = ca*E
[5] d(cbbbar)/d(t) = cb*E
[6] d(ccbar)/d(t) = cc*E
[7] d(cd)/d(t) = rd
[8] d(ce)/d(t) = re
[9] d(cdbar)/d(t) = cd*E
[10] d(cebar)/d(t) = ce*E
```

**Explicit equations as entered by the user**

- ```
[1] k1 = 1
[2] k2 = 1
[3] k3 = 1
[4] E1 = -2.104*t^4+4.167*t^3-1.596*t^2+0.353*t-0.004
[5] E2 = -2.104*t^4+17.037*t^3-50.247*t^2+62.964*t-27.402
[6] rc = k1*ca*cb
[7] re = k3*cb*cd
[8] ra = -k1*ca*cb-k2*ca
[9] rb = -k1*ca*cb-k3*cb*cd
[10] E = if(t<=1.26)then(E1)else(E2)
[11] rd = k2*ca-k3*cb*cd
```

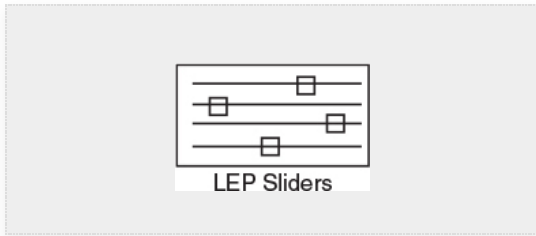


TABLE E17-6.2 SEGREGATION MODEL RESULTS

<i>Asymmetric Distribution</i>		<i>Bimodal Distribution</i>	
The solution for $E_1(t)$ is:		The solution for $E_2(t)$ is:	
$\bar{C}_A = 0.151$	$\bar{C}_E = 0.178$	$\bar{C}_A = 0.245$	$\bar{C}_E = 0.162$
$\bar{C}_B = 0.454$	$\bar{X} = 83.7\%$	$\bar{C}_B = 0.510$	$\bar{X} = 74.8\%$
$\bar{C}_C = 0.357$	$S_{C/D} = 1.18$	$\bar{C}_C = 0.321$	$\tilde{S}_{C/D} = 1.21$
$\bar{C}_D = 0.303$	$S_{D/E} = 1.70$	$\bar{C}_D = 0.265$	$\tilde{S}_{D/E} = 1.63$

Analysis: We note that while the conversion and the exit concentration of species A are significantly different for the two distributions, the selectivities are not. In Problem P17-6B (b), you are asked to calculate the mean residence time for each distribution to try to explain these differences.

Maximum Mixedness Model

The equations for each species are

$$\frac{dC_A}{d\lambda} = k_1 C_A C_B + k_2 C_A + (C_A - C_{A0}) \frac{E(\lambda)}{1-F(\lambda)} \quad (\text{E17-6.7})$$

$$\frac{dC_B}{d\lambda} = k_1 C_A C_B + k_3 C_B C_D + (C_B - C_{B0}) \frac{E(\lambda)}{1-F(\lambda)} \quad (\text{E17-6.8})$$

$$\frac{dC_C}{d\lambda} = k_1 C_A C_B + (C_C - C_{C0}) \frac{E(\lambda)}{1-F(\lambda)} \quad (\text{E17-6.9})$$

$$\frac{dC_D}{d\lambda} = k_2 C_A + k_3 C_B C_D + (C_D - C_{D0}) \frac{E(\lambda)}{1-F(\lambda)} \quad (\text{E17-6.10})$$

$$\frac{dC_E}{d\lambda} = k_3 C_B C_D + (C_E - C_{E0}) \frac{E(\lambda)}{1-F(\lambda)} \quad (\text{E17-6.11})$$

The Polymath program for the bimodal distribution, $E(t)$, is shown in [Table E17-6.3](#). The Polymath program for the asymmetric distribution is identical, with the exception of the polynomial fit for $E_1(t)$ and is given in the [Chapter 17 Living Example Problems](#), [Web 17-1e](#) and [Web 17-1h](#), on the CRE Web site. A comparison of the exit concentration and selectivities of the two RTD distributions is shown in [Table E17-6.4](#).

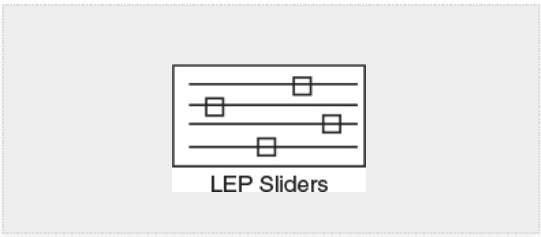


TABLE E17-6.3 POLYMATH PROGRAM FOR MAXIMUM MIXEDNESS MODEL WITH BIMODAL DISTRIBUTION (MULTIPLE REACTIONS)

<p><u>ODE Report (RK45)</u></p> <p>Differential equations as entered by the user</p> <p>[1] $d(ca)/d(z) = -(-ra+(ca-cao)*EF)$</p> <p>[2] $d(cb)/d(z) = -(-rb+(cb-cbo)*EF)$</p> <p>[3] $d(cc)/d(z) = -(-rc+(cc-cco)*EF)$</p> <p>[4] $d(F)/d(z) = -E$</p>

$$[5] \frac{d(cd)}{d(z)} = -(-rd + (cd - cdo) * EF)$$

$$[6] \frac{d(ce)}{d(z)} = -(-re + (ce - ceo) * EF)$$

Explicit equations as entered by the user

$$[1] cbo = 1$$

$$[2] cao = 1$$

$$[3] cco = 0$$

$$[4] cdo = 0$$

$$[5] ceo = 0$$

$$[6] lam = 6 - z$$

$$[7] k2 = 1$$

$$[8] k1 = 1$$

$$[9] k3 = 1$$

$$[10] rc = k1 * ca * cb$$

$$[11] re = k3 * cb * cd$$

$$[12] E1 = 0.47219 * lam^4 - 1.30733 * lam^3 + 0.31723 * lam^2 + 0.85688 * lam + 0.20909$$

$$[13] E2 = 3.83999 * lam^6 - 58.16185 * lam^5 + 366.2097 * lam^4 - 1224.66963 * lam^3 + 2289.84857 * lam^2 - 2265.62125 * lam + 925.46463$$

$$[14] E3 = 0.00410 * lam^4 - 0.07593 * lam^3 + 0.52276 * lam^2 - 1.59457 * lam + 1.84445$$

```

[15] rb = -k1*ca*cb-k3*cb*cd

[16] ra = -k1*ca*cb-k2*ca

[17] rd = k2*ca-k3*cb*cd

[18] E =
if(lam<=1.82)then(E1)else(if(lam<=2.8)then(E2)else(E3))

[19] EF = E/(1-F)

```

TABLE E17-6.4 MAXIMUM MIXEDNESS MODEL
RESULTS

<i>Asymmetric Distribution</i>		<i>Bimodal Distribution</i>	
The solution for $E_1(t)$ (1) is:		The solution for $E_2(t)$ (2) is:	
$C_A = 0.161$	$C_E = 0.192$	$C_A = 0.266$	$C_E = 0.190$
$C_B = 0.467$	$\bar{X} = 83.9\%$	$C_B = 0.535$	$\bar{X} = 73.4\%$
$C_C = 0.341$	$\tilde{S}_{C/D} = 1.11$	$C_C = 0.275$	$S_{C/D} = 1.02$
$C_D = 0.306$	$\tilde{S}_{D/E} = 1.59$	$C_D = 0.269$	$S_{D/E} = 1.41$

Analysis: In this example, we have applied the segregation model and the maximum mixedness models to complex reactions. While the concentrations of species A exiting the reactors for the two distributions are different, the selectivities are not so different for the same mean residence time.

Calculations similar to those in [Example 17-6](#) are given in an example on the CRE Web site for the series reaction



Living Example CD17-RTD (**LEP**), parts (a) through (h), explores the earlier series reaction and also multiple reactors with different residence time distributions (e.g., asymmetric, bimodal).

17.6 AND NOW... A WORD FROM OUR SPONSOR—SAFETY 17 (AWFOS—S17 BRIEF CASE HISTORY ON AN AIR PREHEATER)

Crude oil furnace APH fouling: In crude heaters, air preheaters (APHs) are installed to preheat the ambient air using hot flue gas exiting from the furnace. The preheater, shown schematically in Figure 17-7, reduces the heat input required to heat the air and thus increasing heater efficiency. In a turnaround of a crude distillation unit plant, the existing APH was replaced with a new design having a narrow passage on the flue gas side. The purpose of replacing the old design was to increase the heat-transfer surface area so as to increase heat recovery from flue gas and thus heater efficiency. However, after the plant was started-up, heavy and frequent fouling (e.g., depositing of material) was observed in the APH, requiring cleaning once in 2 weeks. The APH was shut down for 3–4 days for cleaning and during this period heaters were aggressively operated at high fuel rates (to maintain same plant rate). This increase in rates caused an increase in tube metal temperatures and increasing risk of tube failures. Further, hot flue gas was released to atmosphere and causing the heater to operate at a lower efficiency. Overall, it was estimated that the heater reliability had decreased and the financial loss from the APH outage outweighed the benefit of increased heat recovery when APH was in service. Management concluded that the narrow passage is leading to fouling and thus design is flawed. It was therefore, proposed to revert to the older design.

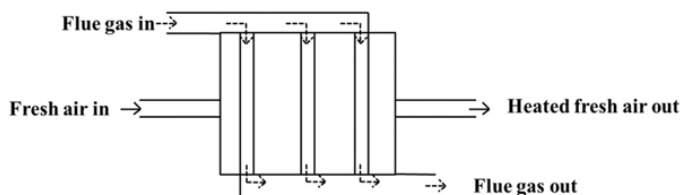


Figure 17-7 Air preheater.

Apply R.W. Paul's six types of critical thinking questions to this situation to help management decide whether or not to revert to the older design APH.

Solution

1. Questions about the question or problem statement

Manan: Why do you think the APH design is flawed considering design would have been reviewed at various levels

before installation?

2. Questions for clarification:

Manan: Are there any other case studies where this new design APH has been installed and performed as per expectations?

3. Questions that probe assumptions

Manan: How did you assume that heater conditions remained the same and there was no change in flue gas quality or temperature?

4. Questions that probe reasons and evidences

Manan: Did the laboratory analysis of foulant show there was no increase in carbon particles or corrosion products (which are known foulant) in flue gas post new APH installation?

5. Questions that probe viewpoints and perspectives

Manan: What is the counterargument that reverting back to the older design will not work?

6. Questions that probe implications and consequences?

Manan: What are the consequences of taking APH offline on environment as hot flue gas is released to atmosphere?

What are the implications on the operator's behavior/mind-set who now has the additional task of frequently cleaning the APH?

Thanks to Manan Agrawal, Indian Institute of Technology, Bombay, and to Mayur Tikmani, Indian Institute of Technology, Guwahati.

Closure. In this chapter, we showed how the reader can use the RTD data along with reaction-rate law and rate-law parameters to predict the conversion and exit concentrations. We first choose the segregation and the maximum mixedness models, which do not use any adjustable parameters to predict conversion for single reactions and exit concentrations for multiple reactions. The reader can use the $E(t)$ determined from experimental data or use the $E(t)$ function for ideal CSTRs, PFRs, LFRs, or combinations thereof, along with the rate law to predict the conversion. The reader will be able to use software packages to fit experimental RTD to polynomials and use the polynomials to represent $E(t)$ and to predict conversion. By analyzing the second derivative of the reaction rate with respect to concentration, the reader will be able to

determine whether the segregation model or maximum mixedness model will give the greater conversion.

SUMMARY

1. The RTD functions for an ideal reactor are

PFR:

$$E(t) = \delta(t - \tau) \quad (\text{S17-1})$$

CSTR:

$$E(t) = \frac{e^{-t/\tau}}{\tau} \quad (\text{S17-2})$$

LFR:

$$E(t) = 0 \quad t < \frac{\tau}{2} \quad (\text{S17-3})$$

$$E(t) = \frac{\tau^2}{2t^3} \quad t \geq \frac{\tau}{2} \quad (\text{S17-4})$$

2. The dimensionless residence time is

$$\Theta = \frac{t}{\tau} \quad (\text{S17-5})$$

and is equal to the number space times. Then

$$E(\Theta) = \tau E(t) \quad (\text{S17-6})$$

3. The internal-age distribution, $[I(\alpha) d\alpha]$, gives the fraction of material inside the reactor that has been inside between a time α and a time $(\alpha + d\alpha)$.

4. Segregation model: The conversion is

$$\bar{X} = \int_0^\infty X(t) E(t) dt \quad (\text{S17-7})$$

and for multiple reactions

$$\bar{C}_A = \int_0^\infty C_A(t) E(t) dt$$

5. Maximum mixedness: Conversion can be calculated by solving the following equations

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{A0}} + \frac{E(\lambda)}{1-F(\lambda)} (X) \quad (\text{S17-8})$$

6. Tanks-in-series model: Use RTD data to estimate the number of tanks in series,

$$n = \frac{\tau^2}{\sigma^2} \quad (\text{S17-9})$$

For a first-order reaction

$$X = 1 - \frac{1}{(1 + \tau_1 k)^n}$$

7. The exit concentration predicted for multiple reactions using the maximum mixedness model can be found by solving the equation

$$\frac{dC_A}{d\lambda} = -r_{A_{\text{net}}} + (C_A - C_{A0}) \frac{E(\lambda)}{1-F(\lambda)} \quad (\text{S17-10})$$

$$\frac{dC_B}{d\lambda} = -r_{B_{\text{net}}} + (C_B - C_{B0}) \frac{E(\lambda)}{1-F(\lambda)} \quad (\text{S17-11})$$

from $\lambda = \lambda_{\text{max}}$ to $\lambda = 0$. To use an ODE solver, let $z = \lambda_{\text{max}} - \lambda$.

CRE WEB SITE MATERIALS

(<http://www.umich.edu/~elements/6e/17chap/obj.html#/>)

Useful Links



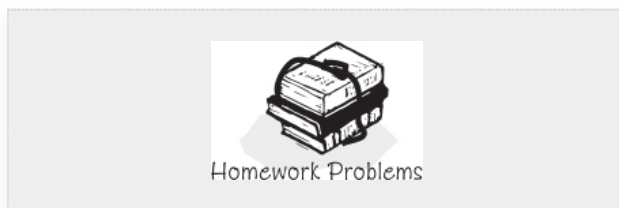
Evaluation



QUESTIONS, SIMULATIONS, AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$\mathbf{A} = \bullet \quad \mathbf{B} = \blacksquare \quad \mathbf{C} = \blacklozenge \quad \mathbf{D} = \blacklozenge\blacklozenge$$



Questions

Q17-1_A QBR (*Question Before Reading*). How does the conversion predicted from the segregation model, X_{seg} , compare with the conversion predicted by the CSTR, PFR, and LFR models for the same mean residence time, t_m ?

Q17-2_A Read over the problems of this chapter. Make up an original problem that uses the concepts presented in this chapter. The guidelines are given in Problem P5-1_B. RTDs from real reactors can be found in *Ind. Eng. Chem.*, 49, 1000 (1957); *Ind. Eng. Chem. Process Des.*

Dev., 3, 381 (1964); *Can. J. Chem. Eng.*, 37, 107 (1959); *Ind. Eng. Chem.*, 44, 218 (1952); *Chem. Eng. Sci.*, 3, 26 (1954); and *Ind. Eng. Chem.*, 53, 381 (1961).

Q17-3 Go to the LearnChemE screencast link for [Chapter 17](http://www.learncheme.com/screencasts/kinetics-reactor-design) (<http://www.learncheme.com/screencasts/kinetics-reactor-design>). View one of the screencast 5- to 6-minute video tutorials and list two of the most important points.

Q17-4 AWFOS–S17. Pick two critical thinking questions and describe why they are the most important questions to ask.

Computer Simulations and Experiments

P17-1_B

1. **Example 17-2: Mean Conversion, X_{seg} , Calculations in a Real Reactor**

Wolfram and Python

- How do C_{A0} , n and k affect the trajectories in X for the segregation model and the LFR?
- Write a set of conclusions based on your experiments in (i).

Polymath

- How does the conversion predicted from the segregation model, X_{seg} , compare with the conversion predicted by the CSTR, PFR, and LFR models for the same mean residence time, t_m ?

2. **Example 17-3: Mean Conversion for Second-Order Reaction in a Laminar-Flow Reactor** *Wolfram and Python*

- For what value of k are X and \bar{X} the farthest apart? Closest together?
- Vary n and describe what you find with regard to X_{seg} .
- Explain how the E -curve varies with n , C_{A0} , and k .
- Vary n , τ , C_{A0} , and k and describe what you find.
- Write a set of conclusions for your experiments (i) through (iv).

Polymath

- (1) Vary k by a factor of 5–10 or so above and below the nominal value given in the problem statement of $4.93 \times 10^{-3} \text{ dm}^3/\text{mol}\cdot\text{s}$. When do X_{PFR} and X_{LFR} come close together and when do they become farther apart? (2) Use the $E(t)$ and $F(t)$ in [Examples 16-1](#) and [16-2](#) to predict conversion, and compare in parts (a), (b), and (c).

3. **Example 17-4: Conversion Bounds for a Nonideal Reactor** *Wolfram and Python*

- For what value of k are X and \bar{X} the farthest apart? Closest together?
- Vary n and describe what you find with regard to X_{seg} .
- Explain how the E -curve varies with n , C_{A0} , and k .
- Vary n , τ , C_{A0} , and k and describe what you find.
- Write a set of conclusions for your experiments (i) through (iv).

Polymath

1. (1) Vary the parameter kC_{A0} , whose nominal value is

$$kC_{A0} = \left(\frac{0.01 \text{ dm}^3}{\text{mol} \cdot \text{s}} \right) \left(\frac{8 \text{ mol}}{\text{dm}^3} \right) = 0.08/\text{s}$$

by a factor of 10 above and below the value nominal of 0.08 s^{-1} and describe when X_{seg} and X_{mm} come closer together and when they become farther apart. (2) How do X_{mm} and X_{seg} compare with X_{PFR} , X_{CSTR} , and X_{LFR} for the same mean residence time? (3) How would your results change if $T = 350 \text{ K}$ with $E = 10 \text{ kcal/mol}$? How would your answer change if the reaction was pseudo first order with $kC_{A0} = 4 \times 10^{-3}/\text{s}$?

4. Example 17-5: Using Software to Make Maximum Mixedness Model Calculations

Wolfram and Python

1. Individually vary k , C_{A0} and n and describe how the profile X as a function of Z changes.
2. Individually vary k , C_{A0} and n and describe how the rate $-r_A$ changes as you vary k , C_{A0} and n .
3. Write a set of conclusions.

Polymath

1. (1) Vary the parameters kC_{A0} , above and below the nominal value 0.08 s^{-1} , by a factor of 10 and describe when X_{mm} and X_{seg} come closer together and when they become farther apart. (2) How do X_{mm} and X_{seg} compare with X_{PFR} , X_{CSTR} , and X_{LFR} for the same t_m ? (3) How would your results change if the reaction was pseudo first order with $k_1 = C_{A0}k = 0.08 \text{ min}^{-1}$? (4) If the reaction was third order with $kC_{A0}^2 = 0.08 \text{ min}^{-1}$? (5) If the reaction was half order with $kC_{A0}^{1/2} = 0.08 \text{ min}^{-1}$? Describe any trends.

5. Example 17-6a: RTD and Complex Reaction for an Asymmetric

RTD (shown on the CRE Web site at

<http://www.umich.edu/~elements/6e/17chap/live.html>)

Wolfram and Python

1. Vary k_1 , k_2 , and k_3 and describe how the conversion changes.
2. Vary k_1 , k_2 , and k_3 and describe how the concentration and selectivity change.
3. Vary k_1 , k_2 , and k_3 and describe how the rate changes.
4. Write a set of conclusions.

Polymath

1. Download the *Living Example Problem* from the CRE Web site. (1) If the activation energies in cal/mol are $E_1 = 5000$, $E_2 = 1000$, and $E_3 = 9000$, how would the selectivities and conversion of A change as the temperature was raised or lowered around 350 K ? (2) If you were asked to compare the results from **Example 17-6** for the asymmetric and bimodal distributions in Tables E17-6.2 and E17-6.4, what similarities and differences do you observe? What generalizations can you make?

6. Example 17-6b: RTD and Complex Reaction with a Bimodal RTD

(shown on the CRE Web site at

<http://www.umich.edu/~elements/6e/17chap/live.html>)

Wolfram and Python

1. Vary k_1 , k_2 , and k_3 and describe how the conversion changes.
2. Vary k_1 , k_2 , and k_3 and describe how the concentration and selectivity change.
3. Vary k_1 , k_2 , and k_3 and describe how the rate changes.
4. Write a set of conclusions.

Problems

P17-2_B OEQ (Old Exam Question). An irreversible first-order reaction takes place in a long cylindrical reactor. There is no change in volume, temperature, or viscosity. The use of the simplifying assumption that there is plug flow in the tube leads to an estimated degree of conversion of 86.5%. What would be the actually attained degree of conversion if the real state of flow is laminar, with negligible diffusion?

P17-3_C Show that for a first-order reaction



the exit concentration maximum mixedness equation

$$\frac{dC_A}{d\lambda} = kC_A + \frac{E(\lambda)}{1-F(\lambda)}(C_A - C_{A0}) \quad (\text{P17-3.1})$$

is the same as the exit concentration given by the segregation model

$$C_A = C_{A0} \int_0^\infty E(t) e^{-kt} dt \quad (\text{P17-3.2})$$

Hint: Verify

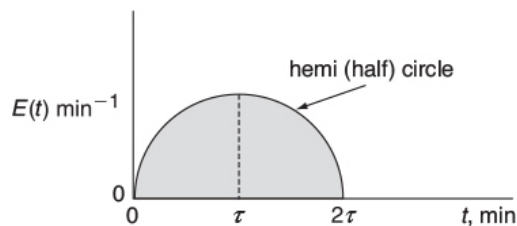
$$C_A(\lambda) = \frac{C_{A0} e^{k\lambda}}{1-F(\lambda)} \int_\lambda^\infty E(t) e^{-kt} dt \quad (\text{P17-3.3})$$

is a solution to Equation (P17-3.1).

P17-4_C OEQ (Old Exam Question). The first-order reaction



with $k = 0.8 \text{ min}^{-1}$ is carried out in a real reactor with the following RTD function:



Mathematically, this hemi circle is described by the equations for $2\tau \geq t \geq 0$ then

$$E(t) = \sqrt{\tau^2 - (t - \tau)^2} \text{ min}^{-1} \text{ (hemi circle)}$$

For $t > 2\tau$, then $E(t) = 0$.

1. What is the mean residence time?
2. What is the variance?
3. What is the conversion predicted by the segregation model?
4. What is the conversion predicted by the maximum mixedness model?
(Ans: $X_{mm} = 0.447$)

5. What is the conversion predicted by the tanks-in-series model?

P17-5B OEQ (Old Exam Question). A step tracer input was used on a real reactor with the following results:

For $t \leq 10$ min, then $C_T = 0$.

For $10 \leq t \leq 30$ min, then $C_T = 10 \text{ g/dm}^3$.

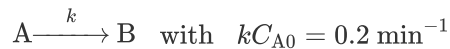
For $t \geq 30$ min, then $C_T = 40 \text{ g/dm}^3$.

The second-order reaction $A \rightarrow B$ with $k = 0.1 \text{ dm}^3/\text{mol} \cdot \text{min}$ is to be carried out in the real reactor with an entering concentration of A of 1.25 mol/dm^3 at a volumetric flow rate of $10 \text{ dm}^3/\text{min}$. Here, k is given at 325 K.

1. What is the mean residence time t_m ?
2. What is the variance σ^2 ?
3. What conversions do you expect from an ideal PFR and an ideal CSTR in a real reactor with t_m ?
4. What is the conversion predicted by
 1. The segregation model?
 2. The maximum mixedness model?
 3. The T-I-S model?
5. What conversion is predicted by an ideal laminar flow reactor?
6. Assume now that the reaction is first order with $k = 0.4 \text{ min}^{-1}$ and calculate the conversion using the tanks-in-series model.

P17-6B OEQ (Old Exam Question). The following $E(t)$ curves were obtained from a tracer test on two tubular reactors in which dispersion is believed to occur.

A second-order reaction



is to be carried out in this reactor. There is no dispersion occurring either upstream or downstream of the reactor, but there is dispersion inside the reactor.

1. What is the final time t_1 (in minutes) for the reactor shown in Figure P17-6B (a)? In Figure P17-6B (b)?

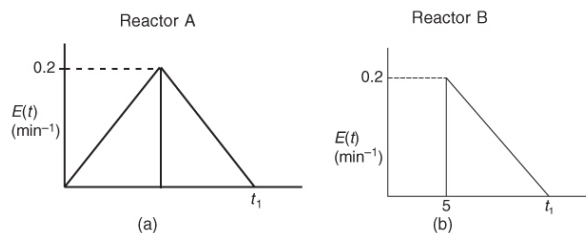
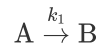


Figure P17-6 B (a) RTD reactor A; (b) RTD reactor B.

- What is the mean residence time, t_m , and variance, σ^2 , for the reactor shown in **Figure P17-6B** (a)? In **Figure P17-6B** (b)?
- What is the fraction of the fluid that spends 7 minutes or longer in **Figure P17-6B** (a)? In **Figure P17-6B** (b)?
- Find the conversion predicted by the segregation model for reactor A.
- Find the conversion predicted by the maximum mixedness model for reactor A.
- Find the conversion predicted by the T-I-S model for reactor A.
- Repeat (d)–(f) for reactor B.
- Now assume the reaction is first order with $k_1 = 0.2 \text{ min}^{-1}$, what are the conversions predicted by the tanks-in-series, the segregation in the maximum mixedness model?

P17-7B The RTD for a nonideal reactor is shown in **Figure P17-6B**. What is the conversion predicted by the tanks-in-series model for a first-order reaction?



- with $k_1 = 0.4 \text{ min}^{-1}$?
- with $k_1 = 0.04 \text{ min}^{-1}$?
- with $k_1 = 4 \text{ min}^{-1}$?

P17-8B The following $E(t)$ curve was obtained from a tracer test on a reactor.

$$\begin{aligned} E(t) &= 0.25t & 0 < t < 2 \text{ min} \\ &= 1 - 0.25t & 2 < t < 4 \text{ min} \\ &= 0 & t < 4 \text{ min} \end{aligned}$$

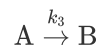
The conversion predicted by the tanks-in-series model for the isothermal elementary reaction



was 50% at 300 K.

If the temperature is to be raised 10°C ($E = 25000 \text{ cal/mol}$) and the reaction carried out isothermally, what will be the conversion predicted by the segregation, maximum mixedness models, and the T-I-S models?

P17-9B OEQ (Old Exam Question). The third-order liquid-phase reaction with an entering concentration of 2M



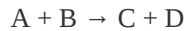
was carried out in a reactor that has the following RTD:

$$\begin{aligned}
 E(t) &= 0 & \text{for } t < 1 \text{ min} \\
 E(t) &= 1.0 \text{ min}^{-1} & \text{for } 1 \leq t \leq 2 \text{ min} \\
 E(t) &= 0 & \text{for } t > 2 \text{ min}
 \end{aligned}$$

- For isothermal operation, what is the conversion predicted by
 - A CSTR, a PFR, an LFR, T-I-S, X_{T-I-S} , and maximum mixedness, X_{mm} , the segregation model, X_{seg} ?
Hint: Find t_m (i.e., τ) from the data and then use it with $E(t)$ for each of the ideal reactors.
 - The maximum mixedness model, X_{mm} ? Plot X versus z (or λ) and explain why the curve looks the way it does.
- Now calculate the exit concentrations of A, B, and C for the reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \text{ with } k_1 = 0.3 \text{ min}^{-1} \text{ and } k_2 = 1 \text{ min}^{-1}$$
 using (1) the segregation model and (2) the maximum mixedness model.

P17-10A Consider again the nonideal reactor characterized by the RTD data in Example 17-5, where $E(t)$ and $F(t)$ are given as polynomials. The irreversible gas-phase nonelementary reaction



is first order in A and second order in B, and is to be carried out isothermally. Calculate the conversion for:

- A PFR, a laminar-flow reactor with complete segregation, and a CSTR all at the same t_m .
- The cases of T-I-S, complete segregation, and maximum mixedness.

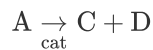
Additional information (obtained at the Jofostan Central Research Laboratory in Riça, Jofostan):

$$\begin{aligned}
 C_{A0} &= C_{B0} = 0.0313 \text{ mol / dm}^3, \quad V = 1000 \text{ dm}^3, \\
 v_0 &= 10 \text{ dm}^3/\text{s}, \quad k = 175 \text{ dm}^6/\text{mol}^2 \cdot \text{s at } 320 \text{ K.}
 \end{aligned}$$

P17-11A Consider an ideal PFR, CSTR, and LFR.

- Evaluate the first moment about the mean $m_1 = \int_0^\infty (t - \tau) E(t) dt$ for a PFR, a CSTR, and an LFR.
- Calculate the conversion in each of these ideal reactors for a second-order liquid-phase reaction with $Da = 1.0$ ($\tau = 2 \text{ min}$ and $kC_{A0} = 0.5 \text{ min}^{-1}$).
- Calculate the conversion predicted by the T-I-S, segregation, and maximum mixedness models.

P17-12B For the catalytic reaction



the rate law can be written as

$$-r'_A = \frac{kC_A}{(1 + K_A C_A)^2}$$

Which will predict the highest conversion, the maximum mixedness model or the segregation model?

Hint: Specify the different ranges of the conversion where one model will dominate over the other.

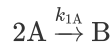
P7-13_B Use the RTD data in Examples 16-1 and 16-2 to predict X_{PFR} , X_{CSTR} , X_{LFR} , $X_{\text{T-I-S}}$, X_{seg} and X_{mm} for the following elementary gas-phase reactions

1. $A \rightarrow B$ $k = 0.1 \text{ min}^{-1}$
2. $A \rightarrow 2B$ $k = 0.1 \text{ min}^{-1}$
3. $2A \rightarrow B$ $k = 0.1 \text{ min}^{-1} \text{ m}^3/\text{kmol}$ $C_{A0} = 1.0 \text{ kmol/m}^3$
4. $3A \rightarrow B$ $k = 0.1 \text{ m}^6/\text{kmol}^2 \text{ min}$ $C_{A0} = 1.0 \text{ kmol/m}^3$

Repeat (a) through (d) for the RTD given by

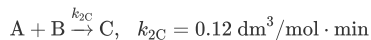
5. Problem P16-3_B
6. Problem P16-4_B
7. Problem P16-5_B

P17-14_C The second-order, elementary liquid-phase reaction



is carried out in a nonideal CSTR. At 300 K, the specific reaction rate is $k_{1A} = 0.5 \text{ dm}^3 / \text{mol} \cdot \text{min}$. In a tracer test, the tracer concentration rose linearly up to $1 \text{ mg} / \text{dm}^3$ at 1.0 minutes and then decreased -linearly to zero at exactly 2.0 minutes. Pure A enters the reactor at a temperature of 300 K.

1. Calculate the conversion predicted by the segregation and maximum mixedness models.
2. Now consider that a second elementary reaction also takes place



Compare the selectivities $\tilde{S}_{B/C}$ predicted by the segregation and maximum mixedness models.

P17-15_C The reaction and corresponding rate data discussed in Example 12-3 are to be carried out isothermally at 613°R in a nonideal reactor where RTD is given by the data (i.e., $E(t)$ and $F(t)$) in Example 16-2.

Determine the exit selectivities

1. Using the segregation model.
2. Using the maximum mixedness model.
3. Compare the selectivities in parts (a) and (b) with those that would be found in an ideal PFR and ideal CSTR in which the space time is equal to the mean residence time.

P17-16_C The reactions described in Example 12-7 are to be carried out isothermally at 1000°C in the reactor whose RTD is described in Example 17-4 with $C_{A0} = C_{B0} = 0.05 \text{ mol/dm}^3$.

1. Determine the exit selectivities using the segregation model.
2. Determine the exit selectivities using the maximum mixedness model.

3. Compare the selectivities in parts (a) and (b) with those that would be found in an ideal PFR and ideal CSTR in which the space time is equal to the mean residence time.
4. What would your answers to parts (a) through (c) be if the RTD curve rose from zero at $t = 0$ to a maximum of 50 mg/dm^3 after 10 minutes, and then fell linearly to zero at the end of 20 minutes?

P17-17_B Using the data in Problem P16-11_B,

1. Plot the internal-age distribution $I(t)$ as a function of time.
2. What is the mean internal age α_m ?
3. The activity of a “fluidized” CSTR is maintained constant by feeding fresh catalyst and removing spent catalyst at a constant rate. Using the preceding RTD data, what is the mean catalytic activity if the catalyst decays according to the rate law $-\frac{da}{dt} = k_D a^2$ with $k_D = 0.1 \text{ s}^{-1}$?
4. What conversion would be achieved in an ideal PFR for a second-order reaction with $kC_{A0} = 0.1 \text{ min}^{-1}$ and $C_{A0} = 1 \text{ mol/dm}^3$?
5. Repeat (d) for a laminar-flow reactor.
6. Repeat (d) for an ideal CSTR.
7. What would be the conversion for a second-order reaction with $kC_{A0} = 0.1 \text{ min}^{-1}$ and $C_{A0} = 1 \text{ mol/dm}^3$ using the segregation model?
8. What would be the conversion for a second-order reaction with $kC_{A0} = 0.1 \text{ min}^{-1}$ and $C_{A0} = 1 \text{ mol/dm}^3$ using the maximum mixedness model?

P17-18_B *OEQ (Old Exam Question)*. The relative tracer concentrations obtained from pulse tracer tests on a commercial packed-bed desulfurization reactor are shown in [Figure P17-18_B](#). After studying the RTD, what problems are occurring with the reactor during the period of poor operation (thin line)? The bed was repacked and the pulse tracer test again carried out with the results shown in [Figure P17-18_B](#) (thick line). Calculate the conversion that could be achieved in the commercial desulfurization reactor during poor operation and during good operation ([Figure P17-18_B](#)) for the following reactions:

1. A first-order isomerization with a specific reaction rate of 0.1 h^{-1}
2. A first-order isomerization with a specific reaction rate of 2.0 h^{-1}
3. What do you conclude upon comparing the four conversions in parts (a) and (b)?

From Additional Home Problem CDP17-I_B (3rd ed. P13-5)

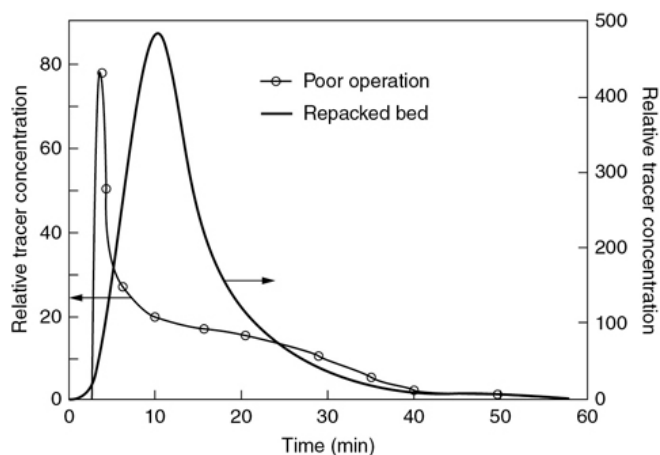


Figure P17-18_B Pilot-plant RTD. [Murphree, E. V., A. Voorhies, and F. Y. Mayer, *Ind. Eng. Chem. Process Des. Dev.*, 3, 381 (1964). Copyright © 1964, American Chemical Society.]

Application Pending for a Problem Hall of Fame



SUPPLEMENTARY READING

1. Discussions of the measurement and analysis of residence time distribution can be found in

R. L. CURL and M. L. MCMILLIN, "Accuracies in residence time measurements," *AIChE J.*, 12, 819–822 (1966).

O. LEVENSPIEL, *Chemical Reaction Engineering*, 3rd ed. New York: Wiley, 1999, Chaps. 11–16.

2. An excellent discussion of segregation can be found in

J. M. DOUGLAS, "The effect of mixing on reactor design," *AIChE Symp. Ser.*, 48, 60, 1 (1964).

3. Also see

M. DUDUKOVIC and R. FELDER, in *CHEMI Modules on Chemical Reaction Engineering*, vol. 4, ed. B. Crynes and H. S. Fogler. New York: AIChE, 1985.

E. B. NAUMAN, "Residence time distributions and micromixing," *Chem. Eng. Commun.*, 8, 53 (1981).

E. B. NAUMAN and B. A. BUFFHAM, *Mixing in Continuous Flow Systems*. New York: Wiley, 1983.

B. A. ROBINSON and J. W. TESTER, "Characterization of flow maldistribution using inlet-outlet tracer techniques: an application of internal residence time distributions," *Chem. Eng. Sci.*, 41 (3), 469–483 (1986).

J. VILLERMAUX, "Mixing in chemical reactors," in *Chemical Reaction Engineering—Plenary Lectures*, ACS Symposium Series 226. Washington, DC: American Chemical Society, 1982.

18. Models for Nonideal Reactors

Success is a journey, not a destination.

—Ben Sweetland

Overview. Not all tank reactors are perfectly mixed nor do all tubular reactors exhibit plug-flow behavior. In these situations, some means must be used to allow for deviations from ideal behavior. Chapter 17 showed how the RTD was sufficient if the reaction was first order or if the fluid was either in a state of complete segregation or maximum mixedness. We use the segregation and maximum mixedness models to bound the conversion when no adjustable parameters are used. For reactions other than first-order, more information than just the RTD is needed to predict conversion and exit concentrations; we need a model for the nonideal reactor. Suppose, we may have an existing reactor in storage and want to carry out a new reaction in that reactor. To predict conversions and product distributions for such systems, a model of reactor flow patterns and/or RTD is necessary. The models we discuss will have at most two adjustable parameters. In this chapter we first use the one-parameter model for dispersion. This topic is followed by a very (did I say very?), yes very brief introduction on how to use combinations of ideal reactors to model a reactor with nonideal flow patterns.

Use the RTD to evaluate parameters.

After completing this chapter you will be able to

- Discuss guidelines for developing one- and two-parameter models for nonideal reactors ([Section 18.1](#)).
- Model axial dispersion and flow of inert tracers in isothermal reactors ([Section 18.2](#)).
- Develop equations for a one-parameter model for isothermal flow with axial dispersion ([Section 18.3](#)) to predict conversion profiles ([Section 18.3](#)).
- Develop equations to model flow, axial dispersion, and reaction in isothermal laminar-flow reactors ([Section 18.4](#)) and explain four ways to find Men_o (i.e., D_a , Pe_l)
 - Theory LFR
 - Pipes correlations
 - Packed-bed correlations
 - RTD
- Discuss the equivalency between the tanks-in-series and dispersion models ([Section 18.5](#)).
- Use COMSOL to study a tubular reactor with axial and radial variations ([Section 18.6](#)).
- Model nonisothermal flow with radial and axial concentration and temperature variations ([Section 18.7](#)).
- Suggest combinations of ideal reactors to model the nonideal reactor to predict conversion and use RTD data to evaluate the model parameters (e.g., α , β ; [Section 18.8](#)).

- Discuss how combinations of ideal reactors can be used to model a nonideal reactor (Section 18.9).
- Identify how combinations of ideal reactors can be used in pharmacokinetics modeling (Section 18.10).
- AWFO–S18: An Algorithm for Management of Change.

Using the above models, we will first measure the RTD to characterize the reactor at the new operating conditions of temperature and flow rate. After selecting a model for the reactor, we use the RTD to evaluate the parameter(s) in the model after which we calculate the conversion and/or product distributions.

18.1 SOME GUIDELINES FOR DEVELOPING MODELS

The overall goal is to use the following equation:

$$\text{RTD Data} + \text{Model} + \text{Kinetics} = \text{Prediction}$$

By *Kinetics* we usually mean the rate law and rate-law parameters. The choice of the particular model to be used depends largely on the chemical reaction engineer's judgment and analysis of the reaction system. It is your job to choose the model that best combines the *conflicting goals* of mathematical simplicity and physical realism. There is a certain amount of art in the development of a model for a particular reactor, and the examples presented here can only point toward a direction that a chemical reaction engineer's thinking might follow.

Conflicting goals

A Model must

- Fit the data
- Be able to extrapolate theory and experiment
- Have realistic parameters

For a given real reactor, it is not uncommon to use all the models discussed previously to predict conversion and then make comparisons. Usually, the real conversion will be *bounded* by the model calculations.

The following guidelines are suggested when developing models for non-ideal reactors:

1. *The model must be mathematically tractable.* The equations used to describe a chemical reactor should be solved without an inordinate

expenditure of human or computer time.

- 2. *The model must realistically describe the characteristics of the nonideal reactor.* The phenomena occurring in the nonideal reactor must be reasonably described physically, chemically, and mathematically.
- 3. *The model should not have more than two adjustable parameters.* This constraint is often used because an expression with more than two adjustable parameters can be fitted to a great variety of experimental data, and the modeling process in this circumstance is nothing more than an exercise in curve fitting. The statement “Give me four adjustable parameters and I can fit an elephant; give me five and I can include his tail!” is one that I have heard from many colleagues. Unless one is into modern art, a substantially larger number of adjustable parameters is necessary to draw a reasonable-looking elephant.¹ A one-parameter model is, of course, superior to a two-parameter model if the one-parameter model is sufficiently realistic. To be fair, however, in complex systems (e.g., internal diffusion and conduction, mass transfer limitations) where other parameters may be measured *independently*, then more than two parameters are quite acceptable.

¹ J. Wei, *CHEMTECH*, 5, 128 (1975).



Table 18-1 gives some guidelines that will help your analysis and model building of nonideal reaction systems.

The Guidelines

TABLE 18-1 A PROCEDURE FOR CHOOSING A MODEL TO PREDICT THE OUTLET CONCENTRATIONS AND THE CONVERSION

1. *Look at the reactor.*

1. Where are the inlet and outlet streams to and from the reactors? (Is by-passing a possibility?)
2. Look at the mixing system. How many impellers are there? (Could there be multiple mixing zones in the reactor?)
3. Look at the configuration. (Is internal recirculation possible? Is the packing of the catalyst particles loose so channeling could occur?)

2. *Look at the tracer data.*

1. Plot the $E(t)$ and $F(t)$ curves.
2. Plot and analyze the shapes of the $E(\Theta)$ and $F(\Theta)$ curves.
Is the shape of the curve such that the curve or parts of the curve can be fit by an ideal reactor model? Does the curve have a long tail suggesting a stagnant zone? Does the curve have an early spike indicating bypassing?
3. Calculate the mean residence time, t_m , and variance, σ^2 .
How does the t_m determined from the RTD data compare with τ as measured with a yardstick and flow meter?
How large is the variance; is it larger or smaller than τ^2 ?

3. *Choose a model or perhaps two or three models.*

4. *Use the tracer data to determine the model parameters (e.g., n , D_a , v_b).*

5. *Use the CRE algorithm in Chapter 5.* Calculate the exit concentrations and conversion for the model system you have

selected.

When using the algorithm in [Table 18-1](#), we classify a model as being either a one-parameter model (e.g., tanks-in-series model or dispersion model) or a two-parameter model (e.g., reactor with bypassing and dead volume or combinations of ideal reactors). In [Sections 18.1.1](#) and [18.1.2](#), we give an overview of these models, which will be discussed in greater detail later in the chapter.

18.1.1 One-Parameter Models

Here, we use a single parameter to account for the nonideality of our reactor. This parameter is most always evaluated by analyzing the RTD determined from a tracer test.

CSTRs. Examples of one-parameter models for nonideal CSTRs include either a reactor dead volume, V_D , where no reaction takes place, or volumetric flow rate with part of the fluid bypassing the reactor, v_b , thereby exiting unreacted.

Tubular Reactors. Examples of one-parameter models for tubular reactors include the tanks-in-series model and the dispersion model. For the tanks-in-series model, the one parameter is the number of tanks, n , and for the dispersion model, the one parameter is the dispersion coefficient, D_a .[†] Knowing these parameter values, we then proceed to determine the conversion and/or effluent concentrations for the reactor.

[†] Nomenclature note: Da_1 (or Da_2) is the Damköhler number and D_a is the dispersion coefficient.

Nonideal tubular reactors

First let's consider nonideal tubular reactors. Tubular reactors may be empty (i.e., no packing), or they may be packed with some material that acts as a catalyst, heat-transfer medium, or means of promoting interphase contact. Until [Chapters 16–18](#), we have modeled the fluid to move through the reactor in a piston-like flow where every atom spends an identical length of time in the reaction environment. Here, the *velocity profile is flat*, and there is no axial mixing. Both of these assumptions

are false, to some extent in every tubular reactor; frequently, they are sufficiently false to warrant some modification of our CRE algorithm. Tubular reactor models need to have the flexibility to allow for failure of the plug-flow assumption and the insignificant axial mixing assumption. Cases where these failures occur include the unpacked laminar-flow tubular reactor, the unpacked turbulent flow reactor, and packed-bed reactors. One of two approaches is usually taken to compensate for failure of either or both of the ideal assumptions. One approach involves modeling the nonideal tubular reactor as a series of identically sized CSTRs, which was discussed in [Section 17.4](#). The other approach (the dispersion model) involves a modification of the ideal reactor by including axial and radial dispersion on the flow and is discussed in this chapter.

18.1.2 Two-Parameter Models

The premise for the two-parameter model is that we can use a combination of ideal reactors to model the real reactor (cf. [Section 18.8](#)). For example, consider a packed-bed reactor with channeling and dead zone. Here, the response to a pulse tracer input would show two dispersed pulses in the output as shown in [Figure 16-1](#) and [Figure 18-1](#).

Here, we could model the real reactor as two ideal PBRs in parallel, with the two parameters being the volumetric flow rate that channels or by passes, v_b , and the reactor dead volume, V_D . The real reactor volume is $V = V_D + V_S$ with entering volumetric flow rate $v_0 = v_b + v_s$.

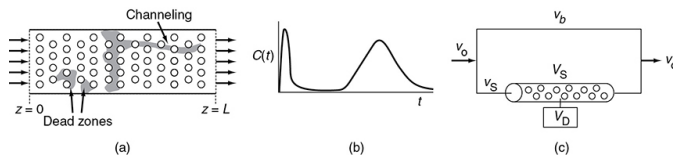


Figure 18-1 (a) Real system; (b) outlet for a pulse input; (c) model system.

18.2 FLOW AND AXIAL DISPERSION OF INERT TRACERS IN ISOTHERMAL REACTORS

The dispersion model is also often used to describe nonideal tubular reactors. In this model, there is an axial dispersion of the material, which is governed by an analogy to Fick's law of diffusion, superimposed on the flow as shown in [Figure 18-2](#).

So in addition to transport by bulk flow, $UA_c C$, every component in the mixture is transported through any cross section of the reactor at a rate equal to $[-D_a A_c (dC/dz)]$ resulting from molecular and convective diffusion. By convective diffusion (i.e., dispersion), we mean either Aris-Taylor dispersion in laminar-flow reactors or turbulent diffusion resulting from turbulent eddies. Radial concentration profiles for plug flow (a) and a representative axial and radial profile for dispersive flow (b) are shown in Figure 18-2. Some molecules will diffuse forward ahead of the molar average velocity, while others will lag behind.

Tracer pulse with dispersion

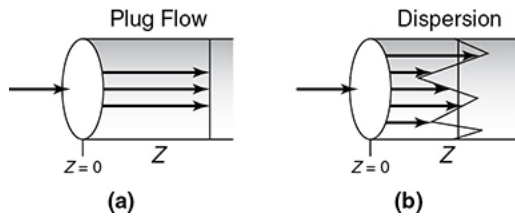


Figure 18-2 Concentration profiles: (a) without and (b) with dispersion.

18.2.1 Balances on Inert Tracers

To illustrate how dispersion affects the concentration profile in a tubular reactor, we consider the injection of a perfect tracer pulse. Figure 18-3 shows how dispersion causes the pulse to broaden as it moves down the reactor and becomes less concentrated.

Why does the tracer pulse broaden?

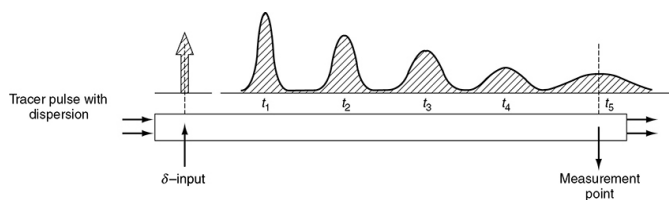


Figure 18-3 Dispersion in a tubular reactor.

(Levenspiel, O., *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.)

Recall Equation (14-14). The molar flow rate of tracer (F_T) by both convection and dispersion is

$$F_T = \left[-D_a \frac{\partial C_T}{\partial z} + UC_T \right] A_c \quad (14-14)$$

In this expression, D_a is the effective dispersion coefficient (m^2/s) and U (m/s) is the superficial velocity. To better understand how the pulse broadens, we refer to the concentration peaks t_2 and t_3 in Figure 18-4. We see that there is a concentration gradient on both sides of the peak causing molecules to diffuse away from the peak and thus broaden the pulse. The pulse then continues to broaden as it moves through the reactor.

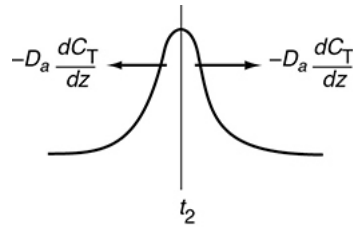


Figure 18-4 Symmetric concentration gradients causing the spreading by dispersion of a pulse input.

Correlations for the dispersion coefficients in both liquid and gas systems may be found in Levenspiel.² Some of these correlations are given in Section 18.4.

² O. Levenspiel, Chemical Reaction Engineering. New York: Wiley, 1962, pp. 290–293.

An unsteady-state mole balance on the inert tracer T gives

$$-\frac{\partial F_T}{\partial z} = A_c \frac{\partial C_T}{\partial t} \quad (18-1)$$

Substituting for F_T and dividing by the cross-sectional area A_c , we have

Pulse tracer balance with dispersion

$$D_a \frac{\partial^2 C_T}{\partial z^2} = \frac{\partial(UC_T)}{\partial z} = \frac{\partial C_T}{\partial t} \quad (18-2)$$

Letting $\psi = C_T/C_{T0}$ and $\lambda = z/L$ and $\Theta = Ut/L$ can put Equation (18-2) in dimensionless form as

$$\frac{1}{Pe_r} \frac{\partial^2 \psi}{\partial \lambda^2} - \frac{\partial \psi}{\partial \lambda} = \frac{\partial \psi}{\partial \Theta} \quad (18-3)$$

where

$$Pe_r = \frac{\text{Rate of Transport by Convection}}{\text{Rate of Transport by Diffusion or Dispersion}} = \frac{UL}{D_a}$$

Here ℓ is the characteristic length, for example, d_p for spherical particle or for the case at hand, L , the length of the reactor. The Péclet number, Pe_r gives a measure of the degree of dispersion. Small Péclet numbers indicate significant dispersion and high Pe_r indicates little dispersion. In the following sections, we will discuss how the dispersion coefficient, D_a , and Péclet number can be obtained either from correlations in the literature (cf. [Section 18.4](#)) or from the analysis obtained from a tracer experiment on the reactor that yields the RTD curve.

Small Pe_r

High Dispersion

Large Pe_r

Small Dispersion

To solve this equation, we need the initial and boundary conditions. The boundary conditions will now be discussed in detail.

For open tubes

$$Pe_r \sim 10^6,$$

$$Pe_r \sim 10^4$$

For packed beds

$$Pe_r \sim 10^3,$$

$$Pe_r \sim 10^1$$

There are two different types of Péclet numbers in common use. One is the *reactor* Péclet number, Pe_r ; It uses the reactor length, L , for the characteristic length, so $Pe_r \equiv UL/D_a$. It is Pe_r that appears in Equation (18-17). The reactor Péclet number, Pe_r , for mass dispersion is often referred to as the Bodenstein number, Bo , in reacting systems rather than the Péclet number. The other type of Péclet number can be called the *fluid* Péclet number, Pe_f ; it uses the characteristic length that determines the fluid's mechanical behavior. In a packed

bed, this length is the particle diameter d_p , and $Pe_f \equiv Ud_p/\phi D_a$. (The term U is the empty tube or superficial velocity. For packed beds, we often wish to use the average interstitial velocity, and thus U/ϕ is commonly used for the packed-bed velocity term.) In an empty tube, the fluid behavior is determined by the tube diameter d_t , and $Pe_f = Ud_t/D_a$. The fluid Péclet number, Pe_f , is given in virtually all literature correlations relating the Péclet number to the Reynolds number because both are directly related to the fluid mechanical behavior. It is, of course, very simple to convert Pe_f to Pe_r : Multiply by the ratio L/d_p or L/d_t . The reciprocal of Pe_r , D_a/UL , is sometimes called the *vessel dispersion number*.

18.2.2 Boundary Conditions for Flow and Reaction

There are two cases that we need to consider: boundary conditions for *closed-closed vessels* and for *open-open vessels*. In the case of *closed-closed vessels*, we assume that there is no dispersion or radial variation in concentration either upstream (closed) or downstream (closed) of the reaction section; hence, this is a closed-closed vessel, as shown in Figure 18-5(a). In an *open-open vessel*, dispersion occurs both upstream (open) and downstream (open) of the reaction section; hence, this is an open-open vessel as shown in Figure 18-5(b). These two cases are shown in Figure 18-5, where fluctuations in concentration due to dispersion are superimposed on the plug-flow velocity profile. A closed-open vessel boundary condition is one in which there is no dispersion in the entrance section but there is dispersion in the reaction and exit sections.

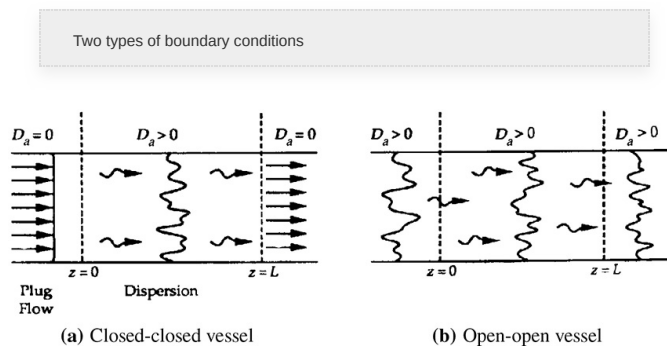


Figure 18-5 Types of boundary conditions.

18.2.2A Closed-Closed Vessel Boundary Condition

For a closed-closed vessel, we have plug flow (no dispersion) to the immediate left of the entrance line ($z = 0^-$) (closed) and to the immediate right of the exit $z = L$ ($z = L^+$) (closed).

However, between $z = 0^+$ and $z = L^-$, we have dispersion and reaction. The corresponding entrance boundary condition for either reactant A or tracer T is

$$\text{At } z = 0 : \quad F_A(0^-) = F_A(0^+)$$



Substituting for F_A yields

$$UA_c C_A(0^-) = -A_c D_a \left(\frac{dC_A}{dz} \right)_{z=0^+} + UA_c C_A(0^+) \quad (18-4)$$

Solving for the entering concentration $C_A(0^-) = C_{A0}$

Concentration boundary conditions at the entrance

$$C_{A0} = \frac{-D_a}{U} \left(\frac{dC_A}{dz} \right)_{z=0^+} + C_A(0^+) \quad (18-5)$$

At the exit to the reaction section, the concentration is continuous, and there is no gradient in tracer concentration.

Concentration boundary conditions at the exit

At $z = L$:

$$\left. \begin{array}{l} C_A(L^-) = C_A(L^+) \\ \frac{dC_A}{dz} = 0 \end{array} \right\} \quad (18-6)$$

Danckwerts boundary conditions

These two boundary conditions, Equations (18-5) and (18-6), first stated by Danckwerts, have become known as the famous **Danckwerts boundary conditions**.³ Bischoff has given a rigorous derivation by solving the differential equations governing the dispersion of component A in the entrance and exit sections, and taking the limit as the dispersion coefficient, D_a in the entrance and exit sections approaches zero.⁴ From the solutions, he obtained boundary conditions on the reaction section identical with those Danckwerts proposed.

³ P. V. Danckwerts, *Chem. Eng. Sci.*, 2, 1 (1953).

⁴K. B. Bischoff, *Chem. Eng. Sci.*, 16, 131 (1961).

The closed-closed concentration boundary condition at the entrance is shown schematically in Figure 18-6. One should not be uncomfortable with the discontinuity in concentration at $z = 0$ because if you recall for an ideal CSTR, the concentration drops immediately on entering from C_{A0} to $C_{A\text{exit}}$. For the other boundary condition at the exit $z = L$, we see the concentration gradient, (dC_A/dz) , has gone to zero. At steady state, it can be shown that this Danckwerts boundary condition at $z = L$ also applies to the open-open system at steady state.

Closed-Closed Boundary Condition

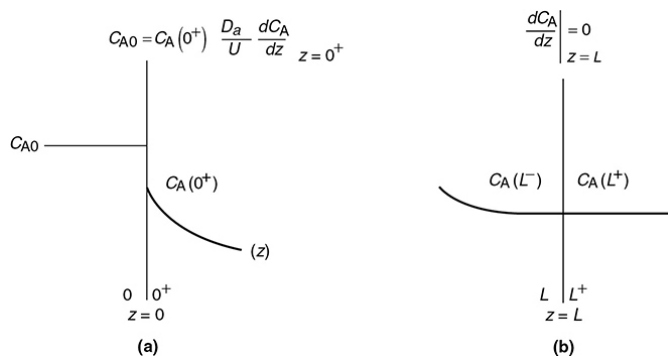


Figure 18-6 Schematic of Danckwerts boundary conditions: **(a)** entrance; **(b)** exit.

Prof. P. V. Danckwerts, Cambridge University, United Kingdom

18.2.2B Open-Open System

For an open-open system, there is continuity of flux at the boundaries at $z = 0$

$$F_A(0^-) = F_A(0^+)$$

Open-open boundary condition

$$\left[-D_a \frac{\partial C_A}{\partial z} \right]_{z=0^-} + U C_A(0^-) = -D_a \frac{\partial C_A}{\partial z} \Big|_{z=0^+} + U C_A(0^+) \quad (18-7)$$

At $z = L$, we have continuity of concentration and

$$\left[\frac{dC_A}{dz} \right]_{z=L} = 0 \quad (18-8)$$

18.3 FLOW, REACTION, AND AXIAL DISPERSION

Now that we have an intuitive feel for how dispersion affects the transport of molecules in a tubular reactor, we shall consider two types of dispersion in a tubular reactor, *laminar* and *turbulent*.

18.3.1 Balance Equations

In [Chapter 14](#), we showed that the mole balance on reacting species A flowing in a tubular reactor was

$$D_a \frac{d^2 C_A}{dz^2} - U \frac{dC_A}{dz} + r_A = 0 \quad (14-17)$$

Rearranging Equation (14-17) we obtain

$$\frac{D_a}{U} \frac{d^2 C_A}{dz^2} - \frac{dC_A}{dz} + \frac{r_A}{U} = 0 \quad (18-9)$$

This equation is a second-order ordinary differential equation. It is nonlinear when r_A is other than zero or first order.

When the reaction rate r_A is first order, $r_A = -kC_A$, then Equation (18-10)

Flow, reaction, and dispersion

$$\frac{D_a}{U} \frac{d^2 C_A}{dz^2} - \frac{dC_A}{dz} - \frac{kC_A}{U} = 0 \quad (18-10)$$

is amenable to an analytical solution. However, before obtaining a solution, we put our Equation (18-10) describing dispersion and reaction in dimensionless form by letting $\psi = C_A/C_{A0}$ and $\lambda = z/L$

D_a = Dispersion coefficient

$$\frac{1}{Pe_r} \frac{d^2 \psi}{d\lambda^2} - \frac{d\psi}{d\lambda} - Da_1 \cdot \psi = 0 \quad (18-11)$$

Da_1 = Damköhler number

We recall from [Chapter 5](#) that the quantity Da_1 appearing in Equation (18-11) is called the *Damköhler number* for a first-order conversion and physically represents the ratio

Damköhler number for a first-order reaction

$$Da_1 = \frac{\text{Rate of consumption of A by reaction}}{\text{Rate of transport of A by convection}} = k\tau \quad (18-12)$$

18.3.2 Solution for a Closed-Closed System

We now shall solve the dispersion reaction balance for a first-order reaction

$$\frac{1}{Pe_r} \frac{d^2\psi}{d\lambda^2} - \frac{d\psi}{d\lambda} - Da_1 \cdot \psi = 0 \quad (18-11)$$

For the closed-closed system, the Danckwerts boundary conditions in dimensionless form are

$$\text{At } \lambda = 0 \text{ then } 1 = -\frac{1}{Pe_r} \frac{d\psi}{d\lambda} \bigg|_{\lambda=0^+} + \psi(0^+) \quad (18-13)$$

$$\text{At } \lambda = 1 \text{ then } \frac{d\psi}{d\lambda} = 0 \quad (18-14)$$

$$Da_1 = \tau k$$

$$Pe_r = UL/D_a$$

Danckwerts[†] solved the closed-closed system to give the dimensionless concentration profile as

[†] Lit cit

Dimensionless concentration profile for dispersion and reaction in a tubular reactor

$$\psi = 2 * \exp\left(\frac{Pe_r \lambda}{2}\right) * \frac{(1+q) \exp\left(\frac{Pe_r}{2} q(1-\lambda)\right) - (1-q) \exp\left(-\frac{Pe_r}{2} q(1-\lambda)\right)}{(1+q)^2 \exp\left(\frac{Pe_r q}{2}\right) - (1-q)^2 \exp\left(-\frac{Pe_r q}{2}\right)} \quad (18-15)$$

where

$$q = \sqrt{1 + \frac{4Da_1}{Pe_r}}$$

The conversion profile is

$$X = 1 - \psi \quad (18-16)$$

To find the conversion leaving the reactor, X , we simply set $\lambda = 1$ to obtain

Nomenclature note:

Da_1 is the Damköhler number for a first-order reaction, τk . D_a is the dispersion coefficient in cm^2/s and $Pe_r = UL/D_a$.

$$\psi_L = \frac{C_{AL}}{C_{A0}} = 1 - X = \frac{4q \exp(Pe_r/2)}{(1+q)^2 \exp(Pe_r q/2) - (1-q)^2 \exp(-Pe_r q/2)} \quad (18-17)$$

where $q = \sqrt{1 + 4Da_1/Pe_r}$

This solution was first obtained by Danckwerts and has been published in many places (e.g., Levenspiel).^{5,6} With a slight rearrangement of Equation (18-17), we obtain the conversion as a function of Da_1 and Pe_r .

⁵ P. V. Danckwerts, *Chem. Eng. Sci.*, 2, 1 (1953).

⁶ Levenspiel, *Chemical Reaction Engineering*, 3rd ed. New York: Wiley, 1999.

$$X = 1 - \frac{4q \exp(Pe_r/2)}{(1+q)^2 \exp(Pe_r q/2) - (1-q)^2 \exp(-Pe_r q/2)} \quad (18-18)$$



Outside the limited case of a first-order reaction, a numerical solution of the equation is required, and because this is a split-boundary-value problem, for example, conditions given at $z = 0$ and $z = L$, an iterative technique is needed. We have to be a little cautious here with conversion defined as $[(C_{A0} - C_A)/C_{A0}]$. We see that at entrance to the reactor $\lambda = 0$, C_A is less than C_{A0} meaning $X > 0$. This value of X greater than zero is a result of A being dispersed at the entrance, not because of reaction.

To evaluate the exit concentration given by Equation (18-17) or the conversion given by Equation (18-18), we need to know the Damköhler and Péclet numbers. The first-order reaction-rate constant, k , and hence $Da_1 = \tau k$, can be found using the techniques in Chapter 7. In Section 18.4, we discuss three methods to determine the Péclet number and dispersion coefficient.

**Example 18-1 Concentration and Conversion
Profiles for Dispersion and Reaction in a Tubular
Reactor**

A first-order reaction with $k = 0.25 \text{ min}^{-1}$ is occurring in a tubular reactor with dispersion where the space time is $\tau = 5.15 \text{ min}$ and the Péclet number is $Pe_r = 7.5$. In Example 18-2, we will show how to use this tracer data to calculate the Damköhler number and Péclet number.



Plot the concentration and conversion profiles for a closed-closed system.

Solution

The dimensionless concentration profile is given by Equation (18-15)

$$\psi = 2 * \exp\left(\frac{Pe_r \lambda}{2}\right) * \frac{\left(1+q\right) \exp\left(\frac{Pe_r}{2} q(1-\lambda)\right) - \left(1-q\right) \exp\left(\frac{Pe_r}{2} q(1-\lambda)\right)}{\left(1+q\right)^2 \exp\left(\frac{Pe_r q}{2}\right) - \left(1-q\right)^2 \exp\left(-\frac{Pe_r q}{2}\right)} \quad (18-15)$$

where

$$q = \sqrt{1 + \frac{4Da_1}{Pe_r}}$$

The conversion profile is

$$X = 1 - \psi \quad (18-16)$$

The Damköhler number for this first-order reaction is

$$Da_1 = \tau k = (5.15 \text{ min})(0.25 \text{ min}^{-1}) = 1.29 \quad (\text{E18-1.1})$$

$$\text{Given: } Pe_r = 7.5 \quad (\text{E18-1.2})$$

$$q = \sqrt{1 + 4 \frac{Da_1}{Pe_r}} = \sqrt{1 + 4 \frac{(1.29)}{7.5}} = 1.30 \quad (\text{E18-1.3})$$

$$\frac{Pe_r q}{2} = \frac{(7.5)(1.3)}{2} = 4.87 \quad (\text{E18-1.4})$$

Substituting for q , Da_1 , and Pe_r , the following concentration profiles can be obtained using Polymath, MatLab, Python, or Wolfram simulations in the *Living Example Problem (LEP)* on the Web site.

Be sure to use the LEP Sliders to get a full understanding of how the parameters affect the profile.



Figure E18-1.1 shows the concentration profiles for three Péclet numbers. The dimensionless residence time function $E(\theta)$ is shown in the upper right-hand corner for the three corresponding Péclet numbers.

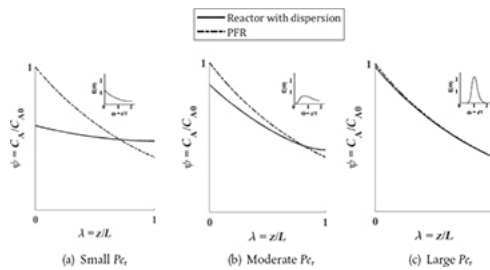


Figure E18-1.1 Concentration profiles for tubular reactor with dispersion.

Analysis: Figure E18-1.1 shows the comparative concentration profiles for a PFR and a reactor with dispersion. For small values of the Péclet number, Figure (a), the dispersion is large and the concentration is distributed throughout the tube and the concentration profiles approach that of a CSTR, one again notes that for a CSTR the entering feed concentration immediately drops from C_{A0} to C_A . For large values of Pe_r , Figure (c), there is virtually no dispersion and the profile approaches that of a PFR. Figure (b) shows the profiles for Péclet numbers in between the extremes of (a) and (c).

As we will see in [Example 18-2](#), the solution to find the exit reactant concentration or the conversion requires both Da and Pe_r which will be discussed in [Section 18.5](#).

18.4 FLOW, REACTION, AND AXIAL DISPERSION IN ISOTHERMAL LAMINAR-FLOW REACTORS AND FINDING MENO

Three ways to find D_a

Nemo in the Disney movie is a fish, but here our fish Meno is the dispersion coefficient, D_a . There are three ways we can use to find D_a and hence Pe_r :

1. Laminar flow with radial and axial molecular diffusion theory
2. Correlations from the literature for pipes and packed beds
3. Experimental tracer data



At first sight, simple models described by Equation (18-11) appear to have the capability of accounting only for axial mixing effects. It will be shown, however, that this approach can compensate not only for problems caused by axial mixing, *but also for those caused by radial mixing and other nonflat velocity profiles*.⁷ These fluctuations in concentration can result from different flow velocities and pathways and from molecular and turbulent diffusion.

⁷ R. Aris, *Proc. R. Soc. (London)*, A235, 67 (1956).

18.4.1 Determine the Dispersion Coefficient (D_a) and the Péclet Number (Pe_r)

Let's first discuss a qualitative description of how dispersion can occur in a laminar-flow tubular reactor. We know that the axial velocity varies in the radial direction according to the well-known parabolic velocity profile:

$$u(r) = 2U \left[1 - \left(\frac{r}{R} \right)^2 \right]$$

where U is the average velocity. For laminar flow, we saw that the RTD function $E(t)$ was given by

$$E(t) = \begin{cases} 0 & \text{for } t < \frac{\tau}{2} \\ \frac{\tau^2}{2t^3} & \text{for } t \geq \frac{\tau}{2} \end{cases} \quad \left(\tau = \frac{L}{U} \right) \quad (16-47)$$

In arriving at this distribution $E(t)$, it was assumed that there was no transfer of molecules in the radial direction between streamlines. Consequently, with the aid of Equation (16-47), we know that the molecules on the center streamline ($r = 0$) exited the reactor at a time $t = \tau/2$, and molecules traveling on the streamline at $r = 3R/4$ exited the reactor at time

$$\begin{aligned} t &= \frac{L}{u} = \frac{L}{2U[1-(r/R)^2]} = \frac{\tau}{2[1-(3/4)^2]} \\ &= \frac{8}{7} \cdot \tau \end{aligned}$$

Qualitative description of dispersion

The question now arises: What would happen if some of the molecules traveling on the streamline at $r = 3R/4$ jumped (i.e., diffused) onto the streamline at $r = 0$? The answer is that they would exit sooner than if they had stayed on the streamline at $r = 3R/4$. Analogously, if some of the molecules from the faster streamline at $r = 0$ jumped (i.e., diffused) onto the streamline at $r = 3R/4$, they would take a longer time to exit (Figure 18-7). In addition to the molecules diffusing between streamlines, they can also move forward or backward relative to the average fluid velocity by molecular diffusion (Fick's law). With both axial and radial diffusion occurring, the question arises as to what will be the distribution of residence times when molecules are transported between and along streamlines by diffusion. To answer this question, we will derive an equation for the axial dispersion coefficient, D_a , that accounts for the axial and radial diffusion mechanisms. In deriving D_a , which is often referred to as the *Aris-Taylor dispersion coefficient*, we closely follow the development given by Brenner and Edwards.⁸

⁸ H. Brenner and D. A. Edwards, *Macrotransport Processes*. Boston: ButterworthHeinemann, 1993.

Molecules diffusing back and forth between streamlines

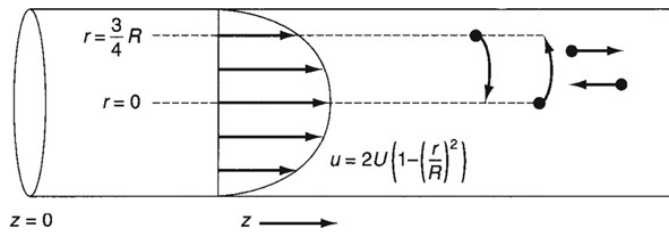


Figure 18-7 Radial diffusion in laminar flow.

The convective–diffusion equation for solute (e.g., tracer) transport in both the axial and radial direction can be obtained by combining Equation (14-2) with the diffusion equation (cf. Equation (14-11)) applied to the tracer concentration, c , and transformed to radial coordinates

$$\frac{\partial c}{\partial t} + u(r) \frac{\partial c}{\partial z} = D_{AB} \left\{ \frac{1}{r} \frac{\partial [r(\partial c / \partial r)]}{\partial r} + \frac{\partial^2 c}{\partial z^2} \right\} \quad (18-19)$$

where c is the solute concentration at a particular r , z , and t , and D_{AB} is the molecular diffusion coefficient of species A in B.

We are going to change the variable in the axial direction z to z^* , which corresponds to an observer moving with the fluid

$$z^* = z - Ut \quad (18-20)$$

A value of $z^* = 0$ corresponds to an observer moving with the average velocity of the fluid, U . Using the chain rule, we obtain

$$\left(\frac{\partial c}{\partial t} \right)_{z^*} + [u(r) - U] \frac{\partial c}{\partial z^*} = D_{AB} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) + \frac{\partial^2 c}{\partial z^{*2}} \right] \quad (18-21)$$

Because we want to know the concentrations and conversions at the exit to the reactor, we are really only interested in the average axial concentration, \bar{C} , which is given by

$$\bar{C}(z, t) = \frac{1}{\pi R^2} \int_0^R c(r, z, t) 2\pi r \, dr \quad (18-22)$$



Consequently, we are going to solve Equation (18-21) for the solution concentration as a function of r and then substitute the solution $c(r, z, t)$ into Equation (18-22) to find $\bar{C}(z, t)$. All the intermediate steps are given on the CRE Web site in the *Professional Reference Shelf*, and the partial differential equation describing the variation of the average axial concentration with time and distance is

$$\frac{\partial \bar{C}}{\partial t} + U \frac{\partial \bar{C}}{\partial z^*} = D^* \frac{\partial^2 \bar{C}}{\partial z^{*2}} \quad (18-23)$$

where D^* is the Aris-Taylor dispersion coefficient

Aris-Taylor dispersion coefficient

$$D^* = D_{AB} + \frac{U^2 R^2}{48 D_{AB}} \quad (18-24)$$

That is, for laminar flow in a pipe

$$D_a \equiv D^*$$

Figure 18-8 shows the dispersion coefficient D^* in terms of the ratio $D^*/U(2R) = D^*/Ud_t$ as a function of the product of the Reynolds (Re) and Schmidt (Sc) numbers.

It was surprising to me how D^* could account for both radial and axial dispersion in laminar flow.



Memo! 1.

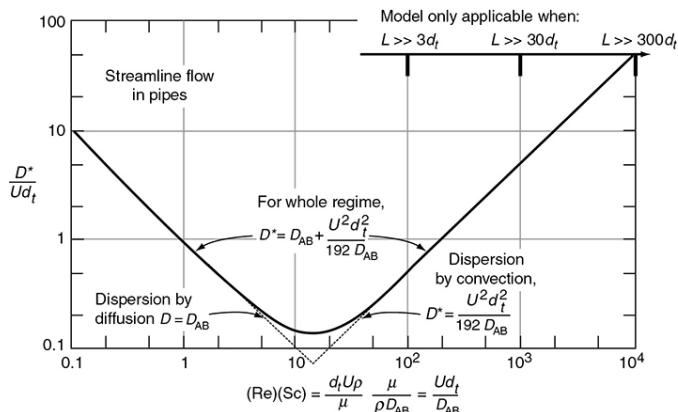


Figure 18-8 Correlation for dispersion for streamline flow in pipes. (Levenspiel, O., *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) Note: $D \equiv D_a$

18.4.2 Correlations for D_a

We will use correlations from the literature to determine the dispersion coefficient D_a for flow in cylindrical tubes (pipes) and for flow in packed beds.

An estimate of the dispersion coefficient, D_a , for laminar and turbulent flow in pipes, can be determined from [Figure 18-9](#). Here, d_t is the tube diameter and Sc is the Schmidt number discussed in [Chapter 14](#). The flow is laminar (streamline) below 2,100, and we see the ratio (D_a/Ud_t) increases with increasing Schmidt and Reynolds numbers. Between Reynolds numbers of 2,100 and 30,000, one can put bounds on D_a by calculating the maximum and minimum values at the top and bottom of the shaded regions.

1. Meno, i.e., Pe and D_a , has been found



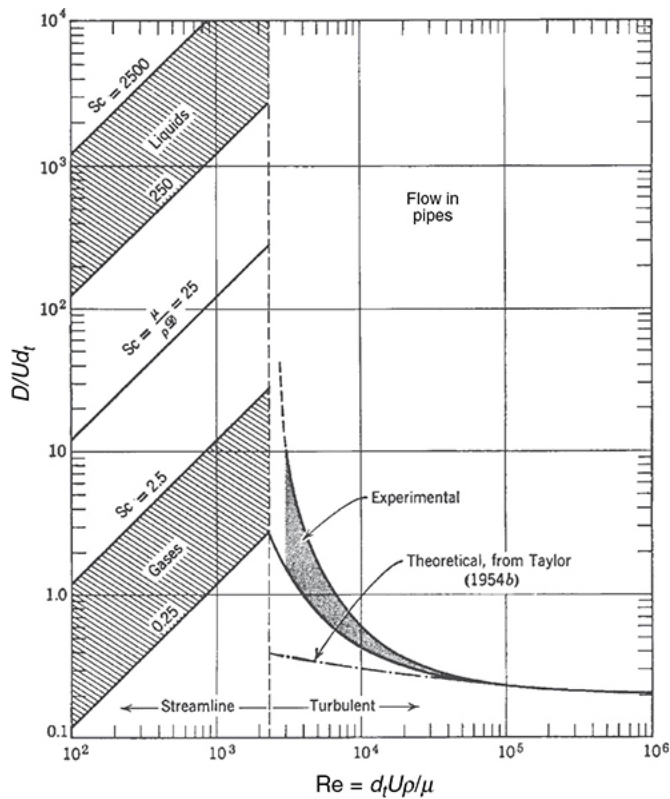


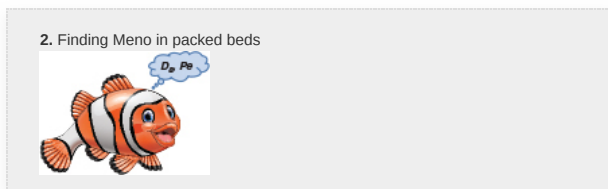
Figure 18-9 Correlation for dispersion of fluids flowing in pipes. (Levenspiel, O., *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) Note: $D \equiv D_a$

18.4.3 Dispersion in Packed Beds

For the case of gas–solid and liquid–solid catalytic reactions that take place in packed-bed reactors, the dispersion coefficient, D_a , can be estimated by using Figure 18-10. Here, d_p is the particle diameter and ε is the porosity.

18.4.4 Experimental Determination of D_a

The dispersion coefficient can be determined from a pulse tracer experiment. Here, we will use t_m and σ^2 to solve for the dispersion coefficient D_a and then



Once the Reynolds number is calculated, D_a can be found.

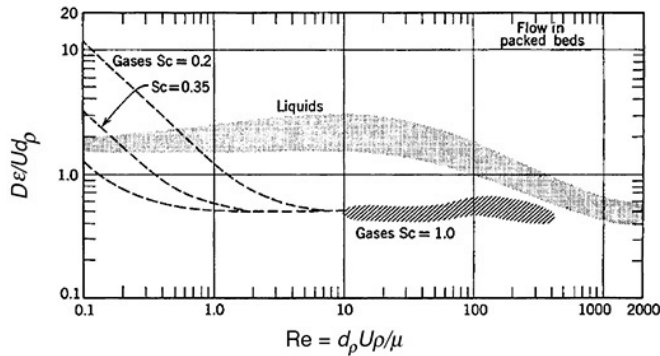


Figure 18-10 Experimental findings on dispersion of fluids flowing with mean axial velocity u in packed beds. (Levenspiel, O., *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) Note: $D \equiv D_a$, ε = void fraction

the Péclet number, Pe_r . Here the effluent concentration of the reactor is measured as a function of time. From the effluent concentration data, the mean residence time, t_m , and variance, σ^2 , are calculated, and these values are then used to determine D_a . To show how this is accomplished, we will write the unsteady-state mass balance on the tracer flowing in a tubular reactor

$$D_a \frac{\partial^2 C_T}{\partial z^2} - \frac{\partial(UC_T)}{\partial z} = \frac{\partial C_T}{\partial t} \quad (18-2)$$

in dimensionless form, discuss the different types of boundary conditions at the reactor entrance and exit, and then solve for the exit concentration as a function of dimensionless time ($\Theta = t / \tau$), and then relate D_a , σ^2 , and τ .

18.4.4A What If ... Those Correlations Don't Apply to My Reactors

If I cannot use any of the earlier correlations or graphs, I will just need to find $Meno$ on my own. To do this, I will need to do some theoretical analysis and some experiments to determine the RTD, which we can then analyze to find t_m and σ^2 and then calculate $D_a(Pe_r)$. The first step to find $Meno$ is to put Equation (18-2) in dimensionless form to arrive at the dimensionless group(s) that characterize the process. Again let

$$\psi = \frac{C_T}{C_{T0}}, \quad \lambda = \frac{z}{L}, \quad \text{and} \quad \Theta = \frac{tU}{L} \quad \lambda = \frac{z}{L}, \quad \Theta = \frac{tU}{L}$$

For a pulse input, C_{T0} is defined as the mass of tracer injected, M , divided by the vessel volume, V . Then

$$\frac{1}{Pe_r} \frac{\partial^2 \psi}{\partial \lambda^2} - \frac{\partial \psi}{\partial \lambda} = \frac{\partial \psi}{\partial \Theta} \quad (18-3)$$

The initial condition is

Initial condition

$$\text{At } t = 0, \quad z > 0, \quad C_T(0^+, 0) = 0, \quad \psi(0^+) = 0 \quad (18-25)$$

The mass of tracer injected, M , is

$$M = UA_c \int_0^\infty C_T(0^-, t) dt$$

18.4.4B Solution for a Closed-Closed System

In dimensionless form, the Danckwerts boundary conditions are



$$\text{At } \lambda = 0 : \quad \left(-\frac{1}{Pe_r} \frac{\partial \psi}{\partial \lambda} \right)_{\lambda=0^+} + \psi(0^+) = \frac{C_T(0^-, t)}{C_{T0}} = 1 \quad (18-26)$$

$$\text{At } \lambda = 1 : \quad \frac{\partial \psi}{\partial \lambda} = 0 \quad (18-27)$$

Equation (18-3) has been solved numerically for a pulse injection, and the resulting dimensionless effluent tracer concentration at the exit of the reactor, ψ_{exit} , is shown as a function of the dimensionless time Θ in [Figure 18-11](#) for various Péclet numbers. Although analytical solutions for ψ can be found, the result is an infinite series. The corresponding equations for the mean residence time, t_m , and the variance, σ^2 , are⁹

⁹ See K. Bischoff and O. Levenspiel, *Adv. Chem. Eng.*, 4, 95 (1963).

$$t_m = \tau \quad (18-28)$$

Effects of dispersion on the effluent tracer concentration

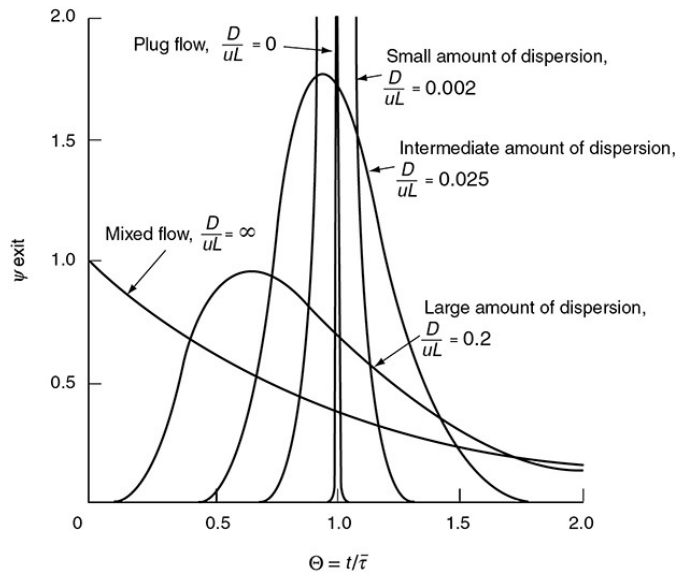


Figure 18-11 C-curves in closed vessels for various extents of back-mixing as predicted by the dispersion model. (Levenspiel, O., *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) Note: $D \equiv D_a^{10}$

¹⁰ O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed. New York: Wiley, 1972, p. 277.

and



$$\frac{\sigma^2}{t_m^2} = \frac{1}{\tau^2} \int_0^\infty (t - \tau)^2 E(t) dt$$

which can be used with the solution to Equation (18-3) to obtain

Calculating Pe_r using t_m and σ^2 determined from RTD data for a closed-closed system

$$\boxed{\frac{\sigma^2}{t_m^2} = \frac{2}{Pe_r} - \frac{2}{Pe_r^2} (1 - e^{-Pe_r})} \quad (18-29)$$

Consequently, we see that the Péclet number, Pe_r (and hence D_a), can be found experimentally by determining t_m and σ^2 from the RTD data and then solving Equation (18-29) for Pe_r .

18.4.4C Solution for Open-Open Vessel Boundary Conditions to Find Meno

When a tracer is injected into a packed bed at a location more than two or three particle diameters downstream from the entrance and measured some distance upstream from the exit, the open-open vessel boundary conditions apply. For an open-open system, an analytical solution to Equation (18-11) can be obtained for a pulse tracer input.

For an open-open system, the boundary conditions at the entrance are

$$F_T(0^-, t) = F_T(0^+, t)$$

Then, for the case when the dispersion coefficient is the same in the entrance and reaction sections

Open at the entrance

$$-D_a \left(\frac{\partial C_T}{\partial z} \right)_{z=0^-} + UC_T(0^-, t) = -D_a \left(\frac{\partial C_T}{\partial z} \right)_{z=0^+} + UC_T(0^+, t) \quad (18-30)$$

Because there are no discontinuities across the boundary at $z = 0$

$$C_T(0^-, t) = C_T(0^+, t) \quad (18-31)$$

At the exit

Open at the exit

$$-D_a \left(\frac{\partial C_T}{\partial z} \right)_{z=L^-} + UC_T(L^-, t) = -D_a \left(\frac{\partial C_T}{\partial z} \right)_{z=L^+} + UC_T(L^+, t) \quad (18-32)$$

$$C_T(L^-, t) = C_T(L^+, t) \quad (18-33)$$

There are a number of perturbations of these boundary conditions that can be applied. The dispersion coefficient can take on different values in each of the three regions ($z < 0$, $0 \leq z \leq L$, and $z > L$), and the tracer can also be injected at some point z_1 rather than at the boundary, $z = 0$. These cases and others can be found in the supplementary readings cited at the end of

this chapter. We shall consider the case when there is no variation in the dispersion coefficient for all z and an impulse of tracer is injected at $z = 0$ at $t = 0$.

Again, we let $\psi = C_A/C_{A0}$ and $\theta = t/\tau$.

For long tubes ($Pe_r > 100$) in which the concentration gradient at $\pm\infty$ will be zero, the solution to Equation (18-3) giving the dimensionless tracer concentration at the exit is¹¹

¹¹ W. Jost, *Diffusion in Solids, Liquids and Gases*. New York: Academic Press, 1960, pp. 17, 47.

Valid for $Pe_r > 100$

$$\psi(1, \Theta) = \frac{C_T(L, t)}{C_{T0}} = \frac{1}{2\sqrt{\pi\Theta/Pe_r}} \exp\left[-\frac{(1-\Theta)^2}{4\Theta/Pe_r}\right] \quad (18-34)$$

The mean residence time for an open-open system is

Calculate τ for an open-open system.

$$t_m = \left(1 + \frac{2}{Pe_r}\right)\tau \quad (18-35)$$

Diffuse in and out.

where τ is based on the volume between $z = 0$ and $z = L$ (i.e., reactor volume measured with a yardstick). We note that the mean residence time for an open system is greater than that for a closed system. The reason is that the molecules can diffuse out of the reactor at the entrance and then diffuse, or be carried, back into the reactor. The variance for an open-open system is

Calculate Pe_r for an open-open system.

$$\frac{\sigma^2}{\tau^2} = \frac{2}{Pe_r} + \frac{8}{Pe_r^2} \quad (18-36)$$

We found Meno 3.



We now consider two cases for which we can use Equations (18-29) and (18-36) to determine the system parameters:

Case 1. The space time τ is *known*. That is, V and v_0 are measured independently. Here, we can determine the Péclet number by determining t_m and σ^2 from the concentration–time data and then use Equation (18-36) to calculate Pe_r . We can also calculate t_m and then use Equation (18-35) as a check, but this is usually less accurate.

Case 2. The space time τ is *unknown*. This situation arises when there are dead or stagnant pockets that exist in the reactor along with the dispersion effects. To analyze this situation, we first calculate mean residence time, t_m , and the variance, σ^2 , from the data as in case 1. Then, we use Equation (18-35) to eliminate τ^2 from Equation (18-36) to arrive at

$$\frac{\sigma^2}{t_m^2} = \frac{2Pe_r + 8}{Pe_r^2 + 4Pe_r + 4} \quad (18-37)$$

Finding the effective reactor volume

We now can solve for the Péclet number in terms of our experimentally determined variables σ^2 and t_m^2 . Knowing Pe_r , we can solve Equation (18-35) for τ , and hence V . The dead volume is the difference between the measured volume (i.e., with a yardstick) and the effective volume calculated from the RTD.



Once we have determined D_a and Pe_r from the RTD for our *real reactor* (i.e., found Meno), we can solve for the conversion from an analytical solution, or for a first-order reaction as in **Example 18-1**, or solve numerically for other reaction orders.

Example 18–2 Comparing Conversion Using Dispersion, PFR, CSTR, and Tanks-in-Series Models for Isothermal Reactors

The first-order reaction



is carried out in a 10-cm-diameter tubular reactor 6.36 m in length. The specific reaction rate is 0.25 min^{-1} . The results of a tracer test carried out on this reactor are shown in [Table E18-2.1](#).

TABLE E18-2.1 EFFLUENT TRACER CONCENTRATION AS A FUNCTION OF TIME

t (min)	0	1	2	3	4	5	6	7	8	9	10	11	12
C (mg/L)	0	1	5	8	10	8	6	4	3	2	1	0	0

Calculate the conversion using **(a)** the closed vessel dispersion model, **(b)** PFR, **(c)** the tanks-in-series model, and **(d)** a single CSTR.

Solution

1. We will use Equation (18-18) to calculate the conversion at the exit

$$X = 1 - \frac{4q \exp(Pe_r/2)}{(1+q)^2 \exp(Pe_r/2) - (1-q)^2 \exp(-Pe_r/2)} \quad (18-18)$$

where

$$q = \sqrt{1 + 4Da_1/Pe_r} \quad Da_1 = \tau k, \text{ and } Pe_r = UL/D_a.$$

(1) Parameter evaluation using the RTD data to evaluate Pe_r :

We can calculate Pe_r from Equation (18-29)

$$\frac{\sigma^2}{\tau^2} = \frac{2}{Pe_r} - \frac{2}{Pe_r^2} (1 - e^{-Pe_r}) \quad (18-29)$$

First calculate t_m and σ^2 from RTD data.

However, we must find τ^2 and σ^2 from the tracer concentration data first.

$$\tau = \frac{V}{v} = \int_0^\infty tE(t) dt \quad (\text{E18-2.1})$$

$$\sigma^2 = \int_0^\infty (t - \tau)^2 E(t) dt \quad (\text{E18-2.2})$$

Here again, spreadsheets can be used to calculate τ^2 and σ^2 .

TABLE E18-2.2 POLYMATH PROGRAM AND RESULTS TO CALCULATE THE MEAN RESIDENCE TIME, t_m , AND THE VARIANCE σ^2

Calculated values of DEQ variables			Differential equations	
Variable	Initial value	Final value	1 d(Sigma2)/dt = (t-tmf)^2 * E	
1 Area	51.	51.	Explicit equations	
2 C	0.0038746	0.0148043	1 C1 = 0.0038746 + 0.2739782*t + 1.574621*t^2 - 0.2550041*t^3	
3 C1	0.0038746	-387.266	2 Area = 51	
4 C2	-33.43818	0.0148043	3 C2 = -33.43818 + 37.18972*t - 11.58838*t^2 + 1.695303*t^3 - 0.1298667*t^4 + 0.005028*t^5 - 7.743*10^-5*t^6	
5 E	7.597E-05	0.0002903	4 C = If(t<=4 and t>=0) then C1 else If(t>4 and t<=14) then C2 else 0	
6 Sigma2	0	6.212473	5 E = C/Area	
7 t	0	14.	6 tmf = 5.1	
8 tmf	5.1	5.1		



Don't fall asleep. These are calculations we need to know how to carry out.

We note that the data in Table E18-2.1 is the same data set used in Examples 16-1 and 16-2 where we found

and

$$\begin{aligned} t_m &= 5.15 \text{ minutes} \\ \sigma^2 &= 6.2 \text{ minutes}^2 \end{aligned}$$

Are we lucky or what? We will use these values in Equation (18-29) to calculate Pe_r . Dispersion in a closed vessel is represented by

$$\begin{aligned}\frac{\sigma^2}{\tau^2} &= \frac{2}{Pe_r^2} (Pe_r - 1 + e^{-Pe_r}) \quad (18-29) \\ &= \frac{6.2}{(5.15)^2} = 0.23 = \frac{2}{Pe_r^2} (Pe_r - 1 + e^{-Pe_r})\end{aligned}$$

Calculate Pe_r from t_m and σ^2 .

Solving for Pe_r either by trial and error or using Polymath, we obtain

$$Pe_r = 7.5 \quad (\text{E18-2.3})$$

Next, calculate Da_1 , q , and X .

(2) Next, we calculate Da_1 and q :

$$Da_1 = \tau k = (5.15 \text{ min}) (0.25 \text{ min}^{-1}) = 1.29 \quad (\text{E18-2.4})$$

Using the equations for q and X gives

$$q = \sqrt{1 + \frac{4Da_1}{Pe_r}} = \sqrt{1 + \frac{4(1.29)}{7.5}} = 1.30 \quad (\text{E18-2.5})$$

Then

$$\frac{Pe_r q}{2} = \frac{(7.5)(1.3)}{2} = 4.87 \quad (\text{E18-2.6})$$

(3) Finally, we calculate the conversion:

Substitution into Equation (18-18) yields

Dispersion model

$$\begin{aligned}X &= 1 - \frac{4(1.30)e^{(7.5/2)}}{(2.3)^2 \exp(4.87) - (-0.3)^2 \exp(-4.87)} \\ X &= 0.68 \quad 68\% \text{ conversion for the dispersion model}\end{aligned}$$

When dispersion effects are present in this tubular reactor, 68% conversion is achieved.

(b) If the reactor were operating ideally as a plug-flow reactor, the conversion would be

PFR

$$X = 1 - e^{-\tau k} = 1 - e^{-Da_1} = 1 - e^{-1.29} = 0.725 \quad (\text{E18-2.7})$$

That is, 72.5% conversion would be achieved in an ideal plug-flow reactor.

Tanks-in-series model

(c) Conversion using the tanks-in-series model: We recall Equation (17-25) to calculate the number of tanks in series:

$$n = \frac{\tau^2}{\sigma^2} = \frac{(5.15)^2}{6.1} = 4.35 \quad (\text{E18-2.8})$$

To calculate the conversion for the T-I-S model, we recall Equation (5-15). For a first-order reaction for n tanks in series, the conversion is

$$X = 1 - \frac{1}{(1 + \tau_1 k)^n} = 1 - \frac{1}{[1 + (\tau/n)k]^n} = 1 - \frac{1}{(1 + 1.29/4.35)^{4.35}} \quad (\text{E18-2.9})$$

$X = 67.7\%$ for the tanks-in-series model

(d) For a single CSTR

CSTR

$$X = \frac{\tau k}{1 + \tau k} = \frac{1.29}{2.29} = 0.563 \quad (\text{E18-2.10})$$

So, 56.3% conversion would be achieved in a single ideal tank. Summary:

Summary

PFR: X	=	72.5%
Dispersion: X	=	68.0%
Tanks in series: X	=	67.7%
Single CSTR: X	=	56.3%

In this example, correction for finite dispersion, whether by a dispersion model or a tanks-in-series model, is significant when compared with a PFR.

Analysis: This example is a very important and comprehensive one. We showed how to calculate the conversion by (1) choosing a model, (2) using the RTD to evaluate the model parameters, and (3) substituting the reaction-rate parameters in the chosen model. As

expected, the dispersion and T-I-S model gave essentially the same result and this result fell between the limits predicted by an ideal PFR and an ideal CSTR.

18.5 TANKS-IN-SERIES MODEL VERSUS DISPERSION MODEL

We have seen that we can apply both of these one-parameter models to tubular reactors using the variance of the RTD. For first-order reactions, the two models can be applied with equal ease. However, the tanks-in-series model is mathematically easier to use to obtain the effluent concentration and conversion for reaction orders other than one, and for multiple reactions. However, we need to ask what would be the accuracy of using the tanks-in-series model over the dispersion model. These two models are equivalent when the Péclet–Bodenstein number is related to the number of tanks in series, n , by the equation¹²

¹² K. Elgeti, *Chem. Eng. Sci.*, 51, 5077 (1996).

$$Bo = 2(n - 1) \quad (18-38)$$

Equivalency between models of tanks-in-series and dispersion

or

$$n = \frac{Bo}{2} + 1 \quad (18-39)$$

where

$$Bo = UL/Da \quad (18-40)$$

where U is the superficial velocity, L the reactor length, and D_a the dispersion coefficient.

For the conditions in [Example 18-2](#), we see that the number of tanks calculated from the Bodenstein number, Bo (i.e., Pe_r), Equation (18-39), is 4.75, which is very close to the value of 4.35 calculated from Equation (17-25). Consequently, for reactions other than first order, one would solve successively for the exit concentration and conversion from each tank in series for both a battery of four tanks in series and for five tanks in series in order to bound the expected values.

In addition to the one-parameter models of tanks-in-series and dispersion, many other one-parameter models exist when a combination of ideal reactors is used to model the real reactor shown in [Section 18.8](#) for reactors with bypassing and dead volume. Another example of a one-parameter model would be to model the real reactor as a PFR and a CSTR in series with the one parameter being the fraction of the total volume that behaves as a CSTR. We can dream up many other situations that would alter the behavior of ideal reactors in a way that adequately describes a real reactor. However, it may be that one parameter is not sufficient to yield an adequate comparison between theory and practice. We explore these situations with combinations of ideal reactors in the section on two-parameter models.

The reaction-rate parameters are usually known (e.g., **Da**), but the Péclet number is usually not known because it depends on the flow and the vessel. Consequently, we need to find Pe_r using one of the three techniques discussed earlier in the chapter.

18.6 NUMERICAL SOLUTIONS TO FLOWS WITH DISPERSION AND REACTION

We now consider dispersion and reaction in a tubular reactor. We first write our mole balance on species A in cylindrical coordinates by recalling [Equation \(18-19\)](#) and including the rate of formation of A, r_A . At steady state we obtain

$$D_{AB} \left[\frac{1}{r} \frac{\partial \left(r \frac{\partial C_A}{\partial r} \right)}{\partial r} + \frac{\partial^2 C_A}{\partial z^2} \right] - u(r) \frac{\partial C_A}{\partial z} + r_A = 0 \quad (18-41)$$

Analytical solutions to dispersion with reaction can only be obtained for iso-thermal zero- and first-order reactions. We are now going to use COMSOL to solve the flow with reaction and dispersion with reaction.

We are going to compare two solutions: one which uses the Aris-Taylor approach and one in which we numerically solve for both the axial and radial concentration using COMSOL. These solutions are on the CRE Web site.

Case A. Aris-Taylor Analysis for Laminar Flow

For the case of an nth-order reaction, [Equation \(18-9\)](#) becomes

$$\frac{D_a}{U} \frac{d^2 \bar{C}_A}{dz^2} - \frac{d\bar{C}_A}{dz} - \frac{k\bar{C}_A^n}{U} = 0 \quad (18-42)$$

where \bar{C}_A is the radially averaged axial concentration from $r = 0$ to $r = R$, that is,

$$\bar{C}_A(z) = \frac{\int_0^R 2\pi r C_A(z,r) dr}{\pi R^2}$$

If we use the Aris-Taylor analysis, we can use Equation (18-9) with a caveat that $\bar{\psi} = \bar{C}_A/C_{A0}$ and $\lambda = z/L$ we obtain

$$\frac{1}{Pe_r} \frac{d^2 \bar{\psi}}{d\lambda^2} - \frac{d\bar{\psi}}{d\lambda} - Da_n \bar{\psi}^n = 0 \quad (18-43)$$

where

$$Pe_r = \frac{UL}{D_a} \text{ and } Da_n = \tau k C_{A0}^{n-1}$$

For the closed-closed boundary conditions we have

$$\text{At } \lambda = 0 : -\frac{1}{Pe_r} \frac{d\bar{\psi}}{d\lambda} \Big|_{\lambda=0^+} + \bar{\psi}(0^+) = 1 \quad (18-44)$$

$$\text{At } \lambda = 1 : \frac{d\bar{\psi}}{d\lambda} = 0$$

Danckwerts boundary conditions

For the open-open boundary conditions we have

$$\text{At } \lambda = 0 : \bar{\psi}(0^-) - \frac{1}{Pe_r} \frac{d\bar{\psi}}{d\lambda} \Big|_{\lambda=0^-} = \bar{\psi}(0^+) - \frac{1}{Pe_r} \frac{d\bar{\psi}}{d\lambda} \Big|_{\lambda=0^+} \quad (18-45)$$

$$\text{At } \lambda = 1 : \frac{d\bar{\psi}}{d\lambda} = 0$$

Equation (18-43) gives the dimensionless concentration profiles for dispersion and reaction in a laminar-flow reactor.

For a first-order reaction, we can use Equation (18-26) and (18-27) to obtain the concentration and conversion profiles.

For a second-order reaction, the equation becomes nonlinear that needs to be solved numerically. We have used COMSOL in the LEP on the Web site (see

http://www.umich.edu/~elements/6e/18chap/expanded_ch18_example2comsol.pdf) to solve for the concentration profiles.

Case B. Full Numerical Solution

To obtain profiles, $C_A(r, z)$, we now solve Equation (18-41)

$$D_{AB} \left[\frac{1}{r} \frac{\partial \left(r \frac{\partial C_A}{\partial r} \right)}{\partial r} + \frac{\partial^2 C_A}{\partial z^2} \right] - u(r) \frac{\partial C_A}{\partial z} + r_A = 0 \quad (18-46)$$

First, we will put the equations in dimensionless form by letting $\psi = C_A/C_{A0}$, $\lambda = z/L$, and $\phi = r/R$. Following our earlier transformation of variables, Equation (18-46) becomes

$$\left(\frac{L}{R} \right) \frac{1}{Pe_r} \left[\frac{1}{\phi} \frac{\partial \left(\phi \frac{\partial \psi}{\partial \phi} \right)}{\partial \phi} \right] + \frac{1}{Pe_r} \frac{d^2 \psi}{d\lambda^2} - 2(1 - \phi^2) \frac{d\psi}{d\lambda} - Da_n \psi^n = 0 \quad (18-47)$$

Example 18–3 Isothermal Reaction with Radial and Axial Dispersion in an LFR

COMSOL

We now consider flow, reaction and dispersion in cylindrical pipes. The parameter values (e.g., k , U_0) will be varied using a COMSOL program. Initially we will use the following values, $k = 8.33 \times 10^{-6} \text{ m}^3/\text{mol} \cdot \text{s}$, $C_{A0} = 500 \text{ mol/m}^3$, $U_0 = 0.021 \text{ m/s}$, and $D_{A0} = 1.25 \times 10^{-6} \text{ m}^2/\text{s}$.

1. Plot the concentration surface for $\phi = 0$ to $\phi = 1$ and $\lambda = 0$ to $\lambda = 1$. To make this plot, go to the CRE Web site and load the COMSOL LEP instruction on *How to Access COMSOL* (http://www.umich.edu/~elements/6e/comsol/comsol_access_instructions.html). Vary the parameters and run the simulation.
2. Plot the radial concentration profile.
3. Plot the axial profiles at $\phi = 0$ and $\phi = 1/2$.
4. Plot the radially averaged axial concentration profiles $C_A(z)$ (i.e., $\phi(\lambda)$).

Solution

The dimensionless form of the equation describing flow, reaction, and dispersion was given in Equation (18-47)

$$\left(\frac{L}{R}\right) \frac{1}{Pe_r} \left[\frac{1}{\phi} \frac{\partial \left(\phi \frac{\partial \psi}{\partial \phi} \right)}{\partial \phi} \right] + \frac{1}{Pe_r} \frac{d^2 \psi}{d\lambda^2} - 2(1 - \phi^2) \frac{d\psi}{d\lambda} - Da_n \psi^n = 0 \quad (18-47)$$

Boundary and Initial Conditions

A. Boundary conditions

1. Radial

1. At $r = 0$, we have symmetry $\partial C_i / \partial r = 0$; in dimensionless form,

$$\partial \psi / \partial \lambda = 0 \text{ at } \phi = 0 \quad (\text{E18-3.1})$$

2. There is no mass flow through the tube walls therefore $\partial C_i / \partial_r = 0$, at $r = R$, in dimensionless form

$$\partial \psi / \partial \lambda = 0 \text{ at } \phi = 1 \quad (\text{E18-3.2})$$

3. Radially averaged axial concentration is given by

$$\bar{C}_A(z) = \frac{\int_0^R 2\pi r C_A(z, r) dr}{\pi R^2}$$

2. Axial

1. At the entrance to the reactor $z = 0$, $\lambda = 0$ for all r (i.e., ϕ)

$$C_i = C_{i0}, \text{ (i.e., } \psi = 1 \text{ for all } \phi) \quad (\text{E18-3.3})$$

COMSOL

2. At the exit of the reactor $z = L$, i.e., $\lambda = 1$

$$\frac{\partial C_i}{\partial z} = 0 \text{ and therefore } \frac{\partial \psi}{\partial \lambda} = 0 \quad (\text{E18-3.4})$$

#COMSOL

Equation (18-47) and Equations (E18-3.1)–(E18-3.4) were solved using COMSOL. Go to the COMSOL module

(<http://www.umich.edu/~elements/6e/18chap/obj.html#/comsol/>) and run the module and find the following surface plots and profiles. It will really be a great experience for you.

A COMSOL tutorial for this example is given on the Web site in the LEP section for Chapter 18.

The results for a reactor of length 4 m from running the COMSOL simulation are shown in Figure E18-3.1(a), (b), (c), and (d).

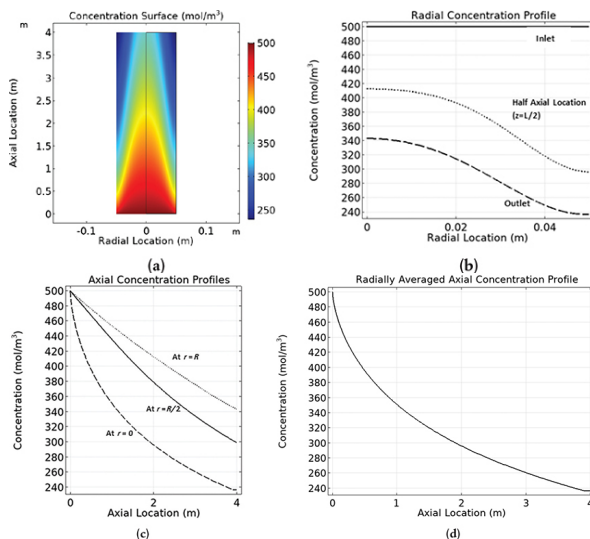


Figure E18-3.1 COMSOL output for laminar flow in the reactor.

In Figure E18-3.1(b) we observe a concentration profiles at the entrance, halfway down the reactor and at the end of the reactor.

Figure E18-3.1(c) shows the axial concentration at different radius while Figure E18-3.1(d) shows the radially averaged axial concentration profile $\bar{C}_A(z)$.

Analysis: We observe in Figure E18-3.1(a) and (b) that the concentration profile is flat (plug flow like) at the reactor entrance and then develops into a parabolic shape. This profile shape remains approximately the same from the halfway point until the fluid exits the reactor. In Figure E18-3.1(c) the steepest axial profile was near the wall. One notes the axial profile in Figure E18-3.1(c) is similar to the radial averaged concentration profile shown in Figure E18-3.1(d). Why do you think they are similar?

18.7 NONISOTHERMAL FLOW WITH RADIAL AND AXIAL VARIATIONS IN A TUBULAR REACTOR

In the previous sections, we have assumed that there were no radial variations in temperature in the tubular and packed-bed reactors. In this section, we will consider the nonisothermal case where we have both axial and radial variations in the system variables. Here, we will again use COMSOL for solving partial differential equation such as shown in the Radial Effects COMSOL Web Module on the CRE Web site (http://umich.edu/~elements/6e/web_mod/radialeffects/index.htm).¹³

¹³ An introductory webinar on COMSOL can be found on the AIChE webinar Web site: <http://www.aiche.org/resources/chemeondemand/webinars/modeling-non-ideal-reactors-and-mixers>.

COMSOL application

We are going to carry out differential mole and energy balances on the differential cylindrical annulus shown in Figure 18-12.

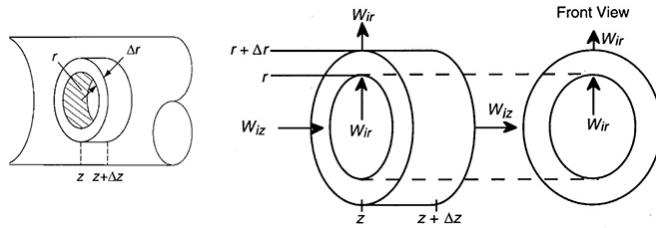


Figure 18-12 Cylindrical shell of thickness Δr , length Δz , and volume $2\pi r \Delta r \Delta z$.

18.7.1 Molar Flux

In order to derive the governing equations, we need to define a couple of terms. The first is the molar flux of species i , W_i ($\text{mol}/\text{m}^2 \cdot \text{s}$). The molar flux has two components, the radial component, W_{ir} , and the axial component, W_{iz} .

The molar flow rates are just the product of the molar fluxes and the cross-sectional areas normal to their direction of flow A_{cz} . For example, for species i flowing in the axial (i.e., z) direction

$$F_{iz} = W_{iz} A_{cz}$$

where W_{iz} is the molar flux in the axial z direction ($\text{mol}/\text{m}^2/\text{s}$), and A_{cz} (m^2) is the cross-sectional area of the tubular reactor.

In [Chapter 14](#) we discussed the molar fluxes in some detail, but for now let's just say they consist of a diffusional component, $-D_e(\partial C_i/\partial z)$, and a convective-flow component, $U_z C_i$, so that the flux W_{iz} in the axial direction is

$$W_{iz} = -D_e \frac{\partial C_i}{\partial z} + U_z C_i \quad (14-8a)$$

where D_e is the effective diffusivity (or dispersion coefficient) (m^2/s), and U_z is the axial molar average velocity (m/s).

Similarly, the flux W_{ir} in the radial direction, r , is

$$W_{ir} = -D_e \frac{\partial C_i}{\partial r} + U_r C_i \quad (18-48)$$

Radial direction

where U_r (m/s) is the average velocity in the radial direction. For now, we will neglect the velocity in the radial direction, that is, $U_r = 0$.

We first recall the mole balance for cylindrical coordinates in Chapter 14.

$$\left[-\frac{1}{r} \frac{\partial(rW_{ir})}{\partial r} - \frac{\partial W_{iz}}{\partial z} + r_i = 0 \right] \quad (14-2)$$

Using Equations (14-8b) and (18-48) to substitute for W_{iz} and W_{ir} in Equation (14-2) and then setting the radial velocity to zero, $U_r = 0$, we obtain

$$-\frac{1}{r} \frac{\partial}{\partial r} \left[\left(-D_e \frac{\partial C_i}{\partial r} r \right) \right] + \left(-\frac{\partial}{\partial z} \left[-D_e \frac{\partial C_i}{\partial z} + U_z C_i \right] \right) + r_i = 0 \quad (18-49)$$

For steady-state conditions and assuming U_z does not vary in the axial direction

$$\left[D_e \frac{\partial^2 C_i}{\partial r^2} + \frac{D_e}{r} \frac{\partial C_i}{\partial r} + D_e \frac{\partial^2 C_i}{\partial z^2} - U_z \frac{\partial C_i}{\partial z} + r_i = 0 \right] \quad (18-50)$$

18.7.2 Energy Flux

When we applied the first law of thermodynamics to a reactor to relate either temperature and conversion or molar flow rates and concentration, we arrived at Equation (11-10). Neglecting the work term we have for steady-state conditions

$$\underbrace{\dot{Q}}_{\text{Conduction}} + \underbrace{\sum_{i=1}^n F_{i0} H_{i0} - \sum_{i=1}^n F_i H_i}_{\text{Convection}} = 0 \quad (18-51)$$

In terms of the molar fluxes, $\mathbf{F}_i = \mathbf{W}_i A_C$, the cross-sectional area, A_C , and $(q = \dot{Q}/A_c)$

$$A_c [q + (\sum W_{i0} H_{i0} - \sum W_i H_i)] = 0 \quad (18-52)$$

The \mathbf{q} term is the heat added to the system and almost always includes a conduction component of some form. We now define an **energy flux vector, \mathbf{e}** , ($\text{J/m}^2 \cdot \text{s}$), to include both the conduction and convection of energy.

\mathbf{e} = energy flux $\text{J/s} \cdot \text{m}^2$

\mathbf{e} = Conduction + Convection

$$\left[\mathbf{e} = q + \sum W_i H_i \right] \quad (18-53)$$

where the conduction term \mathbf{q} ($\text{kJ/m}^2 \cdot \text{s}$) is given by Fourier's law. For axial and radial conduction, Fourier's laws are

$$q_z = -k_e \frac{\partial T}{\partial z} \quad \text{and} \quad q_r = k_e \frac{\partial T}{\partial r}$$

where k_e is the thermal conductivity ($\text{J/m} \cdot \text{s} \cdot \text{K}$). The energy transfer (flow) is the flux vector times the cross-sectional area, A_c , normal to the energy flux

$$\text{Energy flow} = \mathbf{e} \cdot A_c$$

18.7.3 Energy Balance

Using the energy flux, e , to carry out an energy balance on our annulus (Figure 12-15) with system volume $2\pi r \Delta r \Delta z$, we have

$$(\text{Energy flow in at } r) = e_r A_{cr} = e_r \cdot 2\pi r \Delta z$$

$$(\text{Energy flow in at } z) = e_z A_{cz} = e_z \cdot 2\pi r \Delta r$$

$$\left(\begin{array}{c} \text{Energy flow} \\ \text{in at } r \end{array} \right) - \left(\begin{array}{c} \text{Energy flow} \\ \text{out at } r + \Delta r \end{array} \right) + \left(\begin{array}{c} \text{Energy flow} \\ \text{in at } z \end{array} \right) + \left(\begin{array}{c} \text{Energy flow} \\ \text{out at } z + \Delta z \end{array} \right) = \left(\begin{array}{c} \text{Accumulation} \\ \text{of energy in} \\ \text{volume } (2\pi r \Delta r \Delta z) \end{array} \right)$$

$$(e_r 2\pi r \Delta z)|_r - (e_r 2\pi r \Delta z)|_{r+\Delta} + e_z 2\pi r \Delta r|_z - e_z 2\pi r \Delta r|_{z+\Delta} = 0$$

Dividing by $2\pi r \Delta r \Delta z$ and taking the limit as Δr and $\Delta z \rightarrow 0$

$$\boxed{-\frac{1}{r} \frac{\partial(r e_r)}{\partial r} - \frac{\partial e_z}{\partial z} = 0} \quad (18-54)$$

The radial and axial energy fluxes are

$$e_r = q_r + \Sigma W_{ir} H_i$$

$$e_z = q_z + \Sigma W_{iz} H_i$$

Substituting for the energy fluxes, e_r and e_z

$$-\frac{1}{r} \frac{\partial[r(q_r + \Sigma W_{ir} H_i)]}{\partial r} - \frac{\partial[q_z + \Sigma W_{iz} H_i]}{\partial z} = 0 \quad (18-55)$$

and expanding the convective energy fluxes, $\Sigma W_i H_i$,

$$\text{Radial: } \frac{1}{r} \frac{\partial}{\partial r} (r \Sigma W_{ir} H_i) = \frac{1}{r} \Sigma H_i \frac{\partial(r W_{ir})}{\partial r} + \underbrace{\Sigma W_{ir} \frac{\partial H_i}{\partial r}}_{\text{Neglect}} \quad (18-56)$$

$$\text{Axial: } \frac{\partial(\Sigma W_{iz} H_i)}{\partial z} = \Sigma H_i \frac{\partial W_{iz}}{\partial z} + \Sigma W_{iz} \frac{\partial H_i}{\partial z} \quad (18-57)$$

Because U_r and the gradient in the flux term W_{ir} are small, we can neglect the last term in Equation (18-56) with regard to the

other terms in the equation. Substituting Equations (18-56) and (18-57) into Equation (18-55), we obtain upon rearrangement

$$-\frac{1}{r} \frac{\partial(rq_r)}{\partial r} - \frac{\partial q_z}{\partial z} - \sum H_i \overbrace{\left(\frac{1}{r} \frac{\partial(rW_{ir})}{\partial r} + \frac{\partial W_{iz}}{\partial z} \right)}^{r_i} - \sum W_{iz} \frac{\partial H_i}{\partial z} = 0$$

Recognizing that the term in brackets is related to Equation (14-2) and is just the rate of formation of species i , r_i , for steady-state conditions we have

$$\left[-\frac{1}{r} \frac{\partial}{\partial r} (rq_r) - \frac{\partial q_z}{\partial z} - \sum H_i r_i - \sum W_{iz} \frac{\partial H_i}{\partial z} \right] = 0 \quad (18-58)$$

Recalling

$$q_r = -k_e \frac{\partial T}{\partial r}, q_z = -k_e \frac{\partial T}{\partial z}, \frac{\partial H_i}{\partial z} = C_{P_i} \frac{\partial T}{\partial z},$$

and

$$r_i = v_i (-r_A) \\ \sum r_i H_i = \sum v_i H_i (-r_A) = \Delta H_{R_x} r_A$$

we have the energy in the form

$$\left[\frac{k_e}{r} \left[\frac{\partial}{\partial r} \left(\frac{r \partial T}{\partial r} \right) \right] + k_e \frac{\partial^2 T}{\partial z^2} + \Delta H_{R_x} r_A - \left(\sum W_{iz} C_{P_i} \right) \frac{\partial T}{\partial z} \right] = 0 \quad (18-59)$$

where W_{iz} is given by Equation (14-8a). Equation (18-59) would be coupled with the *mole balance* (Equation (18-50)), *rate law*, and *stoichiometric* equations to solve for the radial and axial concentration gradients. However, a great amount of computing time would be required. Let's see if we can make some approximations to simplify the solution.

Some Initial Approximations

Assumption 1. Neglect the diffusive term in the axial direction, wrt, the convective term in Equation (14-8a) in the expression involving heat capacities

$$\sum C_{P_i} W_{iz} = \sum C_{P_i} (0 + U_z C_i) = \sum C_{P_i} C_i U_z$$

With this assumption, Equation (18-59) becomes

$$\left[\frac{k_e}{r} \frac{\partial}{\partial r} \left(\frac{r \partial T}{\partial r} \right) + k_e \frac{\partial^2 T}{\partial z^2} + \Delta H_{R_x} r_A - (U_z \sum C_{P_i} C_i) \frac{\partial T}{\partial z} \right] = 0 \quad (18-60)$$

For laminar flow, the velocity profile is

$$U_z = 2U_0 \left[1 - \left(\frac{r}{R} \right)^2 \right] \quad (18-61)$$

where U_0 is the average velocity inside the reactor.

Energy balance with radial and axial gradients

Assumption 2. Assume that the sum

$C_{P_m} = \Sigma C_{P_i} C_i = C_{A0} \Sigma \Theta_i C_{P_i}$ is constant. The energy balance now becomes

$$k_e \frac{\partial^2 T}{\partial z^2} + \frac{k_e}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \Delta H_{Rx} r_A - U_z C_{P_m} \frac{\partial T}{\partial z} = 0 \quad (18-62)$$

Equation (18-61) is the form we will use in our COMSOL problem. In many instances, the term C_{P_m} is just the product of the solution density (kg/m^3) and the heat capacity of the solution ($\text{kJ/kg} \cdot \text{K}$).

Coolant Balance

We also recall that a balance on the coolant gives the variation of coolant temperature with axial distance where U_{ht} is the overall heat transfer coefficient and R is the reactor wall radius

$$\dot{m}_c C_{P_c} \frac{\partial T_a}{\partial z} = U_{ht} 2\pi R [T(R, z) - T_a] \quad (18-63)$$

Boundary and Initial Conditions

A. Initial conditions *if* other than steady state (not considered here) $t = 0$, $C_i = 0$, $T = T_0$, for $z > 0$ all r

B. Boundary conditions

1. Radial

1. At $r = 0$, we have symmetry $\partial T / \partial r = 0$ and $\partial C_i / \partial r = 0$.
2. At the tube wall, $r = R$, the temperature flux to the wall on the reaction side equals the convective flux out of the reactor into the shell side of the heat exchanger.

$$-k_e \frac{\partial T}{\partial r} \Big|_R = U (T(R, z) - T_a)$$
3. There is no mass flow through the tube walls $\partial C_i / \partial r = 0$ at $r = R$

2. Axial

1. At the entrance to the reactor $z = 0$

$$T = T_0 \text{ and } C_i = C_{i0}$$
2. At the exit of the reactor $z = L$

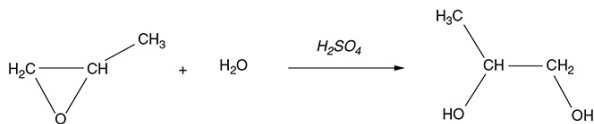
$$\frac{\partial T}{\partial z} = 0 \text{ and } \frac{\partial C_i}{\partial z} = 0$$

The preceding equations were used to describe and analyze flow and reaction in a tubular reactor with heat exchange as described in the following example, which can be found in the Expanded Material on the CRE Web site

(<http://www.umich.edu/~elements/6e/12chap/expanded.html>).

What follows is only a brief outline of that example with a few results from the output of the COMSOL program.

Example 18–4 Tubular Reactor with Axial and Radial Temperature and Concentration Gradients



The liquid phase reaction was analyzed using COMSOL to study both axial and radial variations, and the details can be found on the home page of the CRE Web site, www.umich.edu/~elements/6e/index.html, by clicking on the *Additional Material* for Chapter 18. The algorithm for this example can be found on the Web site: (http://umich.edu/~elements/6e/18chap/expanded_ch18_radial.pdf). Web Figure E12-8.1 is a screen shot from COMSOL of the base case reactor and reaction parameters. In the COMSOL LEP you are asked “What if...” questions about varying the base case parameters. Typical radial (a) and axial (b) temperature profiles for this example are shown in Figure E18-4.1.

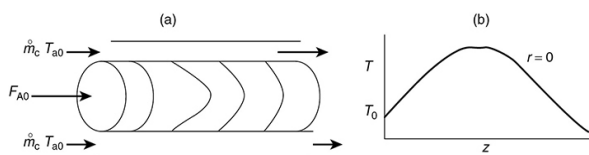


Figure E18-4.1 Radial (a) and axial (b) temperature profiles.

Results. The graphical solutions to the COMSOL code are shown in Figure E18-4.2.

Results of the COMSOL simulation

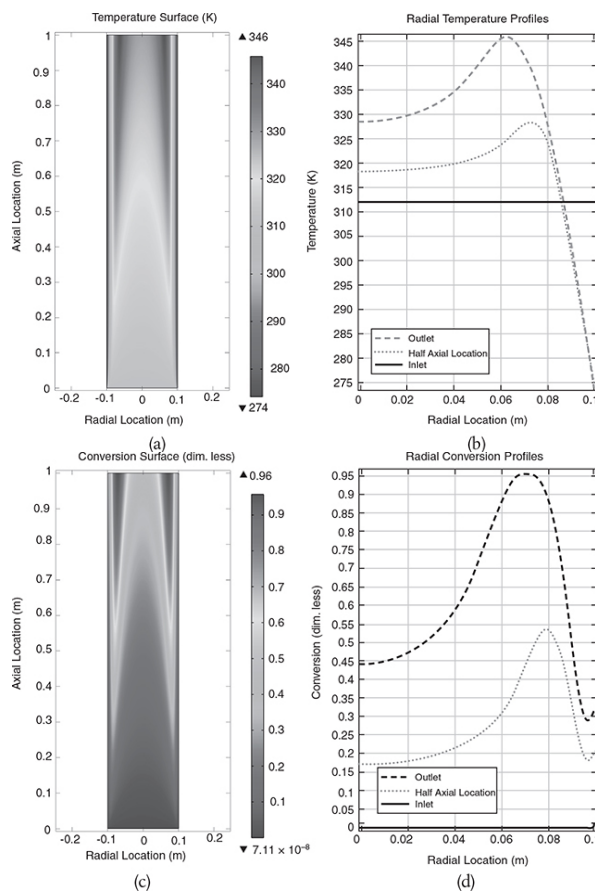


Figure E18-4.2 (a) Temperature surface, (b) temperature surface profiles, (c) conversion surface, and (d) radial profile.

COMSOL

The volumetric flow rate of water is 3.5 times the volumetric flow rate of the mixture of propylene oxide in methanol. Further details of this example are provided in the Chapter 12 Additional Material on the CRE Web site: (http://umich.edu/~elements/6e/software/software_comsol.html).

Analysis: One can observe from the temperature surface plot in Figure E18-4.2(a) how the temperature changes both axially and radially in the reactor from its entering temperature of 312 K. These same profiles can be found in *color* on the CRE Web site in the Web Modules. Be sure to note the predicted maximum and minimum in the temperature and conversion profiles in

Figure E18-4.2(a) to (d). Near the wall, the temperature of the mixture is lower because of the cold wall temperature, which is cooled by the jacket. Consequently, the reaction rate will be lower, and thus the conversion will be lower. However, right next to the wall the flow velocity through the reactor is almost zero, due to the friction with the wall, so the reactants spend a longer time in the reactor; therefore, a greater conversion is achieved, as noted by the upturn right next to the wall.

CRE Web Site—COMSOL

In this interactive Web site and text, you will be able to use the LEP COMSOL program instead of having to write your own code. The CRE LEP COMSOL modules are shown in Figure 18-13. To access these LEPs, you don't need to have COMSOL installed on your computer as you can access it through the CRE Web site. We use the COMSOL codes in a similar manner to the Polymath LEPs where you are able to vary the parameters to explore the radial variations in temperature, conversion, and concentration, in addition to axial profiles.

COMSOL

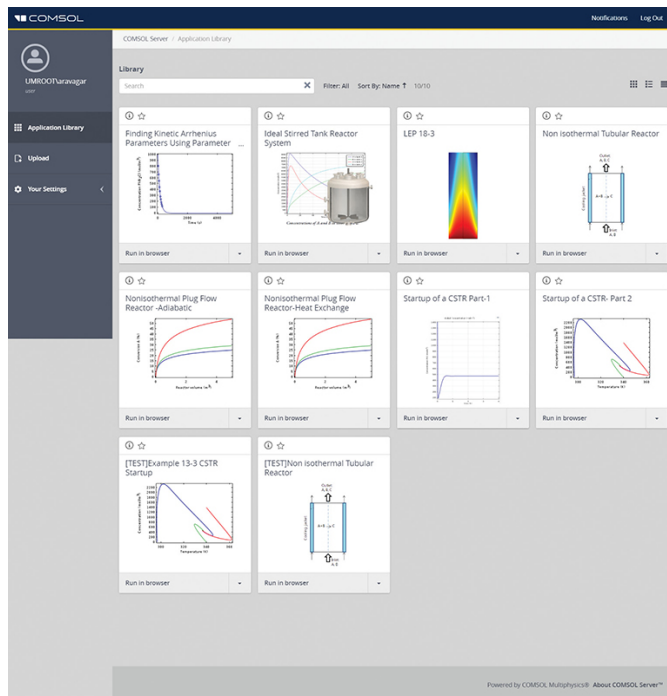


Figure 18-13 COMSOL LEP Modules.

18.8 TWO-PARAMETER MODELS— MODELING REAL REACTORS WITH COMBINATIONS OF IDEAL REACTORS

Creativity and engineering judgment are necessary for model formulation.

A tracer experiment is used to evaluate the model parameters.

We now will see how a real reactor might be modeled by different combinations of ideal reactors. There are an almost unlimited number of combinations that could be made. However, if we limit the number of adjustable parameters to two (e.g., bypass flow rate, v_b , and dead volume, V_D), the situation becomes much more tractable. After reviewing the steps in [Table 18-1](#), choose a model and determine whether it is reasonable by qualitatively comparing it with the RTD and, if it is, determine the model parameters. Usually, the simplest means of obtaining the necessary data is some form of a tracer test. These tests have been described in [Chapters 16 and 17](#), together with their uses in determining the RTD of a reactor system. Tracer tests can be used to determine the RTD, which can then be used in a similar manner to determine the suitability of the model and the value of its parameters.

In determining the suitability of a particular reactor model and the parameter values from tracer tests, it may not be necessary to calculate the RTD function $E(t)$. The model parameters (e.g., V_D) may be acquired directly from measurements of effluent concentration in a tracer test. The theoretical prediction of the particular tracer test in the chosen model system is compared with the tracer measurements from the real reactor. The parameters in the model are chosen so as to obtain the closest possible agreement between the model and experiment. If the agreement is then sufficiently close, the model is deemed reasonable. If not, another model must be chosen.

What is sufficiently close?

The quality of the agreement necessary to fulfill the criterion “*sufficiently close*” again depends on creativity in developing the model and on engineering judgment. The most extreme

demands are that the maximum error in the prediction not exceed the estimated error in the tracer test, and that there be no observable trends with time in the difference between prediction (the model) and observation (the real reactor). In the *Expanded Material* on the CRE Web site, we illustrate how the modeling is carried out. We will now consider two different models for a CSTR: first, a CSTR with a dead zone and bypassing; and second, a CSTR model as two CSTR in interchange. In each of these cases, we will first show how to model the system with two adjustable parameters α and β and then show how to calculate the exit conversion on concentrations.

18.8.1 Real CSTR Modeled Using Bypassing and Dead Space

A real CSTR is believed to be modeled as a combination of an ideal CSTR with a well-mixed volume V_s , a dead zone of volume V_d , and a bypass with a volumetric flow rate v_b (Figure 18-14). We have used a tracer experiment to evaluate the parameters of the model V_s and v_s . Because the total volume and volumetric flow rate are known, once V_s and v_s are found, v_b and V_d can readily be calculated.

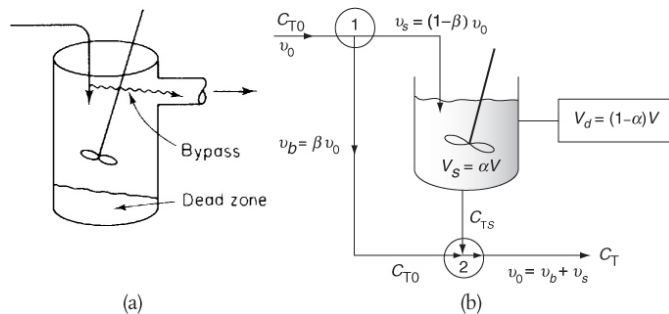


Figure 18-14 (a) Real system; (b) model system.

The model system

18.8.1 A Solving the Model System for C_A and X

The bypass stream and effluent stream from the reaction volume are mixed at the junction point 2. From a balance on species A around this point

$$[\text{In}] = [\text{Out}]$$

$$v_0 C_A = (v_b + v_s) C_A = C_{A0} v_b + C_{As} v_s = C_{A0} v_0 \beta + C_{As} v_0 (1 - \beta) \quad (18 - 64)$$

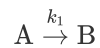
The Duct Tape Council of Jofostan would like to point out the new wrinkle: **The Junction Balance.**

In the absence of reaction (e.g., tracer) the concentration exiting the system is

$$C_A = C_{A0} (1 - X) \quad (18-65)$$

where we will let $\alpha = V_s / V$ and $\beta = v_b / v_0$.

We will use this model to calculate the conversion for the first-order reaction



A mole balance on the well-mixed volume V_s gives

$$v_s C_{A0} - v_s C_{As} - k C_{As} V_s = 0$$

Mole balance on CSTR

As shown in the extended material on the CRE Web site the exit concentration of species A in terms of α and β

$$\frac{C_A}{C_{A0}} = 1 - X = \beta + \frac{(1-\beta)^2}{(1+\beta) + \alpha \tau k} \quad (18-66)$$

Conversion as a function of model parameters

We have used the ideal reactor system shown in [Figure 18-14](#) to predict the conversion in the real reactor (i.e., Equation (18-66)). The model has two parameters, α and β . The parameter α is the dead zone volume fraction and parameter β is the fraction of the volumetric flow rate that bypasses the reaction zone. If these parameters are known, we can readily predict the conversion. In the following section, we shall see how we can use tracer experiments and RTD data to evaluate the model parameters.

Model system

If we were to inject a positive step tracer into the system shown in [Figure 18-14](#), the unsteady-state tracer balance in a well-mixed reactor value V_s is

In – out = accumulation

$$v_s C_{T0} - v_s C_{Ts} = \frac{dN_{Ts}}{dt} = V_s \frac{dC_{Ts}}{dt} \quad (18-67)$$

Tracer balance for step input

The conditions for the positive-step input are

$$\begin{aligned} \text{At } t < 0 \quad C_T &= 0 \\ \text{At } t \geq 0 \quad C_T &= C_{T0} \end{aligned}$$

Solving the tracer balance equations and using a balance around junction point 2, we arrive at the following equation relating C_T and t :

$$\frac{C_T}{C_{T0}} = 1 - (1 - \beta) \exp \left[-\frac{1-\beta}{\alpha} \left(\frac{t}{\tau} \right) \right] \quad (18-68)$$

Example 18–5 Using a Tracer to Determine the Model Parameters in a CSTR with Dead Space and Bypass Model

The following tracer concentration time data was obtained from a step input to the system in Figure 18-14.

TABLE E18-5.1 TRACER DATA FOR STEP INPUT

C_T (mg/dm ³)	1000	1333	1500	1666	1750	1800
t (min)	4	8	10	14	16	18

The entering tracer concentration is $C_{T0} = 2000$ mg/dm³.

1. Determine the model parameters α and β where $\alpha = V_s/V$ and $\beta = v_b/v_0$.
2. Determine the conversion for a second-order reaction with $C_{A0} = 2$ kmol/m³, $\tau = 10$ min, and $k = 0.28$ m³/kmol · min.

Solution

1. Calculating α and β

The model parameters, α and β , are obtained either by regression (Polymath/ MATLAB/Excel) or from the proper plot of the effluent tracer concentration as a function of time. Rearranging Equation (18-68) yields

$$\ln \frac{C_{T0}}{C_{T0} - C_T} = \ln \frac{1}{1 - \beta} + \left(\frac{1 - \beta}{\alpha} \right) \frac{t}{\tau} \quad (\text{E18-5.1})$$

Consequently, using Table E18-5.1 we plot $\ln[C_{T0}/(C_{T0} - C_T)]$ as a function of t . If our model is correct, a straight line should result with a slope of $(1 - \beta)/\tau\alpha$ and an intercept of $\ln[1/(1 - \beta)]$.

TABLE E18-5.2 TRACER DATA FOR STEP INPUT

C_T (mg/dm ³)	1000	1333	1500	1666	1750	1800
$\frac{C_{T0}}{C_{T0} - C_T}$	2	3	4	6	8	10
t (min)	4	8	10	14	16	18

When this data is regressed using Equation (E18-5.1), we obtain

$$\alpha = 0.7 \text{ and } \beta = 0.2$$

$$\tau_s = \frac{V_s}{v_s} = \frac{\alpha V}{(1-\beta)v_0} = \frac{\alpha\tau}{(1-\beta)} = \frac{(0.7)(10 \text{ min})}{(1-0.2)} = 8.7 \text{ min}$$

2. Calculating the Conversion

We now can proceed applying our algorithm to this system. A mole balance on reactor V_s gives

$$v_s C_{A0} - v_s C_A - k C_A^2 V_s = 0 \quad (\text{E18-5.2})$$

For a second-order reaction

$$-r_A = k C_A^2 \text{ with } k = \frac{0.28 \text{ m}^3}{\text{kmol} \cdot \text{min}}$$

The exit concentration is

$$C_A = \beta C_{A0} + (1 - \beta) C_{As} \quad (\text{E18-5.3})$$

$$C_{As} = \frac{-1 + \sqrt{1 + 4\tau_s k C_{A0}}}{2\tau_s k} \quad (\text{E18-5.4})$$

Substituting parameter values we found that the exit concentration and the conversion predicted in the real (nonideal) reactor are

$$C_A = 0.979 \text{ kmol/m}^3 \text{ and}$$

$$X_{\text{model}} = 0.51$$

$$X_{\text{model}} = 0.51$$

$$X_{\text{ideal}} = 0.66$$

Using the same rate-law parameter values for or an *ideal* CSTR we find

$$C_A = 0.685 \text{ kmol/m}^3 \text{ and}$$

$$X_{\text{ideal}} = 0.66$$

Analysis: In this example we used a combination of an ideal CSTR with a dead volume and bypassing to model a nonideal reactor. If the nonideal reactor behaved as an ideal CSTR, a conversion of 66% was expected. Because of the dead volume, not all the space would be available for reaction; also, some of the fluid did not enter the space where the reaction was taking place and, as a result, the conversion in this nonideal reactor was only 51%.

Other Models. In Section 18.8.1 it was shown how we formulated a model consisting of ideal reactors to represent a real reactor. First, we solved for the exit concentration and conversion for our model system in terms of two parameters, α and β . We next evaluated these parameters from data on tracer concentration as a function of time. Finally, we substituted these parameter values into the mole balance, rate law, and stoichiometric equations to predict the conversion in our real reactor.

To reinforce this concept, we will use one more example (yes, just one more, as given in **Example 18-6**).

18.8.2 Real CSTR Modeled as Two CSTRs with Interchange

In this particular model there is a highly agitated region in the vicinity of the impeller; outside this region, there is a region with less agitation (**Figure 18-15**). There is considerable material transfer between the two regions. Both inlet and outlet flow channels connect to the highly agitated region. We shall model the highly agitated region as one CSTR, the quieter region as another CSTR, with material transfer between the two.

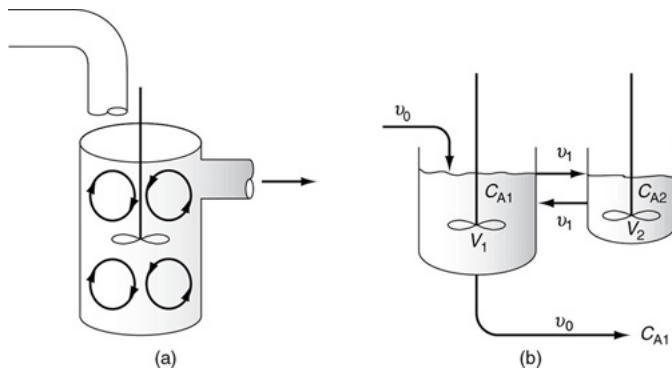


Figure 18-15 (a) Real reaction system; (b) model reaction system.

The model system

18.8.2 A Solving the Model System for C_A and X

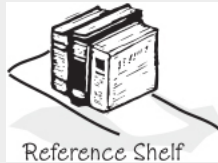
Let β represent that fraction of the total flow that is exchanged between reactors 1 and 2; $v_1 = v_2 = \beta v_0$ and let α represent that fraction of the total volume, V , occupied by the highly agitated region $V_1 = \alpha V$:

The space time is measured as the real reactor volume V divided by the total volumetric flow rate v_0 .

$$\tau = \frac{V}{v_0} = \frac{V_1 + V_2}{v_0}$$

As shown on the CRE Web site *Professional Reference Shelf* R18.2, for a first-order reaction, the exit concentration and conversion are

$$C_{A1} = \frac{C_{A0}}{1 + \beta + \alpha\tau k - \{\beta^2 / [\beta + (1 - \alpha)\tau k]\}} \quad (18-69)$$



and

$$X = 1 - \frac{C_{A1}}{C_{A0}} = \frac{(\beta + \alpha\tau k) [\beta + (1 + \alpha)\tau k] - \beta^2}{(1 + \beta + \alpha\tau k) [\beta + (1 - \alpha)\tau k] - \beta^2} \quad (18-70)$$

where C_{A1} is the reactor concentration exiting the first reactor in Figure 18-15(b).

Conversion for two-CSTR model

18.8.2B Using a Tracer to Determine the Model Parameters in a CSTR with an Exchange Volume

The problem now is to evaluate the parameters α and β using the RTD data. C_{T1} is the measured tracer concentration exiting the real reactor. The tracer is initially dumped only into reactor 1, so that the initial conditions $C_{T10} = N_{T0}/V_1$ and $C_{T20} = 0$.

Using a tracer balance in reactors 1 and 2 in terms of α , β , and τ , we arrive at two coupled differential equations describing the unsteady behavior of the tracer that must be solved simultaneously.

$$\tau\alpha \frac{dC_{T1}}{dt} = \beta C_{T2} - (1 + \beta)C_{T1} \quad (18-71)$$

$$\tau(1-\alpha)\frac{dC_{T2}}{dt} = \beta C_{T1} - \beta C_{T2} \quad (18-72)$$

See Appendix A.3 for method of solution.

Analytical solutions to Equations (18-71) and (18-72) are given on the CRE Web site, in Appendix A.3 and in Equation (18-73), below. However, for more complicated systems, analytical solutions to evaluate the system parameters may not be possible.

$$\left(\frac{C_{T1}}{C_{T10}}\right)_{\text{pulse}} = \frac{(\alpha m_1 + \beta + 1)e^{m_2 t/\tau} - (\alpha m_2 + \beta + 1)e^{m_1 t/\tau}}{\alpha(m_1 - m_2)} \quad (18-73)$$

where

$$m_1, m_2 = \left[\frac{1-\alpha+\beta}{2\alpha(1-\alpha)} \right] \left[-1 \pm \sqrt{\frac{4\alpha\beta(1-\alpha)}{(1-\alpha+\beta)^2}} \right]$$

Example 18-6 CSTR with Interchange

A pulse trace test was carried out on the model system shown in Figure 18-15

(http://www.umich.edu/~elements/6e/18chap/Ch18_Web-Additional%20Material.pdf) with

$$C_{T0} = 2000 \text{ mg/dm}^3 \text{ and } \tau = \frac{V}{v_0} = \frac{1000 \text{ dm}^3}{25 \text{ dm}^3/\text{min}} = 40 \text{ min}$$

, and the results are shown in Table E18-6.1.

TABLE E18-6.1 TRACER DATA FOR PULSE INPUT

t (min)	0 . 0	2 0	4 0	6 0	8 0	1 2 0	16 0	20 0	2 4 0	28 0	3 2 0
$\theta =$ t/τ	0 . 0	0. 5	1 . 0	1 . 5	2 . 0	3 . 0	4. 0	5. 0	6. 0	7.0	8. 0
C	2 0 0 0	1 0 5 0	5 2 0	2 8 0	1 6 0	6 1	29	16 .4	1 0. 0	6.4	4. 0
C/C_1 0	1 . 0	0. 5	0 2	0 1	0 0	0 0	0. 01 45	0. 00 82	0. 0	0.0 2	0. 0 0

Solving for α

$$\alpha = \frac{1}{C_{10}} \int_0^\infty C(\theta) d\theta = \int_0^\infty \frac{C(\theta)}{C_{10}} d\theta \quad (\text{E18-6.2})$$

We see that α is just the area under the curve $C(\theta)$ in Figure E18-6.1 divided by C_{10} .

Evaluating the area we obtain

$$\alpha = 0.80$$

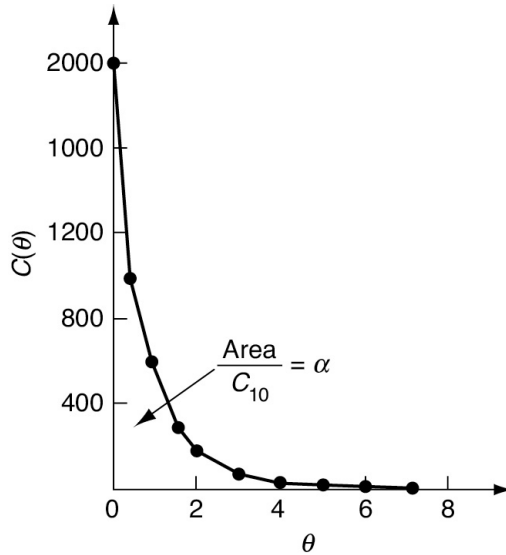


Figure E18-6.1 Dimensionless tracer concentration as a function of dimensionless time.

As shown on the Web site (http://www.umich.edu/~elements/6e/18chap/Ch18_WebAdditonal%20Material.pdf) that by plotting the ratio $C(t)/C_{10}$ as a function of θ on semi-log coordinates, we get the graph shown on the Web site in Figure Web E18-1.3. At long times, in Equation (18-73) the first term containing m_2 in the exponent is negligible with respect to the second term. Consequently, if we extrapolate the portion of the curve for long times back to $\theta = 0$, we have

$$\text{Intercept} = I = -\frac{\alpha m_2 + \beta + 1}{\alpha(m_1 - m_2)} = 0.66 \quad (\text{Web E18-2.4})$$

The values of m_1 and m_2 are obtained from Figure Web E18-1.3.

$$0.066 = \frac{-(0.8)(-1.44) + \beta + 1}{(0.8)[-0.434 - (-1.44)]}$$

Two CSTRs with interchange

Solving for β , we obtain $\beta = 0.1$. The two parameters for this model are then

$$\alpha = 0.8 \text{ and } \beta = 0.1$$

$$\tau k = (40 \text{ min}) (0.03 \text{ min}^{-1}) = 1.2$$

2. Find the conversion for a first-order reaction

For two CSTRs with interchange, recall Equation (18-70)

$$X = 1 - \frac{C_{A1}}{C_{A0}} = \frac{(\beta + \alpha\tau k)[\beta + (1-\alpha)\tau k] - \beta^2}{(1 + \beta + \alpha\tau k)[\beta + (1-\alpha)\tau k] - \beta^2} \quad (18-70)$$

Using regression we find

$$\alpha = 0.8$$

$$\beta = 0.1$$

We now substitute α , β , τk into Equation (18-70), and as also shown on the CRE Web site, Substituting for τk , α and β in Equation (18-69) yields

$$\frac{C_A}{C_{A0}} = 1 - X \frac{1}{1 + \beta + \alpha\tau k - \frac{\beta^2}{\beta + (1-\alpha)\tau k}} \quad (E18-6.3)$$

$$1 - X = \frac{1}{1 + 0.1 + \left(0.8\right)\left(1.2\right) - \frac{(0.1)^2}{0.1 + (1-0.8)(1.2)}} \quad (E18-6.4)$$

$$X = 0.51 \quad \text{Ans.}$$

3. Finding conversion in ideal CSTR and ideal PFR

For a single ideal CSTR,

$$X = \frac{\tau k}{1 + \tau k} = \frac{1.2}{2.2} = 0.55 \quad \text{Ans.}$$

For a single ideal PFR,

$$X = 1 - e^{-\tau k} = 1 - e^{-1.2} = 0.7 \quad \text{Ans.}$$

Two CSTRs with interchange

Comparing models, we find

$$(X_{\text{model}} = 0.51) < (X_{\text{CSTR}} = 0.55) < (X_{\text{PFR}} = 0.7)$$

Analysis: For the two-parameter model chosen, we used the RTD to determine the two parameters' to find the conversion X , i.e., those parameters were the fraction of the larger fluid volume $V_1 = \alpha V$ and the fraction β of fluid exchanged between the reactors, $v_1 = \beta v_0$. We next calculated the exit conversion using an ideal CSTR. The CRE algorithm was then applied to model the reactor system where the conversion was found to be 51%, which is smaller than that for an ideal CSTR ($x = 0.56$).

18.8.3 Other Models of Nonideal Reactors Using CSTRs and PFRs

Several reactor models have been discussed in the preceding pages. All are based on the physical observation that in almost all agitated tank reactors, there is a well-mixed zone in the vicinity of the agitator. This zone is usually represented by a CSTR. The region outside this well-mixed zone may then be modeled in various fashions. We have already considered the simplest models, which have the main CSTR combined with a dead-space volume; if some short-circuiting of the feed to the

outlet is suspected, a bypass stream can be added. The next step is to look at all possible combinations that we can use to model a nonideal reactor using only CSTRs, PFRs, dead volume, and bypassing. The rate of transfer between the two reactors is one of the model parameters. The positions of the inlet and outlet to the model reactor system depend on the physical layout of the real reactor.

Figure 18-16(a) describes a real PFR or PBR with channeling that is modeled as two PFRs/PBRs in parallel. The two parameters are the fraction of flow to the reactors (i.e., β and $(1 - \beta)$) and the fractional volume (i.e., α and $(1 - \alpha)$) of each reactor. Figure 18-16(b) describes a real PFR/PBR that has a backmix region and is modeled as a PFR/PBR in parallel with a CSTR. Figures 18-16(a) and (b) on page 973 show a real CSTR modeled as two CSTRs with interchange. In one case, the fluid exits from the top CSTR (a), and in the other case the fluid exits from the bottom CSTR (b). The parameter β represents the interchange volumetric flow rate, βv_0 , and α = the fractional volume of the top reactor, $\alpha = V/V_0$, where the fluid exits the reaction system. We note that the reactor in Figure 18-16(b) was found to describe extremely well a real reactor used in the production of terephthalic acid.¹⁴ A number of other combinations of ideal reactions can be found in Levenspiel.¹⁵

¹⁴ Proc. Indian Inst. Chem. Eng. Golden Jubilee, a Congress, Delhi, 1997, p. 323.

¹⁵ Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed. New York: Wiley, 1999, pp. 284–292.

A case history for terephthalic acid

Models for nonideal reactors

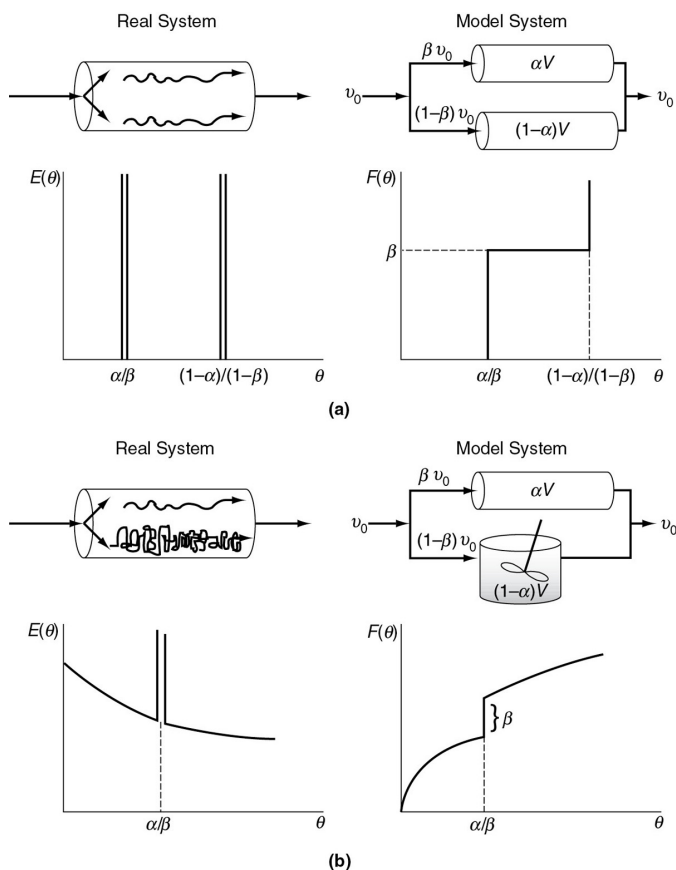


Figure 18-16 Combinations of ideal reactors used to model real tubular reactors: **(a)** two ideal PFRs in parallel; **(b)** ideal PFR and ideal CSTR in parallel.

18.8.4 Applications to Pharmacokinetic Modeling

The use of combinations of ideal reactors to model metabolism and drug distribution in the human body is becoming commonplace. For example, one of the simplest models for drug adsorption and elimination is similar to that shown in Figure 18-17(a). The drug is injected intravenously into a central compartment containing the blood (the top reactor). The blood distributes the drug back and forth to the tissue compartment (the bottom reactor) before being eliminated (top reactor). This model will give the familiar linear semi-log plot found in pharmacokinetics textbooks. As can be seen in Chapter 9, in the figure for *Professional Reference Shelf R9.8* on the CRE Web site on pharmacokinetics, and on pages 408–409, there are two different slopes, one for the drug distribution phase and one for the elimination phase.

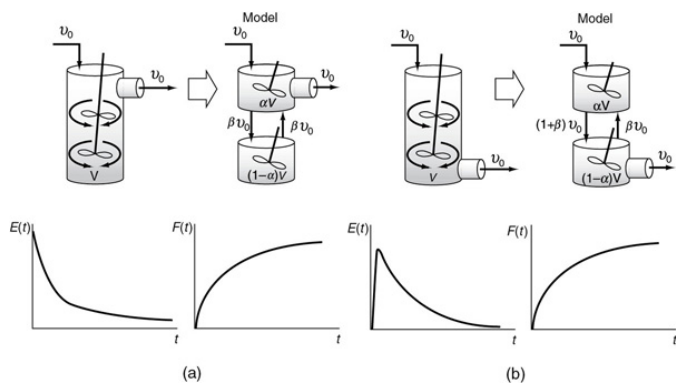


Figure 18-17 Combinations of ideal reactors to model a real CSTR. Two ideal CSTRs with interchange (a) exit from the top of the CSTR; (b) exit from the bottom of the CSTR.

18.9 AND NOW... A WORD FROM OUR SPONSOR—SAFETY 18 (AWFOS—S18 AN ALGORITHM FOR MANAGEMENT OF CHANGE (MOC))

As chemical engineers, it is important for us to understand the aspects of safety involved when we subject a process, plant equipment, or an operating procedure to a change. We must have the ability to look at not only what parameters improve as a result of this change but also at those which may be affected inadvertently and to take proper measures to minimize or at best, nullify the effect of these changes.

We must pay attention to how we define “change.” It is, “anything which is not a like-for-like replacement.”

True Case History

Actual Case History 1: John, Kötloff (Sven’s brother) head of Purchasing at Jofostan Chemical Co. (JCC) was contacted by a new company hoping to sell one of their raw materials to JCC at a cheaper price than their current supplier. They also assured him that they will deliver this highly hazardous liquid to their production facility in the same type of ISO tank (i.e., as per international standards) and with matching connection valves to unload the tank. John went ahead with the purchase without consulting the plant.

Epilogue: The first supply damaged the delivery gantry, because the new supplier used a higher trailer to carry the ISO tank.

Before reading further, let us define risk assessment. Risk assessment is the process of identifying all the possible consequences of an operation and evaluation of their hazards.

Proper and precise description of the change supported with crucial information along with all the paperwork is necessary in order to carry out risk assessment of the change. Before the change is made, the MoC system must identify possible effects and side-effects in order to assess the hazardous consequences and provide a risk assessment of the change.

Actual Case History 2 (Only the names have been changed):

In the early 70s, the Jofostan Mixers produced magnesium oxide (MgO) at one of their plants. The MgO was marketed under the name JofoNutri and was added as a nutritional supplement to the feed for dairy cows. The same plant also manufactured polybrominated biphenyls (PBBs) which were used as flame retardant under the name JofoFire.[†] Sometime in 1973, the paper bags containing JofoFire reached the complex producing dairy feed and was added by the plant operator to the dairy feed assuming that it was JofoNutri.

[†] M. Venier, A. Salamova, and R. A. Hites, "Halogenated flame retardants in the Great Lakes Environment," *Acc. Chem. Res.*, 48, 1853–1861 (2015).

Any activity that classifies as a "change" must go through the following, before implemented, as described in the third edition of "*Strategies for Creative Problem Solving*":

1. Make the **case for change**: identify the need for change and the stakeholders involved.
2. **Vision** for change: what will it be like, after the change?
3. What **skills** are needed to implement the change as far as design, communication, etc. are concerned?
4. What is the **incentive** for the organization to undertake the change?
5. Do we have enough **resources** (personnel, knowledge, etc.) to implement the change?
6. Make an **action plan** (Gantt chart, timetables, etc.) for the change.

In light of the earlier discussion, answer:

1. What should a "change" include?
Any definition of change must clearly include changes in equipment, process, or software as well as addition of a new equipment or process. Any modification to organizational structure or any alteration to an operating procedure must also be defined as a change.

2. What safeguards could have prevented the Jofostan dairy feed incident?

1. *For proper isolation of the harmful chemicals at the facility from the food-grade products, different transport vehicles as well as different personnel should have been employed for JofoNutri and JofoFire.*
2. *A distinctive feature on the packaging of all the harmful chemicals at the facility would have allowed operators to distinguish food-grade products from harmful chemicals.*
3. *The plant operators should have been sensitive to the presence of harmful chemicals that may be accidentally transported to the dairy feed producing mill.*
4. *Use of similar names like JofoNutri and JofoFire should have been avoided as it could have further led to the mix-up.*

3. As the chief of investigation after the Jofostan dairy feed incident, what will be the recommendations of your report to prevent such incidents in the future?

While some of the safeguards in (b) may be recommended, it is important to focus on the “management of change” aspect here.

1. *When the company decided to shift to plain brown bags instead of printed, color-coded bags, it should have flagged this as a “change.”*
2. *All stakeholders—Purchasing, Operations, and Logistics—must be notified of this proposal and consulted for their views.*
3. *A dedicated safety manager must be entrusted to coordinate with all stake-holders and submit his recommendations before such a proposal goes through. He must evaluate the proposal for change in the manner described earlier.*

Closure.

$$\text{RTD Data} + \text{Model} + \text{Kinetics} = \text{Prediction}$$

In this chapter, models were developed for existing reactors to obtain more precise estimates of the exit conversion and concentrations than those from the zero-order parameter models of segregation and maximum mixedness. After completing this chapter, the reader will be able to use the RTD data and kinetic rate law and reactor model to make predictions of the conversion and exit concentrations using the dispersion one-parameter model. In addition, the reader should be able to create two-parameter models consisting of combinations of ideal reactors that mimic the RTD data. Using the models and rate law data, one can then solve for the exit conversions and concentrations. The choice of a proper model is almost pure art *requiring creativity and engineering judgment*. The flow pattern of the model must possess the most important characteristics of that in the real reactor. Standard models are available that have been used with some success, and these can be used as starting points. Models of real reactors usually consist of combinations of ideal PFRs and CSTRs with fluid exchange, bypassing, and dead spaces in a configuration that matches the flow patterns in the reactor. For tubular reactors, the simple dispersion model has proven most popular.

In summary, the parameters in the model, which with rare exception should not exceed two in number, are obtained from the RTD data. Once the parameters are evaluated, the conversion in the model, and thus in the real reactor, can be calculated. For typical tank-reactor models, this can be calculated for the conversion in a series-parallel reactor system. For the dispersion model, the second-order differential equation must be solved, usually numerically. Analytical solutions exist for first-order reactions, but as pointed out previously, no model has to be assumed for the first-order system if the RTD is available.

Correlations exist for the amount of dispersion that might be expected in common packed-bed reactors, so these systems can be designed using the dispersion model without obtaining or estimating the RTD. This situation is perhaps the only one where an RTD is not necessary for designing a non-ideal reactor.

SUMMARY

1. The models for predicting conversion from RTD data are:

1. Zero adjustable parameters

1. Segregation model
2. Maximum mixedness model

2. One adjustable parameter

1. Tanks-in-series model
2. Dispersion model

3. Two adjustable parameters: real reactor modeled as combinations of ideal reactors

2. Dispersion model: For a first-order reaction, use the Danckwerts boundary conditions

$$X = 1 - \frac{4q \exp(Pe_r/2)}{(1+q)^2 \exp(Pe_r q/2) - (1-q)^2 \exp(-Pe_r q/2)} \quad (\text{S18-1})$$

where

$$q = \sqrt{1 + \frac{4Da_1}{Pe_r}} \quad (\text{S18-2})$$

$$Da_1 = \tau k \quad (\text{S18-3})$$

For a first-order reaction

$$Pe_r = \frac{UL}{D_a} \quad Pe_f = \frac{Ud_p}{D_a\phi} \quad (\text{S18-4})$$

3. Determine D_d

1. For laminar flow, the dispersion coefficient is

$$D^* = D_{AB} + \frac{U^2 R^2}{48 D_{AB}} \quad (\text{S18-5})$$

2. Correlations. Use [Figures 18-8 through 18-10](#).

3. Experiment in RTD analysis to find t_m and σ^2 .

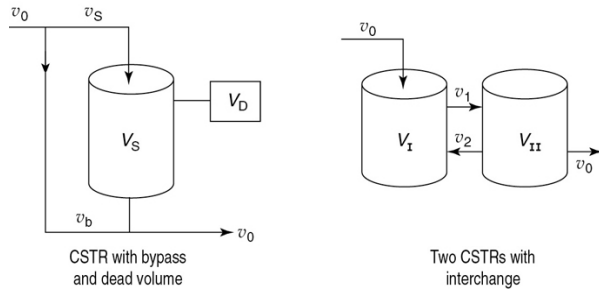
For a *closed-closed system*, use Equation (S18-5) to calculate Pe_r from the RTD data

$$\frac{\sigma^2}{\tau^2} = \frac{2}{Pe_r} - \frac{2}{Pe_r^2} (1 - e^{-Pe_r}) \quad (\text{S18-6})$$

For an *open-open system*, use

$$\frac{\sigma^2}{t_m^2} = \frac{2Pe_r + 8}{Pe_r^2 + 4Pe_r + 4} \quad (\text{S18-7})$$

4. If a real reactor is modeled as a combination of ideal reactors, the model should have at most two parameters.



5. The RTD is used to extract model parameters.
6. Comparison of conversions for a PFR and CSTR with the zero-parameter and two-parameter models. X_{seg} symbolizes the conversion obtained from the segregation model and X_{mm} is that from the maximum mixedness model for reaction orders greater than one.

$$X_{\text{PFR}} > X_{\text{seg}} > X_{\text{mm}} > X_{\text{CSTR}}$$

$$X_{\text{PFR}} > X_{\text{model}} \quad \text{with} \quad X_{\text{model}} < X_{\text{CSTR}} \quad \text{or} \quad X_{\text{model}} > X_{\text{CSTR}}$$

Cautions: For rate laws with unusual concentration functionalities or for nonisothermal operation, these bounds may not be accurate for certain types of rate laws.

7. Axial or radial temperature and concentration gradients. The following coupled, partial differential equations were solved using COMSOL:

$$D_e \frac{\partial^2 C_i}{\partial r^2} + \frac{D_e}{r} \frac{\partial C_i}{\partial r} + D_e \frac{\partial^2 C_i}{\partial z^2} - U_z \frac{\partial C_i}{\partial z} + r_i = 0 \quad (\text{S18-8})$$

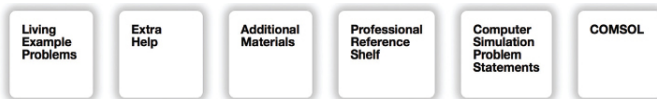
and

$$k_e \frac{\partial^2 T}{\partial z^2} + \frac{k_e}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \Delta H_{\text{Rx}} r_A - U_z C_{\text{P}_m} \frac{\partial T}{\partial z} = 0 \quad (\text{S18-9})$$

CRE WEB SITE MATERIALS

(<http://www.umich.edu/~elements/6e/18chap/obj.html#/>)

Useful Links



Evaluation



QUESTIONS, SIMULATIONS, AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$A = \bullet \quad B = \blacksquare \quad C = \blacklozenge \quad D = \blacklozenge\blacklozenge$$

Questions

Q18-1 QBR (*Question Before Reading*). **What if** you were asked to design a tubular vessel that would minimize dispersion? What would be your guidelines? How would you maximize the dispersion? How would your design change for a packed bed?

Q18-2_B Make up and solve an original problem. The guidelines are given in Problem

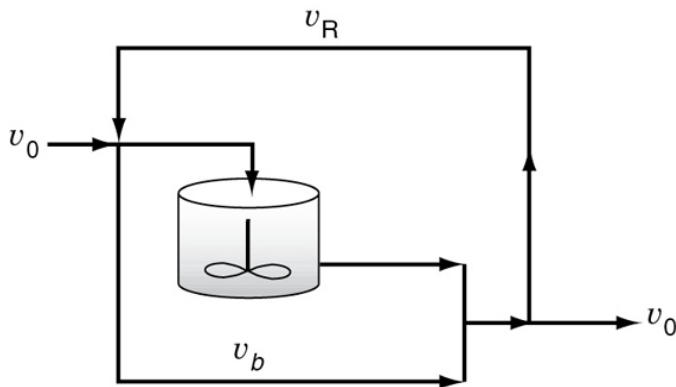


Figure Q18-2_B Model system.



Q18-3_A Can you use Figure 18-2 to find the dispersion coefficient for a liquid with a Schmidt number, $Sc = 0.35$ and a gas porosity $\phi = 0.5$, a particle diameter $d_p = 1$ cm, a gas velocity $U = 10$ cm/s, and a viscosity of a kinematic $\nu = 30$ cm²/s? If so, what is its value?

Q18-4 **What if** someone suggested you could use the solution to the flow-dispersion-reactor equation, Equation (18-18), for a second-order equation by linearizing the rate law by lettering $-r_A = kC_A^2 \cong (kC_{A0}/2)C_A$. (1) Under what circumstances might this be a good approximation? Would you divide C_{A0} by something

other than 2? (2) What do you think of linearizing other non-first-order reactions and using Equation (18-18)? (3) How could you test your results to learn whether the approximation is justified?

Q18-5 Go to the LearnChemE screencast link for Chapter 18 (<http://umich.edu/~elements/6e/18chap/learn-cheme-videos.html>). View one or more of the screencast 5- to 6-minute videos and write a two-sentence evaluation.

Q18-6 AWFOS–S18. An Algorithm for Management of Change (MoC). List three things that would not have occurred if the MoC algorithm had been followed.

Computer Simulations and Experiments

P18-1_b

- Example 18-1. Concentration and Conversion Profiles for Dispersion and Reaction in a Tubular Reactor**
Wolfram and Python



- Vary Péclet number, Pe_r from its largest to smallest value. Describe how the outlet concentration for “reaction with dispersion” deviates from that of “Ideal PFR” as Pe_r is varied.
 - What should be the minimum value of space time, τ , at which conversion reaches at least 95% for reaction with dispersion.
 - If the reaction rate constant is increased to 0.5 min^{-1} , what should be the value of Péclet number, Pe_r , so as to achieve conversion of 90%.
 - Vary the sliders and write a set of conclusions.
- Example 18-2. Comparing Conversion Using Dispersion, PFR, CSTR, and Tanks-in-Series Models for Isothermal Reactors**
Wolfram and Python
 - Which parameter will you vary so that conversion obtained by dispersion model approaches to conversion obtained using ideal PFR model.
 - What is the number of tanks in series required so that conversion obtained by the tank-in-series model is more than conversion obtained by the dispersion model?
 - Write a set of conclusions after you have varied all the parameter values.
- Example 18-3. Isothermal Reaction with Radial and Axial Dispersion in an LFR**

Go to the COMSOL link LEP 18-3 in Chapter 18 on the CRE Web site.

1. Vary the velocity and describe how the radial concentration profiles as well as the surface plot changes.
2. Vary the reactor radius and describe what you find.
3. Vary D_{AB} and describe how the radial concentration profiles and the exit concentration change.
4. Compare the radial concentration profiles at the inlet, exit, and halfway down the reactor with the radially averaged axial concentration when you vary D_{AB} and U and describe what you find.
5. What combination of parameters, for example, (D_a/UL) do not significantly change the base case profile when varied over a wide range? For example, diameter is between 0.01 dm and 1 m and the velocity varies from $U = 0.01$ cm/s to 1 m/s with $D_{AB} = 10^{-5}$ cm²/s with $\nu = \mu/\rho = 0.01$ m²/s. Is there a diameter that minimizes or maximizes your conversion?
6. To what parameters or groups of parameters (e.g., kL^2/D_a) would the conversion be most sensitive? What if the first-order reaction were carried out in tubular reactors of different diameters, but with the space time, τ , remaining constant? The diameters would range from a diameter of 0.1 dm to a diameter of 1 m for a kinematic viscosity $\nu = \mu/\rho = 0.01$ cm²/s, $U = 0.1$ cm/s, and $D_{AB} = 10^{-5}$ cm²/s. How would your conversion change? Is there a diameter that would maximize or minimize conversion in this range?
7. Which type of velocity profile gives the higher outlet concentration?
8. What two parameters would reduce the radial variation in concentration?
9. Which variable has very little effect on radial variation in concentration?
10. What is the effect of diffusivity on the outlet concentration?
11. Keep Da and L/R constant and vary the reaction order n , ($0.5 \leq n \leq 5$) for different Péclet numbers. Are there any combinations of n and Pe where dispersion is more important or less important on the exit concentration? What generalizations can you make? *Hint:* for $n < 1$ use $r_A = -k \cdot (\text{Abs}(C_A^n))$.
12. Write a set of conclusions based on your experiments (i) through (xi).

4. Example 18-4. Tubular Reactor with Axial and Radial Temperature and Concentration Gradients

Use the COMSOL LEP on the Web site to explore radial effects in a tubular reactor. The Additional Material on the Web site describes this LEP in detail

(http://umich.edu/~elements/6e/18chap/expanded_ch18_radial.pdf).

Tutorials on how to access and use COMSOL can be found at (http://umich.edu/~elements/6e/software/software_comsol.html).

1. Vary the heat transfer coefficient, U , and observe the effect on both the conversion and temperature profiles. Why is there an effect of U on the profiles at low values of U , but not at higher values of U ?
2. What is the effect of the different diffusivities, D_a , on the conversion? Should D_a be minimized or maximized?
3. What parameter would you vary so that the maximum of the radial conversion profile becomes 1? What is the value of that parameter?
4. How would your profiles change if the velocity profile was changed to plug flow ($U = U_0$)? Based on your observations, which of the two profiles, namely, laminar flow and plug flow, would you recommend for a larger conversion? How does the change in velocity profile make an effect in the temperature profile?

- Intuitively, how do you expect the radial conversion to vary with diffusion coefficient? Explain the reason behind your intuition. Verify this by varying the diffusion coefficient. Investigate axial and radial conversion and write two conclusions.

5. Example 18-5. Using a Tracer to Determine the Model Parameters in a CSTR with Dead Volume and Bypass Model

Wolfram and Python

- For the case of no dead volume ($\alpha = 1$), vary bypass volume fraction, β , and describe its effect on outlet concentration.
- Repeat part (i) for the case of no bypass volume ($\beta = 0$) and vary α to observe its effect on outlet concentration.
- From your observation in part (i) and part (ii), which of the two model parameters (α or β) have more impact on outlet concentration and conversion? Explain.
- Write a set of conclusions based on your experiments in (i) through (iii).

6. Example 18-6. CSTR with Interchange

Wolfram and Python

- For a fixed value of α (say $\alpha = 0.5$), how does the conversion vary with increase in β ? Explain.
- Vary α and describe its impact on the exit concentration.
- Vary rate constant, k , and describe what you find about its effect on exit concentration.
- Write a set of conclusions based on your experiments in (i) through (iii).

Problems

P18-2_B The gas-phase isomerization



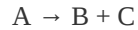
is to be carried out in a flow reactor. Experiments were carried out at a volumetric flow rate of $v_0 = 2 \text{ dm}^3/\text{min}$ in a reactor that had the following RTD

$$E(t) = 10 e^{10t} \text{ min}^{-1}$$

where t is in minutes.

- When the volumetric flow rate was $2 \text{ dm}^3/\text{min}$, the conversion was 9.1%. What is the reactor volume?
- When the volumetric flow rate was $0.2 \text{ dm}^3/\text{min}$, the conversion was 50%. When the volumetric flow rate was $0.02 \text{ dm}^3/\text{min}$, the conversion was 91%. Assuming the mixing patterns don't change as the flow rate changes, what will the conversion be when the volumetric flow rate is $10 \text{ dm}^3/\text{min}$?
- This reaction is now to be carried out in a 1-dm^3 plug-flow reactor where volumetric flow rate has been changed to $1 \text{ dm}^3/\text{min}$. What will be the conversion?
- It is proposed to carry out the reaction in a 10-m-diameter pipe where the flow is highly turbulent ($\text{Re} = 10^6$). There are significant dispersion effects. The superficial gas velocity is 1 m/s. If the pipe is 6 m long, what conversion can be expected? If you were unable to determine the reaction order and the specific reaction-rate constant in part (b), assume $k = 1 \text{ min}^{-1}$ and carry out the calculation!

P18-3_b OEQ (Old Exam Question). The second-order liquid-phase reaction

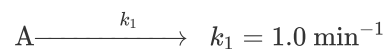


is to be carried out isothermally. The entering concentration of A is 1.0 mol/dm^3 . The specific reaction rate is $1.0 \text{ dm}^3/\text{mol}=\text{min}$. A number of used reactors (shown below) are available, each of which has been characterized by an RTD. There are two crimson and white reactors, and three maize and blue reactors available.

Reactor	$\sigma(\text{min})$	$\tau(\text{min})$	Cost
Maize and blue	2	2	\$25,000
Green and white	4	4	50,000
Scarlet and gray	3.05	4	50,000
Orange and blue	2.31	4	50,000
Purple and white	5.17	4	50,000
Silver and black	2.5	4	50,000
Crimson and white	2.5	2	25,000

1. You have \$50,000 available to spend. What is the greatest conversion you can achieve with the available money and reactors?
2. How would your answer to (a) change if you had an extra \$75,000 available to spend?
3. From which cities do you think the various used reactors came from?

P18-4_B OEQ (Old Exam Question). The elementary liquid-phase reaction



is carried out in a packed-bed reactor in which dispersion is present.

What is the conversion?

Additional information:

Porosity = 50%

Reactor length = 0.1 m

Particle size = 0.1 cm

Mean velocity = 1 cm/s

Kinematic viscosity = $0.01 \text{ cm}^2/\text{s}$

Bed fluidity = 7.3

(Ans: $X = 0.15$)

P18-5A A gas-phase reaction is being carried out in a 5-cm-diameter tubular reactor that is 2 m in length. The velocity inside the pipe is 2 cm/s. As a very first approximation, the gas properties can be taken as those of air (kinematic viscosity = $0.01 \text{ cm}^2/\text{s}$), and the diffusivities of the reacting species are approximately $0.005 \text{ cm}^2/\text{s}$.

1. How many tanks in series would you suggest to model this reactor?
2. If the second-order reaction $A + B \rightarrow C + D$ is carried out for the case of equimolar feed, and with $C_{A0} = 0.01 \text{ mol/dm}^3$, what conversion can be expected at a temperature for which $k = 25 \text{ dm}^3/\text{mol}\cdot\text{s}$?
3. How would your answers to parts (a) and (b) change if the fluid velocity was reduced to 0.1 cm/s? Increased to 1 m/s?
4. How would your answers to parts (a) and (b) change if the superficial velocity was 4 cm/s through a packed bed of 0.2-cm-diameter spheres?
5. How would your answers to parts (a) through (d) change if the fluid was a liquid with properties similar to water instead of a gas, and the diffusivity was $5 \times 10^{-6} \text{ cm}^2/\text{s}$?

P18-6A Use the data in Example 16-2 to make the following determinations. (The volumetric feed rate to this reactor was $60 \text{ dm}^3/\text{min}$.)

1. Calculate the Péclet numbers for both open and closed systems.
2. For an open system, determine the space time τ and then calculate the % dead volume in a reactor for which the manufacturer's specifications give a volume of 420 dm^3 .
3. Using the dispersion calculate the conversion for a closed-closed vessel and tanks-in-series models, for the first-order isomerization

$$A \rightarrow B$$
 with $k = 0.18 \text{ min}^{-1}$.
4. Compare your results in part (c) with the conversion calculated from the tanks-in-series model, a PFR, and a CSTR.

P18-7_A OEQ (Old Exam Question). A tubular reactor has been sized to obtain 98% conversion and to process $0.03 \text{ m}^3/\text{s}$. The reaction is a first-order irreversible isomerization. The reactor is 3 m long, with a cross-sectional area of 25 dm^2 . After being built, a pulse tracer test on the reactor gave the following data: $t_m = 10 \text{ s}$ and $\sigma^2 = 65 \text{ s}^2$. What conversion can be expected in the real reactor?

P18-8_B The following $E(t)$ curve was obtained from a tracer test on a reactor.

$$\begin{aligned} E(t) &= 0.25t & 0 < t < 2 \\ &= 1 - 0.25t & 2 < t < 4 \\ &= 0 & t > 4 \end{aligned}$$

t in minutes, and $E(t)$ in min^{-1} .

The conversion predicted by the tanks-in-series model for the isothermal elementary reaction



was 50% at 300 K.

1. If the temperature is to be raised 10°C ($E = 25000 \text{ cal/mol}$) and the reaction carried out isothermally, what will be the conversion predicted by the maximum mixedness model? The T-I-S model?
2. The elementary reactions

$$\text{A} \xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{C}$$

$$\text{A} \xrightarrow{k_3} \text{D}$$

$$k_1 = k_2 = k_3 = 0.1 \text{ min}^{-1} \text{ at } 300 \text{ K}, C_{A0} = 1 \text{ mol/dm}^3$$
 were carried out isothermally at 300 K in the same reactor. What is the concentration of B in the exit stream predicted by the maximum mixedness model?
3. For the multiple reactions given in part (b), what is the conversion of A predicted by the dispersion model in an isothermal closed-closed system?

P18-9_B Revisit Problem P16-3_C where the RTD function is a hemicircle. The liquid-phase reaction is first order with $k_1 = 0.8 \text{ min}^{-1}$.

What is the conversion predicted by

1. The tanks-in-series model? (**Ans:** $X^{\text{T-I-S}} = 0.447$)
2. The dispersion model? (**Ans:** $X^{\text{Dispersion}} = 0.41$)

P18-10_B Revisit Problem P16-5_B. The liquid-phase reaction $\text{A} \rightarrow \text{B}$ is third order with $k_3 = 0.3 \text{ dm}^6/\text{mol}^2 \text{ min}$ and $C_{A0} = 2 \text{ M}$.

1. What combination of ideal reactors would you use to model the RTD?
2. What are the model parameters?

- What is the conversion predicted for your model?
- What is the conversion predicted by X_{mm} , X_{seg} , X_{T-I-S} , and $X_{Dispersion}$?
- Repeat (a) through (d) for a liquid phase reaction $A \rightarrow B$ is second order with $k_2 C_{A0} = 0.1 \text{ min}^{-1}$.

P18-11_B Below in Figure P18-11_b are two COMSOL simulations for a laminar-flow reactor with heat effects: Run 1 and Run 2. The following figures show the cross-section plot of concentration for species A at the middle of the reactor. Run 2 shows a minimum on the cross-section plot. This minimum could be the result of (circle all that apply and explain your reasoning for each suggestion (a) through (e)).

- The thermal conductivity of reaction mixture decreases
- Overall heat transfer coefficient increases
- Overall heat transfer coefficient decreases
- The coolant flow rate increases
- The coolant flow rate decreases

Hint: Explore “Nonisothermal Reactor II” on the COMSOL LEP.

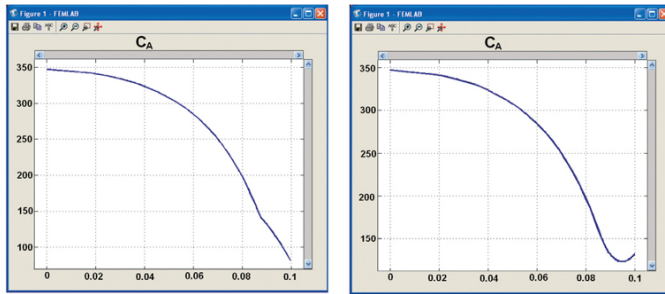


Figure P18-11_B COMSOL screenshots.

P18-12_D Let's continue Problem P16-11_D. Where $\tau = 10 \text{ min}$ and $\tau = 14 \text{ min}^2$

- What would be the conversion for a second-order reaction with $kC_{A0} = 0.1 \text{ min}^{-1}$ and $C_{A0} = 1 \text{ mol/dm}^3$ using the segregation model?
- What would be the conversion for a second-order reaction with $kC_{A0} = 0.1 \text{ min}^{-1}$ and $C_{A0} = 1 \text{ mol/dm}^3$ using the maximum mixedness model?
- If the reactor is modeled as tanks in series, how many tanks are needed to represent this reactor? What is the conversion for a first-order reaction with $k = 0.1 \text{ min}^{-1}$?
- If the reactor is modeled by a dispersion model, what are the Péclet numbers for an open system and for a closed system? What is the conversion for a first-order reaction with $k = 0.1 \text{ min}^{-1}$ for each case?
- Use the dispersion model to estimate the conversion for a second-order reaction with $k = 0.1 \text{ dm}^3/\text{mol}\cdot\text{s}$ and $C_{A0} = 1 \text{ mol/dm}^3$.
- It is suspected that the reactor might be behaving as shown in Figure P18-12_D, with *perhaps (?)* $V_1 = V_2$. What is the “backflow” from the second to the first vessel, as a multiple of u_0 ?

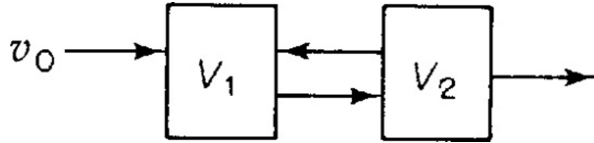


Figure P18-12D Proposed model system.

- If the model above is correct, what would be the conversion for a second-order reaction with $k = 0.1 \text{ dm}^3/\text{mol} \cdot \text{min}$ if $C_{A0} = 1.0 \text{ mol/dm}^3$?
- Prepare a table comparing the conversion predicted by each of the models described above.

P18-13B A second-order reaction is to be carried out in a real reactor that gives the following outlet concentration for a step input:

For $0 \leq t < 10 \text{ min}$, then $C_T = 10 (1 - e^{-1t})$

For $10 \text{ min} \leq t$, then $C_T = 5 + 10 (1 - e^{-1t})$

- What model do you propose and what are your model parameters, α and β ?
- What conversion can be expected in the real reactor?
- How would your model change and conversion change if your outlet tracer concentration was as follows?

For $t \leq 10 \text{ min}$, then $C_T = 0$

For $t \geq 10 \text{ min}$, then $C_T = 5 + 10 (1 - e^{-0.2(t-10)})$

$v_0 = 1 \text{ dm}^3/\text{min}$, $k = 0.1 \text{ dm}^3/\text{mol} \cdot \text{min}$, $C_{A0} = 1.25 \text{ mol/dm}^3$

P18-14b Suggest combinations of ideal reactors to model the real reactors given in Problem P16-2b(b) for either $E(\theta)$, $E(t)$, $F(\theta)$, $F(t)$, or $(1 - F(\theta))$.

P18-15B OEQ (Old Exam Question). The F -curves for two tubular reactors are shown in Figure P18-15B for a closed-closed system.

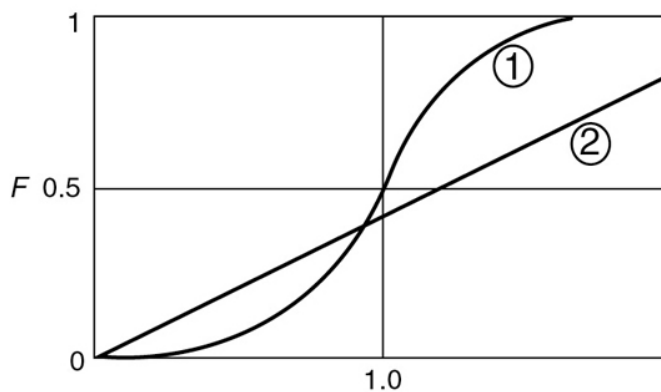


Figure P18-15B F -curves.

- Which curve has the higher Péclet number? Explain.
- Which curve has the higher dispersion coefficient? Explain.
- If this F -curve is for the tanks-in-series model applied to two different reactors, which curve has the largest number of T-I-S, (1) or (2)?

U of M, ChE528 Mid-Term Exam

P18-16_C Consider the following system in Figure P18-16_C used to model a real reactor:

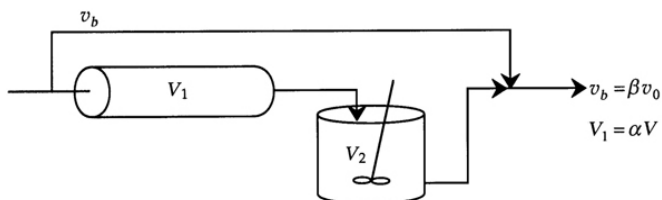


Figure P18-16_C Model system.

Describe how you would evaluate the parameters α and β .

1. Draw the F - and E -curves for this system of ideal reactors used to model a real reactor using $\beta = 0.2$ and $\alpha = 0.4$. Identify the numerical values of the points on the F -curve (e.g., t_1) as they relate to τ .
2. If the reaction $A \rightarrow B$ is second order with $kC_{A0} = 0.5 \text{ min}^{-1}$, what is the conversion assuming the space time for the real reactor is 2 min?

U of M, ChE528 Final Exam

P18-17_B *OEQ (Old Exam Question)*. There is a 2-m^3 reactor in storage that is to be used to carry out the liquid-phase second-order reaction



A and B are to be fed in equimolar amounts at a volumetric rate of $1 \text{ m}^3/\text{min}$. The entering concentration of A is 2 molar, and the specific reaction rate is $1.5 \text{ m}^3/\text{kmol} \cdot \text{min}$. A tracer experiment was carried out and reported in terms of F as a function of time in minutes as shown in Figure P18-17_B.

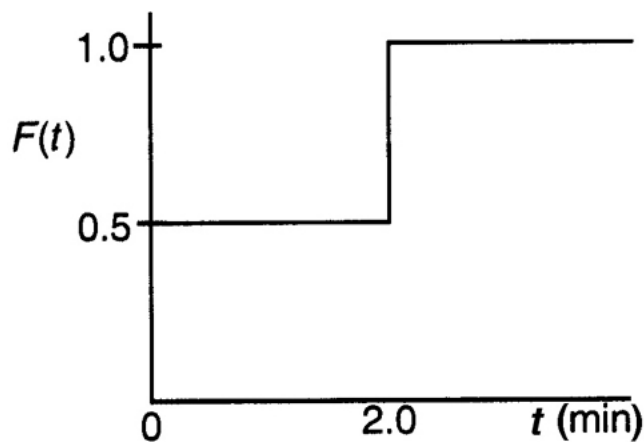


Figure P18-17_B F -curve for a nonideal reactor.

Suggest a two-parameter model consistent with the data; evaluate the model parameters and the expected conversion.

U of M, ChE528 Final Exam

P18-18_b OEQ (*Old Exam Question*). The following E -curve shown in Figure P18-18_b was obtained from a tracer test:

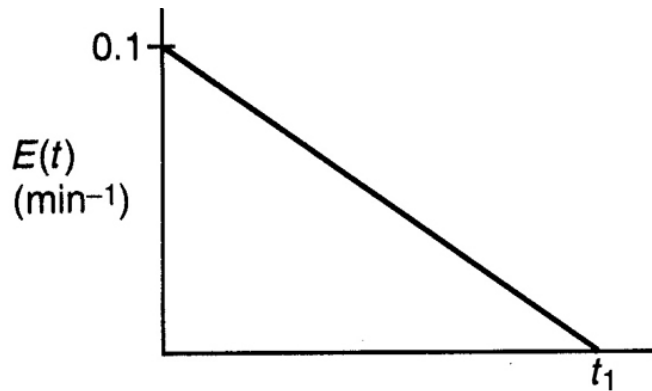


Figure P18-18_B E -curve for a nonideal reactor.

1. What is the mean residence time?
2. What is the Péclet number for a closed-closed system?
3. How many tanks in series are necessary to model this nonideal reactor?

U of M, Doctoral Qualifying Exam (DQE)

P18-19_B OEQ (*Old Exam Question*). A first-order reaction with $k = 0.1 \text{ min}^{-1}$ is to be carried out in the reactor whose RTD is shown in Figure 18-19_B.

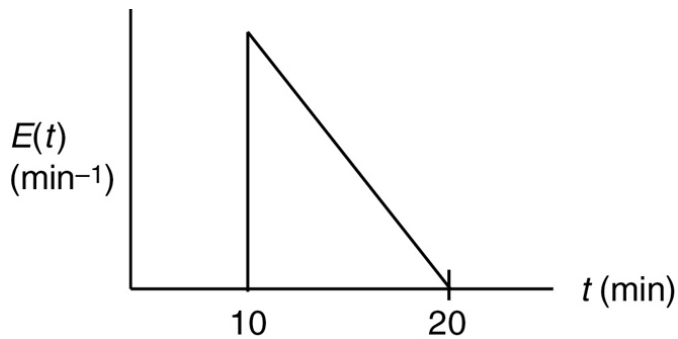


Figure P18-19_B Reactor E -curve.

Fill in Table P18-19_B with the conversion predicted by each type of model/reactor.

TABLE P18-19_B. COMPARISONS OF CONVERSION PREDICTED BY VARIOUS MODELS

Ideal PFR	Ideal CSTR	Ideal Laminar-Flow Reactor	Segregation	Maximum Mixedness	Dispersion	Tanks in Series

P18-20_C Consider a real tubular reactor in which dispersion is occurring.

- For small deviations from plug flow, show that the conversion for a first-order reaction is given approximately as

$$X = 1 - \exp \left[-tk + \frac{(\tau k)^2}{Pe_r} \right] \quad (\text{P18-20.1})$$

- Show that to achieve the same conversion, the relationship between the volume of a plug-flow reactor, V_P , and volume of a real reactor, V , in which dispersion occurs is

$$\frac{V_P}{V} = 1 - \frac{(\tau k)}{Pe_r} = 1 - \frac{kD_e}{U^2} \quad (\text{P18-20.2})$$

- For a Péclet number of 0.1 based on the PFR length, how much bigger than a PFR must the real reactor be to achieve the 99% conversion predicted by the PFR?
- For an n th-order reaction, the ratio of exit concentration for reactors of the same length has been suggested as

$$\frac{C_A}{C_{A,\text{plug}}} = 1 + \frac{n}{Pe_r} \left(\tau k C_{A0}^{n-1} \right) \ln \frac{C_{A0}}{C_{A,\text{plug}}} \quad (\text{P18-20.3})$$

What do you think of this suggestion?

- What is the effect of dispersion on zero-order reactions?

SUPPLEMENTARY READING

- Excellent discussions of maximum mixedness can be found in

J. M. DOUGLAS, "The effect of mixing on reactor design," *AIChE Symp. Ser.* 48, vol. 60, p. 1 (1964).

TH. N. ZWIETERING, *Chem. Eng. Sci.*, 11, 1 (1959).

- Modeling real reactors with a combination of ideal reactors is discussed together with axial dispersion in

O. LEVENSPIEL, *Chemical Reaction Engineering*, 3rd ed. New York: Wiley, 1999.

C. Y. WEN and L. T. FAN, *Models for Flow Systems and Chemical Reactors*. New York: Marcel Dekker, 1975.

3. Mixing and its effects on chemical reactor design have been receiving increasingly sophisticated treatment. See, for example:

K. B. BISCHOFF, "Mixing and contacting in chemical reactors," *Ind. Eng. Chem.*, 58 (11), 18 (1966).

E. B. NAUMAN, "Residence time distributions and micromixing," *Chem. Eng. Commun.*, 8, 53 (1981).

E. B. NAUMAN and B. A. BUFFHAM, *Mixing in Continuous Flow Systems*. New York: Wiley, 1983.

4. See also

M. DUDUKOVIC and R. FELDER, in *CHEMI Modules on Chemical Reaction Engineering*, vol. 4, ed. B. Crynes and H. S. Fogler. New York: AIChE, 1985.

5. Dispersion. A discussion of the boundary conditions for closed-closed, open-open, closed-open, and open-closed vessels can be found in

R. ARIS, *Chem. Eng. Sci.*, 9, 266 (1959).

O. LEVENSPIEL and K. B. BISCHOFF, *Adv. in Chem. Eng.*, 4, 95 (1963).

E. B. NAUMAN, *Chem. Eng. Commun.*, 8, 53 (1981).

6. Now that you have finished this book, suggestions on what to do with the book can be posted on the kiosk in the town square in downtown Riça, Jofostan.

This is not the end.

It is not even the beginning of the end.

But it is, perhaps, the end of the beginning.

Winston Churchill

November 10, 1942

A. Numerical Techniques

Lake Michigan—unsalted and shark-free.

A.1 USEFUL INTEGRALS IN CHEMICAL REACTOR DESIGN

Also see www.integrals.com.

$$\int_0^{\chi} \frac{dx}{1-x} = \ln \frac{1}{1-x} \quad (\text{A-1})$$

$$\int_{x_1}^{x_2} \frac{dx}{(1-x)^2} = \frac{1}{1-x_2} - \frac{1}{1-x_1} \quad (\text{A-2})$$

$$\int_0^x \frac{dx}{(1-x)^2} = \frac{\chi}{1-x} \quad (\text{A-3})$$

$$\int_0^x \frac{dx}{1+\epsilon x} = \frac{1}{\epsilon} \ln (1+\epsilon x) \quad (\text{A-4})$$

$$\int_0^x \frac{(1+\epsilon x)dx}{1-x} = (1+\epsilon) \ln \frac{1}{1-x} - \epsilon x \quad (\text{A-5})$$

$$\int_0^x \frac{(1+\epsilon x)dx}{(1-x)^2} = \frac{(1+\epsilon)x}{1-x} - \epsilon \ln \frac{1}{1-x} \quad (\text{A-6})$$

$$\int_0^x \frac{(1+\varepsilon x)^2 dx}{(1-x)^2} = 2\varepsilon(1+\varepsilon) \ln(1-x) + \varepsilon^2 x + \frac{(1+\varepsilon)^2 x}{1-x} \quad (\text{A-7})$$

$$\int_0^x \frac{dx}{(1-x)(\Theta_B-x)} = \frac{1}{\Theta_B-1} \ln \frac{\Theta_B-x}{\Theta_B(1-x)} \quad \Theta_B \neq 1 \quad (\text{A-8})$$

$$\int_0^W (1-\alpha W)^{1/2} dW = \frac{2}{3\alpha} \left[1 - (1-\alpha W)^{3/2} \right] \quad (\text{A-9})$$

$$\int_0^x \frac{dx}{ax^2+bx+c} = \frac{-2}{2ax+b} + \frac{2}{b} \quad \text{for } b^2 = 4ac \quad (\text{A-10})$$

$$\int_0^x \frac{dx}{ax^2+bx+c} = \frac{1}{a(p-q)} \ln \left(\frac{q}{p} \cdot \frac{x-p}{x-q} \right) \quad \text{for } b^2 > 4ac \quad (\text{A-11})$$

where p and q are the roots of the equation.

$$ax^2 + bx + c = 0, \quad \text{that is, } p, q = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (\text{A-12})$$

$$\int_0^x \frac{a+bx}{c+gx} dx = \frac{bx}{g} + \frac{ag-bc}{g^2} \ln \frac{c+gx}{c}$$

A.2 EQUAL-AREA GRAPHICAL DIFFERENTIATION

There are many ways of differentiating numerical and graphical data (cf. [Chapter 7](#)). We shall confine our discussions to the technique of equal-area differentiation. In the procedure delineated here, we want to find the derivative of y with respect to x .

This method finds use in [Chapter 5](#).

- 1. Tabulate the (y_i, x_i) observations as shown in Table A-1.
- 2. For each *interval*, calculate $\Delta x_n = x_n - x_{n-1}$ and $\Delta y_n = y_n - y_{n-1}$.

TABLE A-1 FINDING DIFFERENTIALS $\left(\frac{dy}{dx}\right)$ FROM DISCRETE DATA

x_i	y_i	Δx	Δy	$\frac{\Delta y}{\Delta x}$	$\frac{dy}{dx}$
-------	-------	------------	------------	-----------------------------	-----------------

x_1	y_1				$\left(\frac{dy}{dx}\right)_1$
-------	-------	--	--	--	--------------------------------

		$x_2 - x_1$	$y_2 - y_1$	$\left(\frac{\Delta y}{\Delta x}\right)_2$	
--	--	-------------	-------------	--	--

x_2	y_2				$\left(\frac{dy}{dx}\right)_2$
-------	-------	--	--	--	--------------------------------

		$x_3 - x_2$	$y_3 - y_2$	$\left(\frac{\Delta y}{\Delta x}\right)_3$	
--	--	-------------	-------------	--	--

x_3	y_3				$\left(\frac{dy}{dx}\right)_3$
-------	-------	--	--	--	--------------------------------

x_4	y_4				and so on.
-------	-------	--	--	--	------------

3. Calculate $\Delta y_n / \Delta x_n$ as an estimate of the *average* slope in an interval x_{n-1} to x_n .
4. Plot these values as a histogram versus x_i . The value between x_2 and x_3 , for example, is $(y_3 - y_2) / (x_3 - x_2)$. Refer to [Figure A-1](#).

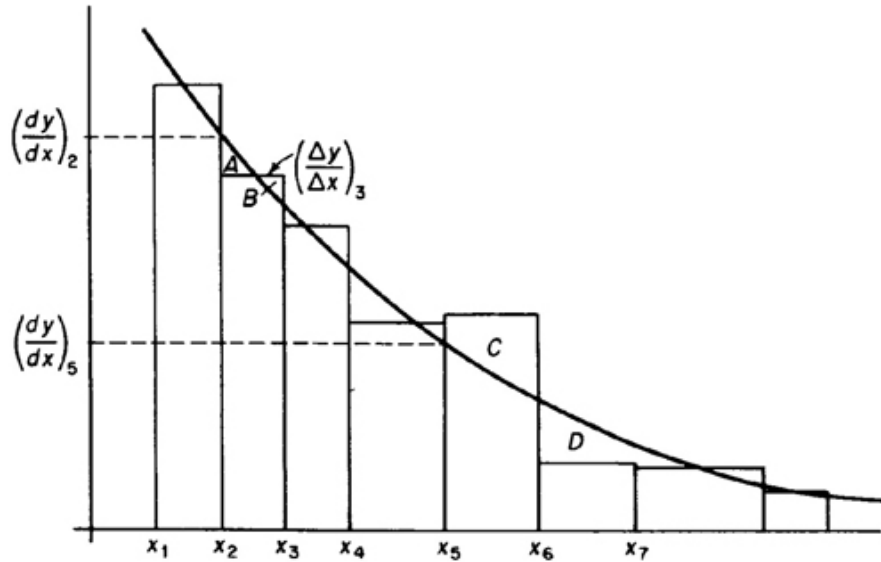


Figure A-1 Equal-area differentiation.

5. Next, draw in the *smooth curve* that best approximates the *area* under the histogram. That is, attempt in each interval to balance areas such as those labeled A and B, but when this approximation is not possible, balance out over several intervals (as for the areas labeled C and D). From our definitions of Δx and Δy , we know that

$$y_n - y_1 = \sum_{i=2}^n \frac{\Delta y}{\Delta x_i} \Delta x_i \quad (\text{A-13})$$

The equal-area method attempts to estimate dy/dx so that

$$y_n - y_1 = \int_{x_1}^{x_n} \frac{dy}{dx} dx \quad (\text{A-14})$$

that is, so that the area under $\Delta y / \Delta x$ is the same as that under dy/dx , *everywhere possible*.

6. Read estimates of dy/dx from this curve at the data points x_1, x_2, \dots and complete the table.

An example illustrating the technique is given on the CRE Web site, [Appendix A](#).

Differentiation is, at best, less accurate than integration. This method also **clearly indicates bad data** and allows for compensation of such data. Differentiation is only valid, however, when the data are presumed to differentiate *smoothly*, as in rate-data analysis and the interpretation of transient diffusion data.

A.3 SOLUTIONS TO DIFFERENTIAL EQUATIONS

A.3.A First-Order Ordinary Differential Equations

See the CRE Web site, [Appendix A.3](#).

$$\frac{dy}{dt} + f(t)y = g(t) \quad (\text{A-15})$$

Using integrating factor = $\exp\left(\int f dt\right)$, the solution is

$$y = e^{-\int f dt} \int g(t) e^{\int f dt} dt + K_1 e^{-\int f dt} \quad (\text{A-16})$$

Example A-1 Integrating Factor for Series Reactions

$$\frac{dy}{dx} + k_2 y = k_1 e^{-k_1 t}$$

Comparing the earlier equation with Equation (A-15) we note

$$f(t) = k_2$$

and the integrating factor = $\exp \int k_2 dt = e^{k_2 t}$

Multiplying both sides by the integrating factor

$$\frac{d(ye^{k_2 t})}{dt} = e^{k_2 t} k_1 e^{-k_1 t} = k_1 e^{(k_2 - k_1)t}$$

Integrating

$$e^{k_2 t} y = k_1 e^{(k_2 - k_1)t} dt = \frac{k_1}{k_2 - k_1} e^{(k_2 - k_1)t} + K_1$$

$$y = \frac{k_1}{k_2 - k_1} e^{-k_1 t} + K_1 e^{-k_2 t}$$

$$t=0 \quad y=0$$

$$y = \frac{k_1}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}]$$

A.3.B Coupled Differential Equations

Techniques to solve coupled first-order linear ODEs such as

$$\frac{dx}{dt} = ax + by$$

$$\frac{dy}{dt} = cx + dy$$

are given in Web Appendix A.3 on the CRE Web site

(http://www.umich.edu/~elements/6e/appendix/AppA.3_Web.pdf).

A.3.C Second-Order Ordinary Differential Equations

Methods of solving differential equations of the type

$$\frac{d^2y}{dx^2} - \beta y = 0 \quad (\text{A-17})$$

can be found in such texts as *Applied Differential Equations* by M. R. Spiegel (Upper Saddle River, NJ: Pearson, 1958, Chapter 4; a great book even though it's old) or in *Differential Equations* by F. Ayres (New York: Schaum Outline Series, McGraw-Hill, 1952). Solutions of this type are required in Chapter 15. One method of solution is to determine the characteristic roots of

$$\left(\frac{d^2}{dx^2} - \beta\right)y = (m^2 - \beta)y$$

which are

$$m = \pm \sqrt{\beta}$$

The solution to the differential equation is

$$y = A_1 e^{-\sqrt{\beta}x} + B_1 e^{+\sqrt{\beta}x} \quad (\text{A-18})$$

where A_1 and B_1 are arbitrary constants of integration. It can be verified that Equation (A-18) can be arranged in the form

$$y = A \sinh \sqrt{\beta}x + B \cosh \sqrt{\beta}x \quad (\text{A-19})$$

Equation (A-19) is the more useful form of the solution when it comes to evaluating the constants A and B because $\sinh(0) = 0$ and $\cosh(0) = 1.0$.

A.4 NUMERICAL EVALUATION OF INTEGRALS

In this section, we discuss techniques for numerically evaluating integrals for solving first-order differential equations.

1. *Trapezoidal rule* (two-point) (Figure A-2). This method is one of the simplest and most approximate, as it uses the integrand evaluated at the limits of integration to evaluate the integral

$$\int_{X_0}^{X_1} f(X) dX = \frac{h}{2} [f(X_0) + f(X_1)] \quad (\text{A-20})$$

when $h = X_1 - X_0$.

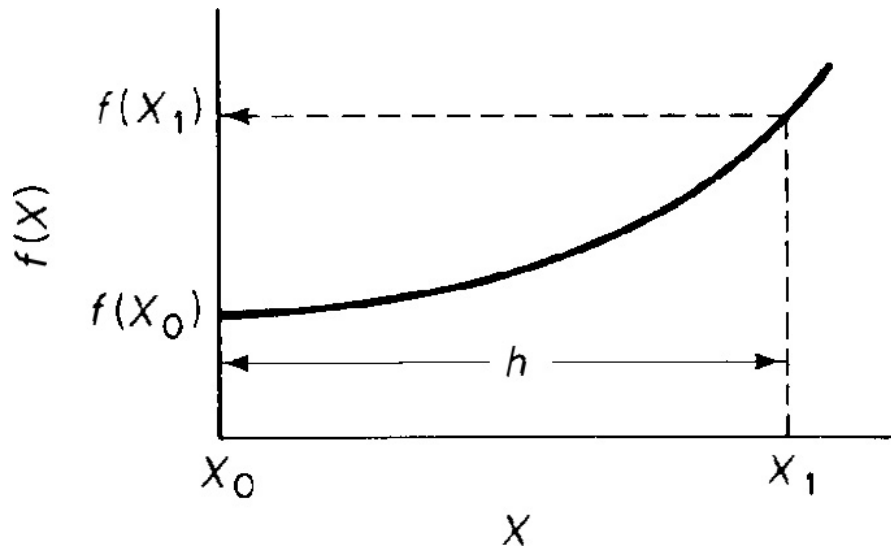


Figure A-2 Trapezoidal rule illustration.

2. *Simpson's one-third rule* (three-point) (Figure A-3). A more accurate evaluation of the integral can be found with the application of Simpson's rule:

$$\int_{X_0}^{X_2} f(X) dX = \frac{h}{3} [f(X_0) + 4f(X_1) + f(X_2)] \quad (\text{A-21})$$

where

$$h = \frac{X_2 - X_0}{2} \quad X_1 = X_0 + h$$

Methods to solve

$$\int_0^X \frac{F_{A0}}{-r_A} dX$$

in Chapters 2, 4, 5, 12, and $\int_0^\infty X(t)E(t)dt$

in Chapter 17

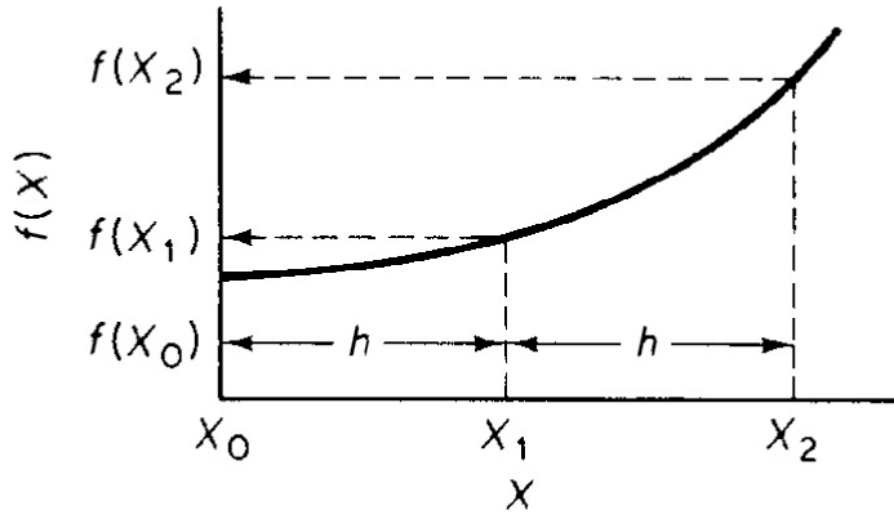


Figure A-3 Simpson's three-point rule illustration.

3. *Simpson's three-eighths rule* (four-point) (Figure A-4). An improved version of Simpson's one-third rule can be made by applying *Simpson's three-eighths rule*:

$$\int_{X_0}^{X_3} f(X) dX = \frac{3}{8}h \left[f(X_0) + 3f(X_1) + 3f(X_2) + f(X_3) \right] \quad (\text{A-22})$$

where

$$h = \frac{X_3 - X_0}{3} \quad X_1 = X_0 + h \quad X_2 = X_0 + 2h$$

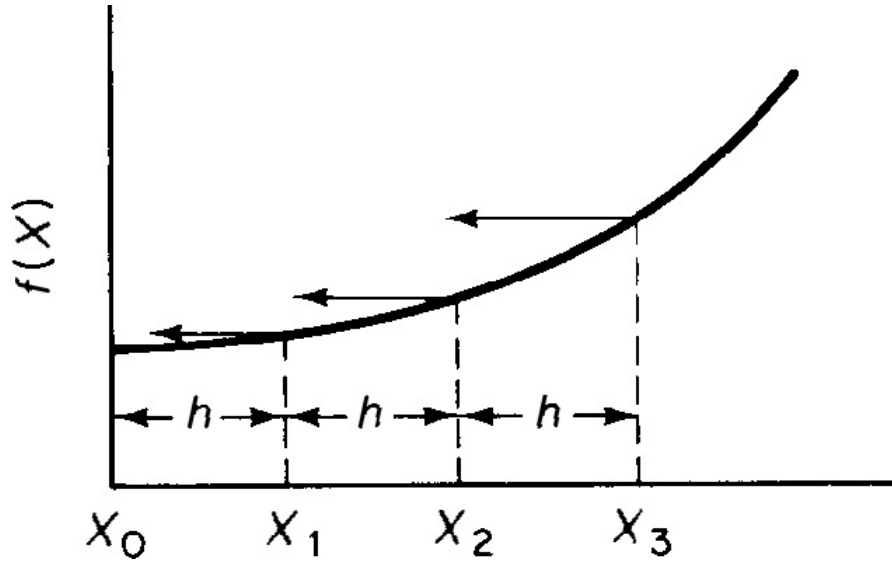


Figure A-4 Simpson's four-point rule illustration.

4. Five-point quadrature formula.

$$\int_{X_0}^{X_4} f(X) dX = \frac{h}{3} (f_0 + 4f_1 + 2f_2 + 4f_3 + f_4) \quad (\text{A-23})$$

where

$$h = \frac{X_4 - X_0}{4}$$

5. For $N = 1$ points, where $(N/3)$ is an integer

$$\int_{X_0}^{X_N} f(X) dX = \frac{3}{8} h [f_0 + 3f_1 + 3f_2 + 2f_3 + 3f_4 + 3f_5 + 2f_6 + \dots + 3f_{N-1} + f_N] \quad (\text{A-24})$$

where $h = \frac{X_N - X_0}{N}$

6. For $N = 1$ points, where N is even

$$\int_{X_0}^{X_N} f(X) dX = \frac{h}{3} (f_0 + 4f_1 + 2f_2 + 4f_3 + 2f_4 + \dots + 4f_{N-1} + f_N) \quad (\text{A-25})$$

where $h = \frac{X_N - X_0}{N}$

These formulas are useful in illustrating how the reaction engineering integrals and coupled ODEs (ordinary differential equation(s)) can be solved, and also when there is an ODE solver power failure or some other malfunction.

A.5 SEMI-LOG GRAPHS

Review how to take slopes on semi-log graphs on the Web.

Also see <https://bolide.cs.uoguelph.ca/tutorials/GLP>. Also see Web Appendix A.5, Using Semi-Log Plots for Data Analysis.

A.6 SOFTWARE PACKAGES

Instructions on how to use Polymath, MATLAB, Python, Wolfram, COMSOL, and Aspen can be found on the CRE Web site.

For the ordinary differential equation solver (ODE solver), contact:

Polymath Software

P.O. Box 523

Willimantic, CT 06226-0523

<https://www.polymath-software.com/fogler>

Wolfram

100 Trade Center Drive

Champaign, IL 61820-7237

Tel: +1-217-398-0700

+1-800-WOLFRAM (965-3726)

Fax: +1-217-398-0747

www.wolfram.com

Python Software

206 East 9th Street

Floor 18

Austin, TX 78701

Tel: +1-512-222-5440

E-mail: webmaster@python.org

www.python.org

MATLAB

The Math Works, Inc.

20 North Main Street, Suite 250

Sherborn, MA 01770

For ordinary *and* partial differentiating equation solvers, contact:

COMSOL, Inc.

1 New England Executive Park

Burlington, MA 01803

Tel: +1-781-273-3322

Fax: +1-781-273-6603

E-mail: info@comsol.com

www.comsol.com

For simulators, contact:

Aspen Technology, Inc.

10 Canal Park

Cambridge, MA 02141-2201

Email: info@aspentech.com

www.aspentech.com

B. Ideal Gas Constant and Conversion Factors

See www.onlineconversion.com.

IDEAL GAS CONSTANT

$$\begin{aligned} R &= \frac{0.73 \text{ ft}^3 \cdot \text{atm}}{\text{lb mol} \cdot ^\circ \text{R}} & R &= \frac{1.987 \text{ Btu}}{\text{lb mol} \cdot ^\circ \text{R}} \\ R &= \frac{8.314 \text{ kPa} \cdot \text{dm}^3}{\text{mol} \cdot \text{K}} & R &= \frac{8.3144 \text{ J}}{\text{mol} \cdot \text{K}} \\ R &= 0.082 \frac{\text{dm}^3 \cdot \text{atm}}{\text{mol} \cdot \text{K}} = \frac{0.082 \text{ m}^3 \cdot \text{atm}}{\text{kmol} \cdot \text{K}} & R &= \frac{1.987 \text{ cal}}{\text{mol} \cdot \text{K}} \end{aligned}$$

$$\begin{aligned} \text{Boltzmann's constant } k_B &= 1.381 \times 10^{-23} \frac{\text{J}}{\text{molecule} \cdot \text{K}} \\ &= 1.381 \times 10^{-23} \text{ kg m}^2/\text{s}^2/\text{molecule/K} \end{aligned}$$

VOLUME OF IDEAL GAS

1 lb-mol of an ideal gas at 32°F and 1 atm occupies 359 ft³ (0.00279 lb-mol/ft³).

1 mol of an ideal gas at 0°C and 1 atm occupies 22.4 dm³ (0.0446 mol/dm³).

$$C_A = \frac{P_A}{RT} = \frac{y_A P}{RT}$$

where C_A = concentration of A, mol/dm³ T = temperature, K

P = pressure, kPa y_A = mole fraction of A

R = ideal gas constant, $8.314 \text{ kPa} \cdot \text{dm}^3 / \text{mol} \cdot \text{K}$

$$1\text{M} = 1 \text{ molar} = 1 \text{ mol/liter} = 1 \text{ mol/dm}^3 = 1 \text{ kmol/m}^3 = 0.062 \text{ lb-mol/ft}^3$$

VOLUME

$$1 \text{ cm}^3 = 0.001 \text{ dm}^3$$

$$1 \text{ in}^3 = 0.0164 \text{ dm}^3$$

$$1 \text{ fluid oz} = 0.0296 \text{ dm}^3$$

$$1 \text{ ft}^3 = 28.32 \text{ dm}^3$$

$$1 \text{ m}^3 = 1000 \text{ dm}^3$$

$$1 \text{ U.S. gal} = 3.785 \text{ dm}^3$$

$$1 \text{ liter (L)} = 1 \text{ dm}^3$$

LENGTH

$$1 \text{ \AA} = 10^{-8} \text{ cm}$$

$$1 \text{ dm} = 10 \text{ cm}$$

$$1 \text{ }\mu\text{m} = 10^{-4} \text{ cm}$$

$$1 \text{ in.} = 2.54 \text{ cm}$$

$$1 \text{ ft} = 30.48 \text{ cm}$$

$$1 \text{ m} = 100 \text{ cm}$$

$$\left(1 \text{ ft}^3 = 28.32 \text{ dm}^3 \times \frac{1 \text{ gal}}{3.785 \text{ dm}^3} = 7.482 \text{ gal} \right)$$

PRESSURE

$$1 \text{ torr (1 mmHg)} = 0.13333 \text{ kPa}$$

$$1 \text{ in. H}_2\text{O} = 0.24886 \text{ kPa}$$

$$1 \text{ atm} = 101.33 \text{ kPa}$$

$$1 \text{ psia} = 6.8943 \text{ kPa}$$

$$1 \text{ megadyne/cm}^2 = 100 \text{ kPa}$$

$$1 \text{ bar} = 100 \text{ kPa}$$

ENERGY (WORK)

$$1 \text{ kg}\cdot\text{m}^2/\text{s}^2 = 1 \text{ J}$$

$$1 \text{ Btu} = 1055.06 \text{ J}$$

$$1 \text{ cal} = 4.1868 \text{ J}$$

$$1 \text{ L}\cdot\text{atm} = 101.34 \text{ J}$$

$$1 \text{ hp}\cdot\text{h} = 2.6806 \times 10^6 \text{ J}$$

$$1 \text{ kWh} = 3.6 \times 10^6 \text{ J}$$

$$\left(1 \text{ bar} = 100 \text{ kPa} \times \frac{1 \text{ atm}}{101.37 \text{ kPa}} = 0.987 \text{ atm} \right)$$

TEMPERATURE

$$^{\circ}\text{F} = 1.8 \times ^{\circ}\text{C} + 32$$

$$^{\circ}\text{R} = ^{\circ}\text{F} + 459.69$$

$$\text{K} = ^{\circ}\text{C} + 273.16$$

$$^{\circ}\text{R} = 1.8 \times \text{K}$$

$$^{\circ}\text{Réaumur} = 1.25 \times ^{\circ}\text{C}$$

MASS

$$1 \text{ lb}_m = 454 \text{ g}$$

$$1 \text{ kg} = 1000 \text{ g}$$

$$1 \text{ grain} = 0.0648 \text{ g}$$

$$1 \text{ oz (avoird.)} = 28.35 \text{ g}$$

$$1 \text{ ton} = 908000 \text{ g}$$

VISCOSITY

$$1 \text{ poise} = 1 \text{ g/cm/s} = 0.1 \text{ kg/m/s}$$

$$1 \text{ centipoise} = 1 \text{ cp} = 0.01 \text{ poise} = 0.1 \text{ micro Pascal} \cdot \text{second}$$

FORCE

$$1 \text{ dyne} = 1 \text{ g} \cdot \text{cm/s}^2$$

$$1 \text{ Newton} = 1 \text{ kg} \cdot \text{m/s}^2$$

PRESSURE

$$1 \text{ Pa} = 1 \text{ Newton/m}^2$$

WORK

$$\text{A. Work} = \text{Force} \times \text{Distance}$$

$$1 \text{ Joule} = 1 \text{ Newton} \cdot \text{meter} = 1 \text{ kg m}^2/\text{s}^2 = 1 \text{ Pa} \cdot \text{m}^3$$

$$\text{B. Pressure} \times \text{Volume} = \text{Work}$$

$$(1 \text{ Newton/ m}^2) \cdot \text{m}^3 = 1 \text{ Newton} \cdot \text{m} = 1 \text{ Joule}$$

TIME RATE OF CHANGE OF ENERGY WITH TIME (POWER)

$$1 \text{ Watt} = 1 \text{ J/s}$$

$$1 \text{ hp} = 746 \text{ J/s}$$

GRAVITATIONAL CONVERSION FACTOR

Gravitational constant

$$g = 32.2 \text{ ft/s}^2$$

American Engineering System

$$g_c = 32.174 \frac{(\text{ft})(\text{lb}_m)}{(\text{s}^2)(\text{lb}_f)}$$

SI/cgs System

$$g_c = 1 \text{ (Dimensionless)}$$

TABLE B-1 TYPICAL PROPERTY VALUES

Liquid (water)	Gas (air, 77°C, 101 kPa)	Solid	
Density	1000 kg/m ³	1.0 kg/m ³	3000 kg/m ³
Concentration	55.5 mol/dm ³	0.04 mol/dm ³	–
Diffusivity	10 ⁻⁸ m ² /s	10 ⁻⁵ m ² /s	10 ⁻¹¹ m ² /s
Viscosity	10 ⁻³ kg/m/s	1.82 × 10 ⁻⁵ kg/m/s	–
Heat capacity	4.31 J/g/K	40 J/mol/K	0.45 J/g/K
Thermal conductivity	1.0 J/s/m/K	10 ⁻² J/s/m/K	100 J/s/m/K
Kinematic viscosity	10 ⁻⁶ m ² /s	1.8 × 10 ⁻⁵ m ² /s	–

Prandtl number	7	0.7	—
Schmidt number	200	2	—

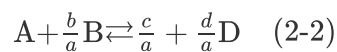
TABLE B-2 TYPICAL TRANSPORT VALUES

	Liquid	Gas
Heat transfer coefficient, h	1000 W/m ² /K	65 W/m ² /K
Mass transfer coefficient, k_c	10 ⁻² m/s	3 m/s

C. Thermodynamic Relationships Involving the Equilibrium Constant¹

¹ For the limitations and for further explanation of these relationships, see, for example, K. Denbigh, *The Principles of Chemical Equilibrium*, 3rd ed. Cambridge: Cambridge University Press, 1971, p. 138.

For the gas-phase reaction



1. The true (dimensionless) equilibrium constant

$$RT \ln K = -\Delta G$$

$$K = \frac{a_C^{c/a} a_D^{d/a}}{a_A a_B^{b/a}}$$

where a_i is the activity of species i

$$a_i = \frac{f_i}{f_i^\circ}$$

where f_i = fugacity of species i

f_i° = fugacity of species i at the standard state. For gases, the standard state is 1 bar, which is in the noise level of 1 atm, so we will use atm.

$$a_i = \frac{f_i}{f_i^\circ} = \gamma_i P_i$$

where γ_i is the activity coefficient

$$K = \underbrace{\frac{\gamma_C^{c/a} \gamma_D^{d/a}}{\gamma_A \gamma_B^{b/a}}}_{K_\gamma} \cdot \underbrace{\frac{P_C^{c/a} P_D^{d/a}}{P_A P_B^{b/a}}}_{K_p} = K_\gamma K_p$$

K = True equilibrium constant
 K_Y Activity equilibrium constant
 K_p = Pressure equilibrium constant
 K_c = Concentration equilibrium constant

K_Y has units of [atm] $[\text{atm}]^{-\left(d/a+c/a-\frac{b}{a}-1\right)} = [\text{atm}]^{-\delta}$

K_p has units of [atm] $[\text{atm}]^{-\left(d/a+c/a-\frac{b}{a}-1\right)} = [\text{atm}]^{\delta}$

For ideal gases $K_Y = 1.0 \text{ atm}^{-\delta}$

2. For the generic reaction (2-2), the pressure equilibrium constant K_p is

$$K_p = \frac{P_C^{c/a} P_D^{d/a}}{P_A P_B^{b/a}} \quad (\text{C-1})$$

P_i = partial pressure of species i , atm, kPa.
 $P_i = C_i RT$

3. For the generic reaction (2-2), the concentration equilibrium constant K_c is

$$K_c = \frac{C_C^{c/a} C_D^{d/a}}{C_A C_B^{b/a}} \quad (\text{C-2})$$

It is important to be able to relate K , K_Y , K_c , and K_p .

4. For ideal gases, K_c and K_p are related by

$$K_p = K_c (RT)^{\delta} \quad (\text{C-3})$$

where for the generic reaction (2-2),

$$\delta = \frac{c}{a} + \frac{d}{a} - \frac{b}{a} - 1 \quad (\text{C-4})$$

5. K_p is a function of temperature only, and the temperature dependence of K_p is given by van't Hoff's equation:

$$\boxed{\frac{d \ln K_p}{dT} = \frac{\Delta H_{R,x}(T)}{RT^2}} \quad (\text{C-5})$$

$$\frac{d \ln K_p}{dT} = \frac{\Delta H_{R,x}^{\circ}(T_R) + \Delta C_p(T - T_R)}{RT^2} \quad (\text{C-6})$$

(<http://www.umich.edu/~elements/6e/11chap/summary-biovan.html>).

6. Integrating, we have

$$\ln \frac{K_p(T)}{K_p(T_1)} = \frac{\Delta H_{R,x}^{\circ}(T_R) - T_R \Delta C_p}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) + \frac{\Delta C_p}{R} \ln \frac{T}{T_1} \quad (\text{C-7})$$

K_p and K_c are related by

$$K_c = \frac{K_p}{(RT)^{\delta}} \quad (\text{C-8})$$

when

$$\delta = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right) = 0$$

then

$$K_P = K_C$$

7. K_P neglecting ΔC_P . Given the equilibrium constant at one temperature, T_1 , $K_P(T_1)$, and the heat of reaction, $\Delta H_{\text{Rx}}^\circ$, the partial pressure equilibrium constant at any temperature T is

$$K_p(T) = K_p(T_1) \exp \left[\frac{\Delta H_{\text{Rx}}^\circ(T_R)}{R} \left(\frac{1}{T} - \frac{1}{T_1} \right) \right] \quad (\text{C-9})$$

8. From Le Châtelier's principle we know that for exothermic reactions, the equilibrium shifts to the left (i.e., K and X_e decrease) as the temperature increases. Figures C-1 and C-2 show how the equilibrium constant varies with temperature for an exothermic reaction and for an endothermic reaction, respectively.

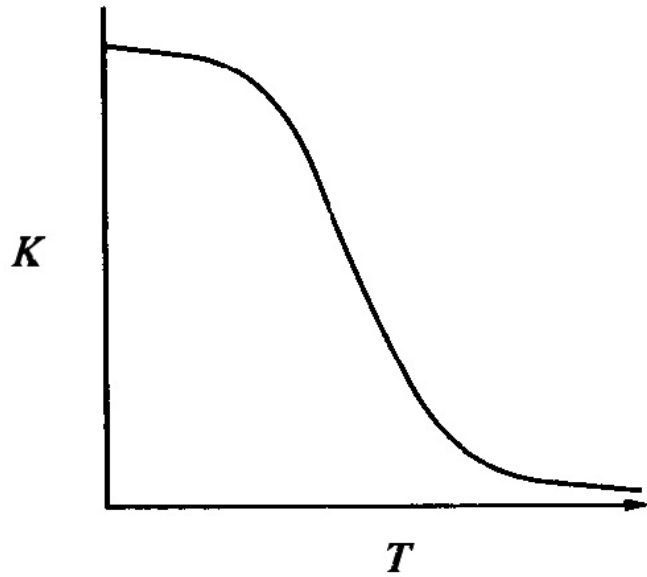


Figure C-1 Exothermic reaction.

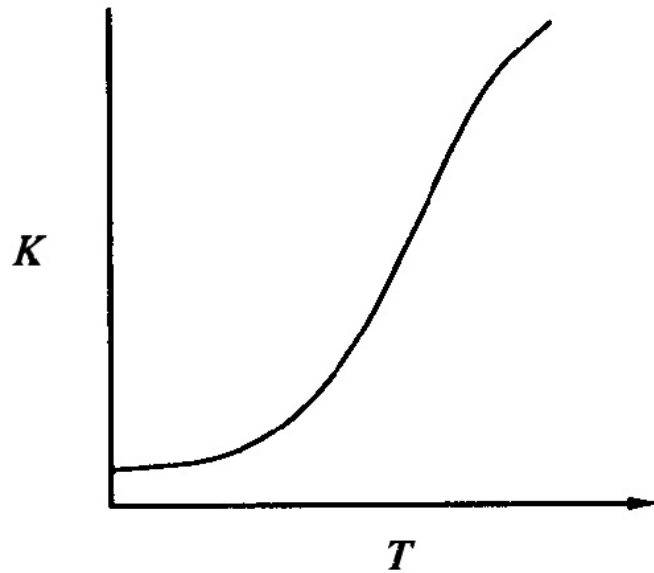


Figure C-2 Endothermic reaction.

9. The equilibrium constant for the reaction (2-2) at temperature T can be calculated from the change in the Gibbs free energy using

$$-RT \ln [K(T)] = \Delta G_{\text{Rx}}^{\circ}(T) \quad (\text{C-10})$$

$$\Delta G_{\text{Rx}}^{\circ} = \frac{c}{a} G_C^{\circ} + \frac{d}{a} G_D^{\circ} - \frac{b}{a} G_B^{\circ} - G_A^{\circ} \quad (\text{C-11})$$

10. Tables that list the standard Gibbs free energy of formation of a given species G_i° are available in the literature (webbook.nist.gov).
11. The relationship between the change in Gibbs free energy and enthalpy, H , and entropy, S , is

$$\Delta G = \Delta H - T\Delta S \quad (\text{C-12})$$

See

<https://www.chm.uri.edu/weuler/chm112/lectures/lecture26.html>. An example on how to calculate the equivalent conversion for ΔG is given on the Web site.

Example C-1 Water-Gas Shift Reaction

The water-gas shift reaction to produce hydrogen



is to be carried out at 1000 K and 10 atm. For an equimolar mixture of water and carbon monoxide, calculate the equilibrium conversion and concentration of each species.

Data: At 1000 K and 10 atm, the Gibbs free energies of formation are

$G_{\text{CO}}^\circ = -47,860 \text{ cal/mol}$; $G_{\text{CO}_2}^\circ = -94,630 \text{ cal/mol}$; $G_{\text{H}_2\text{O}}^\circ = -46,040 \text{ cal/mol}$; and $G_{\text{H}_2}^\circ = 0$.

Solution

We first calculate the equilibrium constant. The first step in calculating K is to calculate the change in Gibbs free energy for the reaction. Applying Equation (C-10) gives us

Calculate $\Delta G_{\text{Rx}}^\circ$

$$\begin{aligned} \Delta G_{\text{Rx}}^\circ &= G_{\text{H}_2}^\circ + G_{\text{CO}_2}^\circ - G_{\text{CO}}^\circ - G_{\text{H}_2\text{O}}^\circ \\ &= 0 + (-94,630) - (-47,860) - (-46,040) \\ &= -730 \text{ cal/mol} \end{aligned} \quad (\text{EC-1.1})$$

$$-RT \ln K = \Delta G_{\text{Rx}}^\circ(T) \quad (\text{C-10})$$

Calculate K

$$\begin{aligned} \ln K &= -\frac{\Delta G_{\text{Rx}}^\circ(T)}{RT} = \frac{-(-730 \text{ cal/mol})}{1.987 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}(1000\text{K})} \quad (\text{EC-1.2}) \\ &= 0.367 \end{aligned}$$

then

$$K = 1.44$$

Expressing the equilibrium constant first in terms of activities and then finally in terms of concentration, we

have

$$K = \frac{a_{\text{CO}_2} a_{\text{H}_2}}{a_{\text{CO}} a_{\text{H}_2\text{O}}} = \frac{f_{\text{CO}_2} f_{\text{H}_2}}{f_{\text{CO}} f_{\text{H}_2\text{O}}} = \frac{\gamma_{\text{CO}_2} P_{\text{CO}_2} \gamma_{\text{H}_2} P_{\text{H}_2}}{\gamma_{\text{CO}} P_{\text{CO}} \gamma_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}} \quad (\text{EC-1.3})$$

where a_i is the activity, f_i is the fugacity, γ_i is the activity coefficient (which we shall take to be 1.0 owing to high temperature and low pressure), and y_i is the mole fraction of species i .² Substituting for the mole fractions in terms of partial pressures gives

$$K = \frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}} \quad (\text{EC-1.4})$$

$$P_i = C_i RT \quad (\text{EC-1.5})$$

$$K = \frac{C_{\text{CO}_2} C_{\text{H}_2\text{O}}}{C_{\text{CO}} C_{\text{H}_2\text{O}}} \quad (\text{EC-1.6})$$

² See Chapter 17 in J. R. Elliott and C. T. Lira, *Introductory Chemical Engineering Thermodynamics*, 2nd ed. Upper Saddle River, NJ: Pearson, 2012, and Chapter 16 in J. W. Tester and M. Modell, *Thermodynamics and Its Applications*, 3rd ed. Upper Saddle River, NJ: Pearson, 1997.

Relate K and X_e .

In terms of conversion for an equimolar feed, we have

$$K = \frac{C_{\text{CO},0} X_e C_{\text{CO},0} X_e}{C_{\text{CO},0} (1-X_e) C_{\text{CO},0} (1-X_e)} \quad (\text{EC-1.7})$$

$$= \frac{X_e^2}{(1-X_e)} = 1.44 \quad (\text{EC-1.8})$$

From Figure EC-1.1 we read at 1000 K that $\log K_P = 0.15$; therefore, $K_P = 1.41$, which is close to the calculated value. We note that there is no net change in the number of moles for this reaction (i.e.,); therefore,

$$K = K_p = K_c \text{ (dimensionless)}$$

Taking the square root of Equation (EC-1.8) yields

$$\frac{X_e}{1-X_e} = (1.44)^{1/2} = 1.2 \quad (\text{EC-1.9})$$

$$X_e = \frac{1.2}{2.2} = 0.55$$

Then

$$\begin{aligned}
 C_{\text{CO},0} &= \frac{y_{\text{CO},0}P_0}{RT_0} \\
 &= \frac{(0.5)(10\text{atm})}{(0.082\text{dm}^3\cdot\text{atm}/\text{mol}\cdot\text{K})(1000\text{ K})} \\
 &= 0.061\text{mol}/\text{dm}^3
 \end{aligned}$$

Calculate $C_{\text{CO},e}$, the equilibrium conversion of CO

$$C_{\text{CO},e} = C_{\text{CO},0}(1 - X_e) = (0.061)(1 - 0.55) = 0.0275\text{mol}/\text{dm}^3$$

$$C_{\text{H}_2\text{O},e} = 0.0275\text{mol}/\text{dm}^3$$

$$C_{\text{CO}_2,e} = C_{\text{H}_2,e} = C_{\text{CO},0}X_e = 0.0335\text{mol}/\text{dm}^3$$

Figure EC-1.1 gives the equilibrium constant as a function of temperature for a number of reactions. Reactions in which the lines increase from left to right are exothermic.

The following links give thermochemical data. (Heats of Formation, C_P , etc.)

1. www.uic.edu/~mansoori/Thermodynamic.Data.and.Property_.html

2. webbook.nist.gov

Also see *Chem. Tech.*, 28 (3) (March), 19 (1998).

D. Software Packages

While Polymath 6.1 is the primary software package for the majority of the problems requiring numerical solutions, Wolfram, Excel, Python, and MATLAB are also available. In addition, one can use COMSOL and Aspen to solve a few selected problems in Chapters 12 and 13 and Chapter 18.

D.1 POLYMATH

D.1.A About Polymath

(<http://www.umich.edu/~elements/6e/software/polymath.html>)

Polymath is an extremely user-friendly software package that is best suited for solving chemical reaction engineering problems. In this text and on the Web site, we mostly use the DEQ for solving coupled differential equations (e.g., conversion and temperature), but also use REG for fitting data to a curve, as well as nonlinear regression to determine the best values of parameters to fit the data to determine the reaction-rate parameters such as the specific reaction-rate k and the activation energy, E_A .

- Simultaneous linear algebraic equations
- Simultaneous nonlinear algebraic equations
- Simultaneous ordinary differential equations

- Data regressions (including the following)
 - Curve fitting by polynomials
 - Multiple linear regression with statistics
 - Nonlinear regression with statistics

Polymath is unique in that the problems are entered just like their mathematical equations and there is a minimal learning curve. Problem solutions are easily found with robust algorithms. Polymath allows very convenient problem-solving to be used in chemical reaction engineering and other areas of chemical engineering, leading to an enhanced educational experience for students.

Polymath is available free on most universities' computers. In addition, if you would like to buy a version to load onto your own personal computer, you could first try a free 15-day trial version of Polymath 6.1. The trial version of Polymath 6.1 will execute up to 15 consecutive days after installation. You will be able to install this version only once on a particular personal computer. Detailed information on ordering specially priced educational versions of Polymath 6.1 that will execute for a variety of time periods (e.g., 4 months, 1 year) is available only from <http://www.polymathsoftware.com/fogler/>.

D.1.B Polymath Tutorials

(<http://www.umich.edu/~elements/6e/software/polymath-tutorial.html>)

Polymath tutorials (LEQ, NLE, DEQ, REG) for the following Polymath Programs are given on the Web site.

- How to Run the LEP Codes
(http://www.umich.edu/~elements/6e/software/Polymath_LEP_tutorial_new.pdf)
- Linear Equation Solver
(http://www.umich.edu/~elements/6e/software/Linear_Equation_%20Solver_Tutorial.pdf)
- Nonlinear Equation Solver
(http://www.umich.edu/~elements/6e/software/Non_linear_equation_tutorial.pdf)
- Ordinary Differential Equation Solver
(http://www.umich.edu/~elements/6e/software/Ordinary_Differential_Equation_Solver_Tutorial.pdf)
- Regression Polynomial Fitting of Data
(http://www.umich.edu/~elements/6e/software/Polymath_linear_and_polynomial_regression_tutorial.pdf)
- Nonlinear Regression Analysis
 - Find Rate Law Parameters (alpha and k)
(http://www.umich.edu/~elements/6e/software/Example_7-3_Polymath_nonlinear_regression_tutorial.pdf)
 - Find Rate Law Parameters for Heterogeneous Reactions
(http://www.umich.edu/~elements/6e/software/Nonlinear_Regression_Tutorial.pdf)
- Nonlinear Regression Tutorial
(http://www.umich.edu/~elements/6e/software/nonlinear_regression_tutorial.pdf)

The Web site shows screen shots of the various steps for each of the Polymath programs. A Polymath tutorial is also given in the LearnChemE videos (<https://www.youtube.com/watch?v=nyJmt6cTiL4>).

D.1.C Living Example Problems (LEPs)

The Living Example Problems (LEPs) are available in Wolfram, Python, MATLAB, and Polymath and can be run by first loading the software package on to your computer and then clicking on the problem of interest. A tutorial on how to download and run the LEPs is on the CRE Web site—for example, Polymath LEPs need to be copied from the CRE Web site and pasted into the Polymath software. The Polymath software is available in most chemical engineering departments and computer labs in the United States and in some other countries as well. If you want to have Polymath on your own laptop or desktop computer, you can purchase special low-priced educational versions of the software for various time periods. Polymath versions are compatible with Windows XP, Vista, Windows 7, Windows 8, and Windows 10. Android users can also use PolyMathLite on phones, tablets, and computers. More information is available from the Web site www.polymathlite.com.

D.2 WOLFRAM

Wolfram CDF Player is used for viewing .cdf files. Its main feature is creating dynamic and interactive examples, which allow users to vary different parameters using sliders and generate results live (allows users to immediately change parameters, and continuously update the plot), although it is not necessary in order to run the Wolfram LEP. If you wish to also edit the code that generates these programs, you need to purchase and download Wolfram Mathematica 12, which can be found here:

<http://www.wolfram.com/mathematica/>. (Note for all University of Michigan students: CAEN computers have Mathematica 12 installed, so you can easily edit and view the Mathematica files.)

Getting Started

- Download Wolfram CDF Player for FREE (<https://www.wolfram.com/cdf-player/>). (Note for all University of Michigan students: CAEN computers have CDF player installed, so you don't need to install CDF player.)
- View the tutorial on installing Wolfram CDF Player (http://www.umich.edu/~elements/6e/software/CDF_installation_tutorial.pdf).
- View the tutorial on running Wolfram LEP codes (http://www.umich.edu/~elements/6e/software/Wolfram_LEP_tutorial.pdf).
- View the tutorial for the initial settings of the Wolfram variable.

D.3 PYTHON

In this edition, Python sliders software is included in the Living Example Problems as a resource. Python is similar to Wolfram in that one uses sliders to change the parameters to study the reactions and reactors in which they take place. A **tutorial** can be found on the Web site (http://www.umich.edu/~elements/6e/tutorials/Python_tutorials.html).

D.4 MATLAB

MATLAB is a high-performance language for technical computing. It is a matrix-based language that allows matrix manipulations, plotting of functions and data, implementation of algorithms, and interfacing with programs written in other languages. To run MATLAB code you need MATLAB software, which is available on most university computers where it is free for your use. If for some reason it is not available at your university, it can be purchased from <https://www.mathworks.com>.

MATLAB programs for the LEPs are given on the CRE Web site. The disadvantage of the MATLAB ODE solver is that it is not particularly user-friendly when trying to determine the variation of secondary parameter values. MATLAB can be used for the same four types of programs as Polymath.

Getting Started

If you already have MATLAB installed on your computer, use the MATLAB program tutorial. If you don't have MATLAB installed, please visit

https://www.mathworks.com/programs/trials/trial_request.html?ref=ggl&s_eid=ppc_5852767522&q=%252Btrial%20%252Bmatlab to download a one-month free trial.

MATLAB Tutorial

Ordinary Differential Equation (ODE) Solver Tutorial
(http://www.umich.edu/~elements/6e/software/matlab_tutorial)

[_LEP-12-1.pdf](#)

D.5 EXCEL

Microsoft Excel is a spreadsheet application that uses a grid of cells arranged in rows and columns to perform basic and complex mathematical computations and functions. It features calculation, graphing tools, pivot tables, and a macro programming language. In this text, we use Excel for performing linear regression.

Getting Started

The tutorial assumes that you have Excel (Microsoft Office) installed on your computer. If you are a student or faculty at a university, you likely have Excel available to you on university computers. If you don't have access to Excel, contact your university computing services or visit products.office.com to download 30-day free trial or to purchase Excel from Microsoft (<https://products.office.com/en-US/excel?legRedirect=true&CorrelationId=f37dfa92-9ec7-41a1-bdd4-d5ccd9210720>). For University of Michigan students, Excel is available on all on-campus computers.

Excel Tutorial

- Determination of Activation Energy
(http://www.umich.edu/~elements/6e/software/Excel_tutorial.pdf)

D.6 COMSOL

[\(HTTP://WWW.UMICH.EDU/~ELEMENTS/6E/](HTTP://WWW.UMICH.EDU/~ELEMENTS/6E/)

12CHAP/COMSOL.HTML)

COMSOL Multiphysics is modeling and simulation software that is available commercially from COMSOL Inc. It solves multiphysics problems in 1D, 1D axisymmetry, 2D, 2D axisymmetry, 3D, and at single points (0D). Internally in the program, these problems are formulated using partial differential equations (PDEs for 1D to 3D) or ordinary differential equations (ODEs).

The textbook features model examples that have been formulated and solved using the COMSOL Multiphysics software. At www.comsol.com/ecre, each problem is described and summarized in the documentation, which also includes step-by-step instructions to reproduce the corresponding models and derive the model equations in detail. In the Web modules, there are five different COMSOL modules (e.g., tubular reactor, plug-flow reactor, CSTR) that can be downloaded. In order to run or reproduce these COMSOL models, a valid COMSOL Multiphysics license is required.

We use COMSOL software to solve both ordinary and partial differential equations (<http://www.comsol.com/ecre>). The Chemical Reaction Engineering Module in COMSOL is used to solve space- and time-dependent problems.

Getting Started

If you have COMSOL software installed on your computer, then you can develop your own COMSOL files or access a

number of COMSOL files present on the COMSOL Web site (<http://www.comsol.com/ecre>). There is a tutorial on downloading and running a COMSOL file from the COMSOL Web site at http://umich.edu/~elements/6e/software/software_comsol.html.

If you don't have COMSOL software, don't worry! We have created a user interface for COMSOL LEP files that enables you to access and run all the COMSOL files, which are in the library. You can sign in to use the COMSOL models using the University of Michigan's Web site as a "Guest." To access and run COMSOL, go to <http://www.umich.edu/~elements/6e/12chap/comsol.html>.

COMSOL tutorials to run COMSOL LEP files for the following COMSOL modules are given on the Web site (http://www.umich.edu/~elements/6e/software/software_comsol.html).

- Nonisothermal tubular reactor
- Startup of a CSTR
- Plug-flow reactor with adiabatic operations
- Plug-flow reactor with heat exchange
- Two CSTR in series

D.7 ASPEN

Aspen is a process simulator that is used primarily in senior design courses. It has the steepest learning curve of the

software packages used in this text. It has a built-in database of the physical properties of reactants and products.

Consequently, one has only to type in the chemicals and the rate-law parameters. It is really too powerful to be used for the types of home problems given here. The pyrolysis of benzene using Aspen is given as an example on the CRE Web site in Chapter 5, *Learning Resources 4.E, Solved Problem E.5-3 Design*. Perhaps one home assignment should be devoted to using Aspen to solve a problem with heat effects in order to help familiarize the student with Aspen.

An Aspen tutorial and example problem from Chapters 5, 11, and 12 can be accessed directly from the CRE Web site home page (under *Let's Get Started*, click on *Additional Software* and then click *Aspen Plus*).

Instructions for using Aspen Plus to solve chemical reaction engineering problems (software not included) can be found on the Aspen Web site at www.aspentech.com.

- Chapter 5—Example 5-3: Producing 300 Million Pounds per Year of Ethylene in a Plug-Flow Reactor: Design of a Full-Scale Tubular Reactor (Tutorial, ASPEN Backup File)
(<http://www.umich.edu/~elements/6e/software/aspen-creating.html>)
- Chapter 8—Supplemental Example: Pyrolysis of Benzene (Tutorial, ASPEN Backup File, Polymath File)
- Chapter 11—Example 11-3: Adiabatic Liquid-Phase Isomerization of Normal Butane (Tutorial, ASPEN Backup File)
(<http://www.umich.edu/~elements/6e/software/aspen-example11-3.html>)

- Chapter 12—Example 12-2a: Adiabatic Production of Acetic Anhydride (Tutorial, ASPEN Backup File)
(<http://www.umich.edu/~elements/6e/software/aspen-example12-2.html#8-6>).
- Chapter 12—Example 12-2b: Constant Heat Exchange Production of Acetic Anhydride (Tutorial, ASPEN Backup File)
(<http://www.umich.edu/~elements/6e/software/aspen-example12-2.html#8-7>).

D.8 VISUAL ENCYCLOPEDIA OF EQUIPMENT—REACTORS SECTION

Additional information on different types of reactors is available at

<http://encyclopedia.che.engin.umich.edu/Pages/Reactors/menu.html>.

D.9 REACTOR LAB

Instructions for using ReactorLab to simulate a variety of chemical reactors are available at <http://reactorlab.net>.

E. *Rate-Law Data*

Reaction-rate laws and data can be obtained from the following Web sites:

1. National Institute of Standards and Technology (NIST)
Chemical Kinetics Database on the Web
Standard Reference Database 17, Version 7.0 (Web Version), Release 1.2
This Web site provides a compilation of kinetics data on gas-phase reactions.
<http://kinetics.nist.gov/kinetics/index.jsp>
2. International Union of Pure and Applied Chemistry (IUPAC)
This Web site provides kinetic and photochemical data for gas kinetic data evaluation.
<http://iupac.pole-ether.fr/>
3. NASA/JPL (Jet Propulsion Laboratory: California Institute of Technology)
This Web site provides chemical kinetics and photochemical data for use in atmospheric studies. <http://jpldataeval.jpl.nasa.gov/download.html>
4. BRENDA: University of Cologne
This Web site provides enzyme data and metabolic information. BRENDA is maintained and developed at the Institute of Biochemistry at the University of Cologne.
<http://www.brenda-enzymes.org/>
5. NDRL Radiation Chemistry Data Center: Notre Dame Radiation Laboratory
This Web site provides the reaction-rate data for transient radicals, radical ions, and excited states in solution.
<http://rad.nd.edu/data-center/>

F. *Nomenclature*

A Chemical species

A_c Cross-sectional area (m^2)

A_p Total external surface area of particle (m^2)

a_p External surface area of catalyst per unit bed volume (m^2/m^3)

a Area of heat exchange per unit volume of reactor (m^{-1})

a_c External surface area per volume of catalyst pellets (m^2/m^3)

B Chemical species

$\mathbf{B_A}$ Flux of A resulting from bulk flow ($\text{mol}/\text{m}^2 \cdot \text{s}$)

Bo Bodenstein number

C Chemical species

C_i Concentration of species i (mol/dm³)

C_{pi} Heat capacity of species i at temperature T (cal/gmol · K)

\tilde{C}_{pi} Mean heat capacity of species i between temperature T_0 and temperature T (cal/mol · K)

\hat{C}_{pi} Mean heat capacity of species i between temperature T_R and temperature T (cal/mol · K)

c Total concentration (mol/dm³) (Chapter 14)

D Chemical species

Da Damköhler number (dimensionless)

D_{AB} Binary diffusion coefficient of A in B (dm²/s)

D_d Dispersion coefficient (cm²/s)

D_e Effective diffusivity (dm²/s)

D_K Knudsen diffusivity (dm²/s)

D^* Taylor dispersion coefficient

E Activation energy (cal/gmol)

(E) Concentration of free (unbound) enzyme (mol/dm³)

F_i Molar flow rate of species i (mol/s)

F_{i0} Entering molar flow rate of species i (mol/s)

f Volumetric flow rate ratio, v/v_0

G Superficial mass velocity (g/dm²·s)

G_i Rate of generation of species i (mol/s)

$G_i^o(T)$ Gibbs free energy of species i at temperature T (cal/gmol · K)

$H_i(T)$ Enthalpy of species i at temperature T (cal/mol i)

$H_{i0}(T)$ Enthalpy of species i at temperature T_0 (cal/mol i)

H_i^o Enthalpy of formation of species i at temperature T_R (cal/gmol i)

h Heat transfer coefficient (cal/m² · s · K)

J_A Molecular diffusive flux of species A ($\text{mol/m}^2 \cdot \text{s}$)

K_A Adsorption equilibrium constant

K_c Concentration equilibrium constant

K_e Equilibrium constant (dimensionless)

K_p Partial pressure equilibrium constant

k Specific reaction rate (constant)

k_c Mass transfer coefficient (m/s)

M_i Molecular weight of species i (g/mol)

MR Mears Number

m_i Mass of species i (g)

N_i Number of moles of species i (mol)

n Overall reaction order

Nu Nusselt number (dimensionless)

Pe Péclet number (Chapter 17)

P_i Partial pressure of species i (atm)

Pr Prandtl number (dimensionless)

p Pressure ratio P/P_0

Q Heat flow from the surroundings to the system (cal/s)

R Ideal gas constant

Re Reynolds number

r Radial distance (m)

r_A Rate of generation of species A per unit volume ($\text{gmol A/s} \cdot \text{dm}^3$)

$-r_A$ Rate of disappearance of species A per unit volume ($\text{mol A/s} \cdot \text{dm}^3$)

$-r'_A$ Rate of disappearance of species A per mass of catalyst ($\text{mol A/g} \cdot \text{s}$)

$-r''_A$ Rate of disappearance of A per unit area of catalytic surface ($\text{mol A/m}^2 \cdot \text{s}$)

S An active site (Chapter 10)

(S) Substrate concentration (gmol/dm^3) (Chapter 7)

S_a Surface area per unit mass of catalyst (m^2/g)

$S_{D/U}$ Instantaneous selectivity (Chapter 8)

$\tilde{S}_{D/U}$ Overall selectivity of D to U

Sc Schmidt number (dimensionless) (Chapter 10)

Sh Sherwood number (dimensionless) (Chapter 10)

SV Space velocity (s^{-1})

T Temperature (K)

t Time (s)

U Overall heat transfer coefficient ($\text{cal}/\text{m}^2 \cdot \text{s} \cdot \text{K}$)

V Volume of reactor (dm^3)

V_0 Initial reactor volume (dm^3)

v Volumetric flow rate (dm^3/s)

v_0 Entering volumetric flow rate (dm^3/s)

W Weight of catalyst (kg)

WP Weisz-Prater criterion

\mathbf{W}_A Molar flux of species A ($\text{mol}/\text{m}^2 \cdot \text{s}$)

X Conversion of key reactant, A

Y_i Instantaneous yield of species i

\tilde{Y}_i Overall yield of species i

y_i Mole fraction of species i

y_{i0} Initial mole fraction of species i

Z Compressibility factor

z Linear distance (cm)

Subscripts

0 Entering or initial condition

b Bed (bulk)

c Catalyst

e Equilibrium

p Pellet Greek Symbols

Greek Symbols

α Reaction order (Chapter 3)

α Pressure-drop parameter (Chapter 5)

α_i Parameter in heat capacity (Chapter 12)

β_i Parameter in heat capacity

β Reaction order

γ_i Parameter in heat capacity

δ Change in the total number of moles per mole of A reacted

ϵ Fraction change in volume per mole of A reacted resulting from the change in total number of moles

η Internal effectiveness factor

Θ_i Ratio of the number of moles of species i initially (entering) to the number of moles of A initially (entering)

λ Dimensionless distance (z/L) (Chapter 15)

λ Life expectancy (s) (Chapter 17)

μ Viscosity ($\text{g}/\text{cm} \cdot \text{s}$)

ρ Density (g/cm^3)

ρ_c Density of catalyst pellet (g/cm^3 of pellet)

ρ_b Bulk density of catalyst (g/cm^3 of reactor bed)

τ Space time (s)

ϕ Void fraction (porosity)

ϕ_n Thiele modulus

ψ Dimensionless concentration (C_A/C_{As})

Ω External (overall) effectiveness factor

ν Kinematic viscosity (m^2/s)

G. Open-Ended Problems

The following are summaries for open-ended problems that have been used as term problems at the University of Michigan.

The complete problem statement of the problems can be found on the CRE Web site, Web Appendix G (<http://www.umich.edu/~elements/6e/appendix/DVDROM-Appendix-G.pdf>).

G.1 CHEME CAR

Each year, the finals of the *Chem-E-Car* competition is held at the annual meeting of the American Institute of Chemical Engineers (AIChE). To be able to compete in the finals, a student chapter must qualify at a regional competition, which is held in the spring. The competition is to design and build a small car that is powered by a chemical reaction, fits in no more than a very large shoebox, carries a specified amount of water (e.g., 500 dm³), travels a certain distance (e.g., 35 m), and stops. The amount of water to be carried and the distance are specified 1 hour before the competition begins. The complete list of rubrics can be found at <https://www.aiche.org/chem-e-car-competitionr-rules>.

G.2 EFFECTIVE LUBRICANT DESIGN

Lubricants used in car engines are formulated by blending a base oil with additives to yield a mixture with the desirable physical attributes. In this problem, students examine the degradation of lubricants by oxidation and design an improved lubricant system. The design should include the lubricant system's physical and chemical characteristics, as well as an explanation as to how it is applied to automobiles. Focus: automotive industry, petroleum industry.

G.3 PEACH BOTTOM NUCLEAR REACTOR

The radioactive effluent stream from a newly constructed nuclear power plant must be made to conform with Nuclear Regulatory Commission standards. Students use chemical reaction engineering and creative problem solving to propose solutions for the treatment of the reactor effluent. Focus: problem analysis, safety, ethics.

G.4 UNDERGROUND WET OXIDATION

You work for a specialty chemicals company that produces large amounts of aqueous waste. Your chief executive officer (CEO) read in a journal about an emerging technology for reducing hazardous waste, and you must evaluate the system and its feasibility. Focus: waste processing, environmental issues, ethics.

G.5 HYDRODESULFURIZATION REACTOR DESIGN

Your supervisor at Kleen Petrochemical wishes to use a hydrodesulfurization reaction to produce ethylbenzene from a process waste stream. You have been assigned the task of designing a reactor for the hydrodesulfurization reaction. Focus: reactor design.

G.6 CONTINUOUS BIOPROCESSING

Most commercial bioreactions are carried out in batch reactors. The design of a continuous bioreactor is desired since it may prove to be more economically rewarding than batch processes. Most desirable is a reactor that can sustain cells that are suspended in the reactor while growth medium is fed in, without allowing the cells to exit the reactor. Focus: mixing modeling, separations, bioprocess kinetics, reactor design.

G.7 METHANOL SYNTHESIS

Kinetic models based on experimental data are being used increasingly in the chemical industry for the design of catalytic reactors. However, the modeling process itself can influence the final reactor design and its ultimate performance by incorporating different interpretations of experimental design into the basic kinetic models. In this problem, students are asked to develop kinetic modeling methods/approaches and apply them in the development of a model for the production of methanol from experimental data. Focus: kinetic modeling, reactor design.

G.8 CAJUN SEAFOOD GUMBO

Most gourmet foods are prepared by batch processes, that is, a batch reactor. In this problem, students are challenged to design a continuous process for the production of gourmet-quality Cajun seafood gumbo from an old family recipe. Some of the most difficult gourmet foods to prepare are Louisiana specialties, owing to the delicate balance between spices (hotness) and subtle flavors that must be achieved. In preparing Creole and Cajun food, certain flavors are released only by cooking some of the ingredients in hot oil for a period of time.

We shall focus on one specialty, Cajun seafood gumbo (http://umich.edu/~elements/6e/appendix/New_Orleans.pdf). Develop a continuous-flow reactor system that would produce 5 gal/h of a gourmet-quality seafood gumbo. Prepare a flow sheet of the entire operation. Outline certain experiments and areas of research that would be needed to ensure the success of your project. Discuss how you would begin to research these problems. Make a plan for any experiments to be carried out (see Chapter 7, R7.5, [<http://www.umich.edu/~elements/6e/07chap/prof-7-5.html>]).

Following is an old family formula for Cajun seafood gumbo for batch operation (10 quarts, serves 40):

1 cup flour 4 bay leaves, crushed

1½ cups olive oil ½ cup chopped parsley

1 cup chopped celery 3 large Idaho potatoes (diced)

2 large red onions (diced) 1 tablespoon ground pepper

5 qt fish stock 1 tablespoon tomato paste

6 lb fish (combination of cod, red snapper, monk fish, and halibut) 5 cloves garlic (diced)

½ tablespoon Tabasco sauce

12 oz crabmeat 1 bottle dry white wine

1 qt medium oysters 1 lb scallops

1 lb medium to large shrimp

1. Make a roux (i.e., add 1 cup flour to 1 cup of boiling olive oil). Cook until dark brown. Add roux to fish stock.
2. Cook chopped celery and onion in boiling olive oil until onion is translucent. Drain and add to fish stock.
3. Add of the fish (2 lb) and of the crabmeat, liquor from oysters, bay leaves, parsley, potatoes, black pepper, tomato paste, garlic, Tabasco, and cup of the olive oil. Bring to a slow boil and cook 4 h, stirring intermittently.

4. Add 1 qt cold water, remove from the stove, and refrigerate (at least 12 h) until 2 h before serving.
5. Remove from refrigerator, add cup of the olive oil, wine, and scallops. Bring to a light boil, then simmer for 2 h. Add remaining fish (cut to bite size), crabmeat, and water to bring total volume to 10 qt. Simmer for 2 h, add shrimp, then 10 minutes later, add oysters and serve immediately.

G.9 ALCOHOL METABOLISM

The purpose of this open-ended problem is for the students to apply their knowledge of reaction kinetics to the problem of modeling the metabolism of alcohol in humans. In addition, the students will present their findings in a poster session. The poster presentations will be designed to bring a greater awareness to the university community of the dangers associated with alcohol consumption.

Students should choose one of the following four major topics to further investigate:

1. Death caused by acute alcohol overdose
2. Long-term effects of alcohol
3. Interactions of alcohol with common medications
4. Factors affecting metabolism of alcohol

General information regarding each of these topics can be found on the CRE Web site.

The metabolism and model equations are given on the CRE Web site. One can load the Living Example problem for

alcohol metabolism directly from the CRE Web site (<http://www.umich.edu/~elements/6e/09chap/prof-pharmacokinetics.html>).

G.10 METHANOL POISONING

The emergency room treatment for methanol poisoning is to inject ethanol intravenously to tie up the alcohol dehydrogenase enzyme so that methanol will not be converted to formic acid and formate, which cause blindness. The goal of this open-ended problem is to build on the physiological-based model for ethanol metabolism to predict the ethanol injection rate for methanol poisoning. One can find a start on this problem by the *Professional Reference Shelf Material* (<http://www.umich.edu/~elements/6e/09chap/prof-pharmacokinetics.html>) on Physiologically Based Pharmacokinetic (PBPK) Models in Chapter 9 that is on the Web.

G.11 SAFETY

As the chemical engineering profession continues to intensify its efforts on safety, examples of runaway reactions are analyzed in Chapter 13. A companion Web site on safety has been developed and can be found at (<http://umich.edu/~safeche/>). Each module contains the safety algorithm (shown in the following) that is to be filled out.

Safety Algorithm

Activity: _____

Hazard: _____

Incident: _____

Initiating Event: _____

Preventative Actions and Safeguards: _____

Contingency Plan/Mitigating Actions: _____

Lessons Learned: _____

Definitions

Activity: The process or situation for which risk to people, property or the environment is being evaluated.

Hazard: A chemical or physical characteristic that has the potential to cause damage to people, property or the environment.

Incident: What happened? Description of the event or sum of the events along with the steps that lead to one or more undesirable consequences, such as harm to

Effects: damage to people, damage to the property, to the environment, or asset/business losses.

Initiating Event: The event that triggers the incident, (e.g. failure of equipment, instrumentation, human actions, flammable release, etc.). If necessary state precursor events, e.g. valve closed, inadvertent human action, nearby ignition source. The root cause of the sum events in causing the incident.

Preventive Actions and Safeguards: Steps that can be taken to prevent the initiating event from occurring and becoming an incident that causes damage to people, property or the environment. Brainstorm all problems that could go wrong and then actions that could be taken to prevent them from occurring.

Contingency Plan/Mitigating Actions: Steps that reduce or mitigate the incident after the preventative action fails and the initiating event occurred.

Lessons Learned: What we have learned and can pass on to others that can prevent similar incidents from occurring

H. Use of Computational Chemistry Software Packages

H.1 COMPUTATIONAL CHEMICAL REACTION ENGINEERING

As a prologue to the future, our profession is evolving to one of molecular chemical engineering. For chemical reaction engineers, computational chemistry and molecular modeling could well be our future.

Thermodynamic properties of molecular species that are used in reactor design problems can be readily estimated from thermodynamic data tabulated in standard reference sources such as Perry's Handbook or the JANAF Tables.

Thermochemical properties of molecular species not tabulated can usually be estimated using group contribution methods. Estimation of activation energies is, however, much more difficult owing to the lack of reliable information on transition-state structures, and the data required to carry out these calculations is not readily available.

Recent advances in computational chemistry and the advent of powerful, easy-to-use software tools have made it possible to estimate important reaction-rate quantities (such as activation

energy) with sufficient accuracy to permit incorporation of these new methods into the reactor design process.

Computational chemistry programs are based on theories and equations from quantum mechanics, which until recently, could only be solved for the simplest systems such as the hydrogen atom. With the advent of inexpensive high-speed desktop computers, the use of these programs in both engineering research and industrial practice is increasing rapidly. Molecular properties such as bond length, bond angle, net dipole moment, and electrostatic charge distribution can be calculated. Additionally, reaction energetics can be accurately determined by using quantum chemistry to estimate heats of formation of reactants, products, and also for transition-state structures.

Examples of commercially available computational chemistry programs include Spartan, developed by Wavefunction, Inc. (www.wavefun.com), and Cerius2 from Molecular Simulations, Inc. (www.accelrys.com). The Web module in Chapter 3 on molecular reaction engineering (http://www.umich.edu/~elements/6e/web_mod/quantum/index.htm) gives an example of what we can expect in the future.



I. *How to Use the CRE Web Resources*

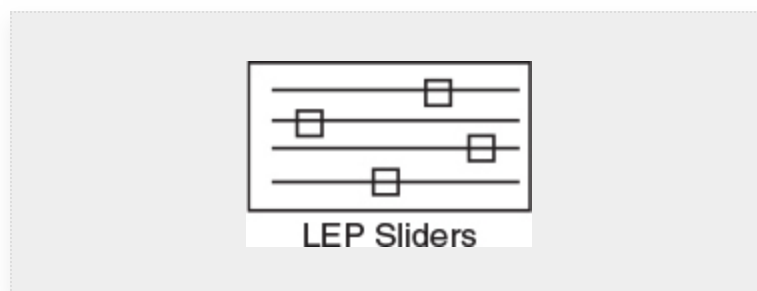
The primary purpose of the CRE Web Resources is to serve as an enrichment resource. The benefits of using the CRE Web Resources are fivefold:

1. To facilitate different student learning styles:
<http://www.umich.edu/~elements/6e/asyLearn/index.htm>
2. To provide the student with the option/opportunity for further study or clarification of a particular concept or topic
3. To provide the opportunity to practice critical thinking, creative thinking, and problem-solving skills
4. To provide additional technical material for the practicing engineer
5. To provide other tutorial information, such as additional homework problems and instructions on using computational software in chemical engineering

I.1 CRE WEB RESOURCES COMPONENTS

There are two types of information in the CRE Web Resources: information that is organized **by chapter** and information organized **by concept**. Material in the “by chapter” section of the CRE Web Resources corresponds to the material found in this book and is further divided into five sections.

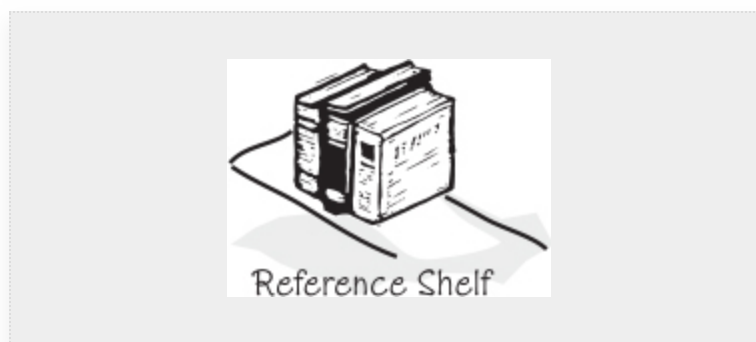
- **Objectives.** The objectives page lists what the students will learn from the chapter. When students are finished working on a chapter, they can come back to the objectives to see whether they have covered everything in that chapter. Or if students need additional help on a specific topic, they can see whether that topic is covered in a chapter from the objectives page.



- **Living Example Problems (LEP).** These problems are usually the second homework problem in each chapter (e.g., Problem P5-2_B), and most require computational software to solve. One can run the LEPs using Polymath, Wolfram, Python, or MATLAB. The LEP programs are provided on the Web site so students can download the program to “play” with the problem and ask “What if . . . ?” questions to practice critical and creative thinking skills. Students can change parameter values, such as the reaction-rate constants, to learn to deduce trends or predict the behavior of a given reaction system.
- **Extra Help.** Multiple resources (screencasts, interactive computer games, lecture notes, and extra problems) promote a deeper understanding of important concepts. These resources provide links to the LearnChemE screencasts related to the material in each chapter and provide extra explanations, examples, and applications to reinforce the basic concepts of chemical reaction engineering. *Summary Notes* serve as an overview of each chapter and contain a logical flow of derived equations and additional examples.
- **LearnChemE Videos.** The University of Colorado has a number of 6- to 8-minute videos on some of the concepts covered in the course.
- **Additional Materials.** There are multiple resources of new material that are not included in the present text. Web modules provide more examples for students to use the knowledge gained in each chapter.

Computer simulation statements, not in previous editions, for the LEPs that use Wolfram and Python Sliders, Polymath, or MATLAB to vary the parameters to answer the questions or solve the problems can be found here.

- **Professional Reference Shelf.** The Professional Reference Shelf contains two types of information. First, it includes material that is important to the practicing engineer but that is typically not included in the majority of chemical reaction engineering courses. Second, it includes material that gives a more detailed explanation of derivations that were abbreviated in the text.



- **Self Tests.** Interactive problems with solutions to provide extra practice of concepts.
- **i>clicker Questions.** A collection of i>clicker questions for each chapter, with answers, are provided for each chapter.
- **Entertainment on the CRE Web Site.**

Links to entertaining **YouTube** videos can be found on the Web site home page. From the University of Alabama the most viewed videos are

Chapter 1: *Fogler Zone (you've got a friend in Fogler).*

Chapter 3: *The Black Widow murder mystery and Baking*

a Potato.

Chapter 4: *CRF Reactor Video*, Crimson Reactor Firm's video of a "semi batch" reactor with Diet Coke and Mentos.

Chapter 5: Learn a new dance and song, *CSTR* to the tune of *YMCA*, *Chemical Good Time Rhythm* rap song, and the University of Michigan students' *Chemical Engineering Gone Wrong*.

From the University of Michigan the most viewed videos are

Chapter 3: *Arrhenius Dream*

Chapter 4: *I Just Found X*

Chapter 5: *Chemical Engineering Gone Wrong; Under Pressure*

- **Visual Encyclopedia of Equipment** (<http://encyclopedia.che.engin.umich.edu>). This section was developed by Dr. Susan Montgomery at the University of Michigan. Here, a wealth of photographs and descriptions of real and ideal

reactors are given. Students with visual, active, sensing, and intuitive learning styles of the Felder/Solomon Index will particularly benefit from this section.

- **Reactor Lab (<http://www.ReactorLab.net>).** Developed by Professor Richard Herz at the University of California at San Diego, this interactive tool allows students not only to test their comprehension of the CRE material, but also to explore different situations and combinations of reaction orders and types of reactions.
- **Interactive Web Modules.** Web site includes both Web Games and ICGs. The Web Games use a Web browser for an interface and give examples of how chemical reaction engineering principles can be applied to a wide range of situations, such as modeling cobra bites and cooking a potato.
- **Interactive Computer Games (ICGs).** The ICGs are games that use a Windows or DOS-based program for an interface. They test knowledge on different aspects of chemical reaction engineering through a variety of games such as basketball and Jeopardy.



Index

A

α -amylase, 378

Acetic anhydride, 897

Acetylation reactions, 249

Activation energy, 809–811

 barrier heights, 90

 barrier to energy transfer, 90

 description, 90

 fraction of molecular collisions. *See* Fraction of molecular collisions

 potential energy surfaces and energy barriers, 90–93

 rate of reaction, 90

Active intermediates

 chain reactions, 377

 collision theory, 369

 computational software packages, 369

 cyclobutane, 369

 decomposition of acetaldehyde, 368

 first-order reactions, 372–373

 mechanism, 373–374

 pseudo-steady-state hypothesis, 369–372

rate laws, 368

reactant concentrations, 369

Stern–Volmer equation, 374–377

translational kinetic energy, 368–369

Activity, 210, 212

Actual rate of reaction, 803

Adenosine diphosphate (ADP), 401

Adenosine triphosphate (ATP), 401

ADH. *See* Alcohol dehydrogenase

Adiabatic CSTR, propylene glycol, 623–628

Adiabatic energy balance, 557–558

Adiabatic equilibrium conversion, 566, 576–577

 equilibrium conversion, 566–571

Adiabatic equilibrium temperature, 576–577

Adiabatic exothermic reactions, 58

Adiabatic gas-phase PFR/PBR reactor, 560

Adiabatic liquid-phase isomerization, 59–61

 of normal butane, 560–566

Adiabatic operation, 557, 609, 610, 614, 651, 652, 687, 690, 692, 697–698, 726

 adiabatic energy balance, 557–558

 adiabatic tubular reactor, 558–566

 of batch reactors, 686

Adiabatic PFR/PBR algorithm, 559

Adiabatic tubular reactor, 558–566

Administration control, 144

ADP. *See* Adenosine diphosphate

Adsorption, 445

Adsorption constants, 136

Adsorption equilibrium constant, 454, 456

Adsorption-limited reaction, 462

Adsorption of cumene, 463, 464, 466–469

Advanced Reactor System Screening Tool (ARSST), 700, 717, 723, 724

Affinity constant, 383

Aging (Sintering), 498

Alarm system, 724

Alcohol dehydrogenase (ADH), 394

Alcohol metabolism, 1023

Algorithm for chemical reaction engineering, 157–160

Alkylation catalyst, 446–447

Alumina-supported iridium catalyst, 768

American Institute of Chemical Engineers (AIChE), 1021

Ammonia, 310

Ammonolysis, 248

Antifreeze, 173

Apparent reaction, 83

Apparent reaction order, 810, 811

Aqueous caustic soda, 123

Aris–Taylor dispersion coefficient, 933, 942, 943

Arrhenius equation, 89, 107

Arrhenius plot

- activation energy, 96
- description, 96
- determination, 97–99
- Polanyi–Semenov equation, 99

at temperature, 99

Arrhenius temperature, 391

ARSST. *See* Advanced Reactor System Screening Tool

Artificial kidney, 380

Aspen, 1013

AspenTech, 566

Aspergillus niger, 400

Aspirin, 392

ATP. *See* Adenosine triphosphate

Autocatalytic reactions, 51, 70, 402

Auto exhaust data, 306

Avogadro's number, 452, 453

AZO. *See* Azomethane

Azomethane (AZO)

decomposition mechanism, 373, 425

gas-phase decomposition, 370

internal rotational and vibrational energies, 371

rate equation, 374

rate law, 370, 373

reaction orders, 372

B

Backmix reactor or vat. *See* Continuous stirred-tank reactor

Backup cooling system, 144

Bacteria growth

batch reactor, 415–417

phases of, 426

Barrier walls, 724

Batch and plug-flow reactors, RTD in, 860–861

Batch and semibatch reactors, with heat exchanger, 700–702

semibatch operation, 707–710

startup of CSTR, 702–706

Batch operation, with heat exchange, 698–699

Batch polymerization process, 163

Batch reaction times, 161–167

algorithm for, 162

first-order reaction, 162

order of magnitude of, 162, 163

second-order reaction, 162

Batch reactor (BR), 10–12, 64, 119, 160, 248, 687, 726, 891, 896, 899. *See also* Mole balance

adiabatic operation of, 686–693

bacteria growth, 415–417

batch reaction times. *See* Batch reaction times

catalyst decay, 500–502

cell growth, 403–404

concentration–time data, 280

design equations, 36–38

energy balance on, 684–685

enzymatic reactions, 389–391

with heat exchanger, 691–693, 700–702

with interrupted isothermal operation, 693–700

mole balance, 276

rate-law parameters, 272

series reactions in, 325–329

Batch systems, 139–140

batch reactors, 119

constant-volume batch reactors, 122

continuous-flow liquid-phase systems, 121

equal molar and stoichiometric feed, 122

kinetic rate law, 121

limiting reactant, 124–125

liquid-phase reactions, 122–123, 123–124

$N_{A0}X$ moles, 119

parameter, 122

reactor volume, 121

stoichiometric table, 120, 121

Bed fluidicity, 770

Behavioral control, 144

Benzene (B), 5

catalytic surface, 464

dependence of, 481

desorption, 465, 467, 469, 471–473

and ethylene, equimolar mixture of, 446–447

and methane, 480

production of, 443

and propylene, 460, 463, 465

Benzene diazonium chloride, 97

Berzelius's work, 442

Bimodal distribution, 916

Bimolecular, 76

Bioconversions, 400

Bioreactors

- bacteria growth in batch reactor, 415–417
- bioconversions, 400
- cell growth and division, 402–404
- cells, 400–401
- chemical and biochemical engineering, 399
- chemostats, 418
- CSTR bioreactor operation, 418–419
- definition, 399
- enzymatic reactions, 399
- marketable chemical products, 400
- mass balances, 413–415
- monoclonal antibodies market, 400
- Monod equation, 400
- rate laws, 404–407
- Sapphire Energy, 400
- stoichiometry, 407–410
- washout, 419–421
- yield coefficients, 411–413

Blood clotting, 333–334

Bodenstein number (Bo), 952

Boltzmann distribution, 96

BowTie diagram, 256–257, 521, 522, 653

BR. See Batch reactor

Bromine cyanide, 252, 254

Bulk catalyst density, 243

Bulk concentration, 814, 815

Bulk density, of catalyst, 189

Bulk flow, 741, 742, 743, 764

Bulk velocity, 748

C

Cajun seafood gumbo, 1022–1023

California Institute of Technology, 1015

California Professional Engineers' Exam Problem, 619, 621

Carbonaceous (coke) material, 502–503

Carbonium ion, 369

Carbon monoxide, 716

Carbonylation, 716

Catalyst deactivation, 524

- batch reactors, 500–502

- by coking or fouling, 502–503

- gas catalytic system, 498

- packed-bed reactor. *See* Packed-bed reactor

- by poisoning, 503–504

- poison in the feed, 504–505

- reaction-rate law parameters, 497

- separable and nonseparable kinetics, 497

- by sintering (aging), 498–500

Catalyst decay

- moving-bed reactors, 510–515

- straight-through transport reactors, 515–519

- temperature–time trajectories, 508–510

Catalyst pellet, shell balance on, 796

Catalysts

- Berzelius's work, 442
- classification, 446–447
- deactivation. *See* Catalyst deactivation
- definitions, 442–443
- gas–solid interactions, 445–446
- properties, 443–444
- uses of, 441–442

Catalyst weight, 241, 243

Catalytic bed, 243, 244

Catalytic membrane reactor (CMR), 239, 240

Catalytic packed-bed reactor, 447

Catalytic rate laws, 147

Catalytic reaction

- adsorption isotherms, 452–458
- desorption, 460–461
- different types and sizes, 447
- external surface, 450–451
- heterogeneous catalytic reaction, 448
- internal diffusion, 451–452
- mechanisms and rate-limiting steps, 449
- packed-bed reactor, 447
- porous catalysts, 447
- rate law, 449
- rate-limiting step, 461–463
- rate of reaction, 447
- steps in, 448, 449

surface reaction, 458–460

Catalytic reactor design, 486–489

CCPS. *See* Center for Chemical Process Safety

C-curve in RTD, 847, 849–850

Center for Chemical Process Safety (CCPS), 654

Ceramic reactors, 240

ChemE Car, 1021

Chemical Engineering Curriculum Web site, 652–653

Chemical kinetics, 1

Chemical plants

- profit, 209
- safety with exothermic runaway reactions, 693–700
- synthesizing the design of, 208–210

Chemical process safety, 25

Chemical reaction, 5

- modeling diffusion with, 748–750

Chemical reaction engineering (CRE), 1, 2, 1021

Chemical reaction-rate-law, 7

Chemical reactors, 844

- design, integrals in, 991–992

Chemical Safety Board (CSB), 210, 716, 717

Chemical species, 4

Chemical vapor deposition (CVD), 490–493, 522, 523–524, 826, 831

Chemisorption, 445–446

Chemostats, 418, 426

Chloral, 6

Chlorination, 248

Chlorobenzene, 6, 97

Chymotrypsin, 379

Circulating fluidized bed (CFB), 515

Clinoptilolite, 480

Closed-closed vessel boundary condition, 936–937, 939

Coagulation of blood, 333–334

Cobalt molybdenum catalyst, 494

Co-current exchange, 606, 616, 648–649

Co-current flow, 609, 612

 heat-transfer fluid, 595–597

Coking or fouling, deactivation, 502–503

Colburn J factor, 767

Collision theory, 80, 83, 84, 108, 369

Col or saddle point, 91

Colquhoun-Lee, I., 768

Combination, 5

Combustion triangle. *See* Fire triangle

Competing reactions. *See* Parallel reactions

Competitive inhibition, 392–394

Completely micromixed fluid, 890

Completely segregated fluid, 890

Complex gas-phase reactions, in PBR, 335–339

Complex liquid-phase reactions

 in CSTR, 339–341

 in semibatch reactor, 341–343

Complex reactions, 310, 311, 335

 complex gas-phase reactions in PBR, 335–339

- complex liquid-phase reactions in CSTR, 339–341
- complex liquid-phase reactions in semibatch reactor, 341–343
- RTD and, 913–917
- Computational chemistry software packages, 1025
- Computational software packages, 369
- COMSOL program, 961, 963, 1012
- Conflicting goals, 930
- Consecutive reactions. *See* Series reactions
- Constant-density, 127
- Constant heat capacities, 553
- Constant-volume batch reactor, 273, 287
- Constant-volume batch systems, 123, 141
- Contingency plan/mitigating actions, 211, 212
- Continuous bioprocessing, 1022
- Continuous-flow liquid-phase systems, 121
- Continuous-flow reactors, 12, 140, 543
 - continuous-stirred tank reactor, 12–14
 - “fluidized” catalytic bed reactor, 20
 - packed-bed reactor, 18–19
 - tubular reactor, 14–18
- Continuous-flow system, 39, 891
- Continuous stirred-tank reactor (CSTR), 1, 12–14, 168, 845, 870–871
 - adiabatic, 623–628
 - bioreactor operation, 418–419
 - bypassing (BP) model, 871–872
 - complex liquid-phase reactions in, 339–341

- complex reactions, 649–652
- conversion, 68
- cooling coil, 628–630
- Damköhler number, 171
- dead space and bypass model, 966–968
- dead volume (DV) model, 872–873
- first-order reaction in, 168–169
- flow reactors, 40
- heat effects, 619–623
 - cooling coil, 628–630
 - propylene glycol in adiabatic CSTR, 623–628
 - reactor, Q , 620–623
 - steady-state energy balance, 619
- heat exchange in, 550–551
 - with heat exchanger, 547
- ideal, 893–894, 895
- isothermal reactors, 865–867
- little batch reactors (globules), 890
- mole balance, 564–565, 633
- multiple reactions, 642–645
- nonideal, 888
- nonideal reactors, 885–887
 - in parallel, 175–176
 - “perfectly mixed,” 890
- perfect operation (P) model, 871
- plug-flow reactor. *See* Plug-flow reactor
- RTD functions, 919

- second-order reaction in, [169–170](#)
- segregation model, [810](#)
- semibatch or unsteady, [548](#)
- semibatch reactors, [248](#)
- series, [52–56](#)
 - in series, [171–178](#)
 - series reactions in, [329–332](#)
- sizing, [46–47](#)
- specify the sizing of, [623](#)
- startup of, [702–706](#)
- stirred reactors, [248](#)
- tanks-in-series model, [865–867](#)
- two-parameter model, [889](#)
- volume, [142–143](#)
- zero-order parameter models, [889](#)

Convective diffusion, [933](#), [942](#)

Convective-flow component, [957](#)

Convective transport, [744–746](#)

Conversion

- basis of calculation, [36](#)
- BR, CSTR, PFR, and PBR, [68](#)
- definition, [36](#)
- function of, [42](#), [69](#)
- heat effects in PFRs and PBRs, [598–599](#), [656](#)
- multiple reactions, [313](#)
- and reaction rate profiles, [50](#)

Conversion surface, [962](#), [963](#)

Coolant

- co-current flow, 596
- energy balance, 595, 596, 597
- enthalpy of, 596
- exothermic reactions, 595, 620
- heat transfer fluid, 596, 597
- mass flow rate, 603

Coolant balance, 961

Cooling coil, 628–630

Cooling water system, 724

Countercurrent flow, 609

- heat-transfer fluid, 597–598

Countercurrent heat exchange, 606–608, 617–619, 649–650

Coupled differential equations, 994

CRC Handbook of Chemistry and Physics, 625

CRE. *See* Chemical reaction engineering

CRE algorithm, 162, 174, 177, 185, 201, 208

CRE Web Resources, 1027–1028

Critical thinking actions (CTAs), 876–877

Crystalline aluminosilicates, 443

CSB. *See* Chemical Safety Board

CSTR. *See* Continuous stirred-tank reactor

Cumulative distribution function $F(t)$, 853, 861, 864, 878

CVD. *See* Chemical vapor deposition

Cyanamide, 252, 254

Cyclobutane, 369

Cyclohexane, 443

Cytidine, [897](#)

D

Damköhler number, [171](#), [176](#), [514–515](#), [893](#), [895](#), [938](#), [940](#)

Danckwerts boundary conditions, [746](#), [888](#), [936](#), [937](#), [946](#)

Danckwerts, Peter V., [844](#), [846](#)

Darcy's law, [247](#)

Database, [81](#)

DDT. *See* [Dichlorodiphenyltrichloroethane](#)

Deactivation

activated water molecule, [375](#)

reverse of reaction, [376](#)

Death phase, [404](#)

Decay rate laws, [507](#), [509](#), [511](#)

Decomposition, [5](#)

acetaldehyde, [368](#)

active intermediate, [374](#)

azomethane, [370](#), [373](#), [425](#)

of cumene, [463](#), [469](#)

hydrogen peroxide, [383](#)

urea, [378](#)

Dehydrogenation

butane to butene, [243](#)

ethylbenzene to styrene, [242](#)

propane, [243](#)

Dehydrogenation catalyst, [446–447](#)

Deoxyribonucleic acid (DNA), [401](#)

- Department of Energy (DOE), [242](#)
- Derivation of differential equation, single spherical catalyst pellet, [795–798](#)
- Design equation, [38](#), [41–42](#)
- Desired reactions, [311](#)
- Determination of limiting situations, from reaction-rate data, [823–824](#)
- Dichlorodiphenyltrichloroethane (DDT), [6](#), [67](#)
- Diethanolamine, [310](#)
- Diethylene glycol dimethyl ether (diglyme), [715](#), [716](#), [723](#)
- Differential catalyst bed, [290](#)
- Differential equations
 - coupled differential equations, [994](#)
 - first-order ordinary differential equations, [994](#)
 - for first-order reaction, [801–802](#)
 - second-order ordinary differential equations, [995](#)
- Differential reactors, [480](#), [515](#), [529](#)
 - catalytic-rate data, [292–297](#)
 - reaction-rate data, [290–292](#)
- Differentiation, [993](#)
- Differentiation formulas, [279](#)
- Diffusion
 - boundary conditions, [746](#), [747](#)
 - chemical reaction, [748–750](#)
 - and convective transport, [744–746](#)
 - definition, [741–742](#)
 - Fick's first law, [743–744](#)
 - molar flux, [742–743](#)

- mole balance, 740
- plug-flow, 740
- and reaction effects, 740–741
- and reactions
 - in homogeneous systems, 792
 - Mears criterion for external diffusion limitations, 816
 - in spherical catalyst pellets. *See* Spherical catalyst pellets
- temperature and pressure dependence, 746, 747
- Diffusivity phase (gases, liquids, and solids), 747
- Dilution rate, 418, 419, 420, 426
- Dimensionless concentration profile, 802
- Dimensionless form of equations, diffusion and reaction, 798–801
- Dimensionless residence time, 878, 919
- Dimerize propylene, 57
- Dimersol G unit, 57
- Diphenyl, 87–88
- Dirac delta function, 860–861, 893
- Dispersion, 446
- Dispersion coefficient (D_a)
 - axial mixing effects, 941
 - closed-closed system, 946–947
 - correlations, 944
 - effluent concentration, 945
 - isothermal reactors, 949–951
 - open-open vessel boundary conditions, 947–949
 - packed beds, 944, 945

and Péclet Number, 941–943

in pipes, 944

tubular reactor, 945

unsteady-state tracer balance, 945

Dispersion model, 888

vs. tanks-in-series model, 951–952

Dissociative adsorption, 453–454, 456–458

DNA. *See* Deoxyribonucleic acid

Doubling times, 406

Dual-site mechanism, 458–460

Dust Explosion Dynamic (Ogle), 763

E

Eadie–Hofstee plot, 385, 386, 387, 388

Early and late mixing for second-order reaction, 867–869

$E(t)$ -curve, 850–851

Effective diffusivity, 793–795

Effective lubricant design, 1021

Effective transport coefficient, 753

EG. *See* Ethylene glycol

Electromotive force (EMF), 461

Elementary rate law, 235, 252, 253

α reaction order, 79

β reaction order, 79

Collision theory, 80

elementary reaction, 80

gas- and liquid-phase reactions, 81

- molecular oxygen, 80
- nonelementary reaction, 80
- power law models, 79
- reaction order, 79–80
- reaction rate laws, 81–82
- units of $-r_A$, 79
- Elementary reaction, 454
- Eley–Rideal mechanism, 460
- EMCD. *See* Equal molar counter diffusion
- Emergency pressure relief systems, 724
- Emergency quenching system, 724
- Endothermic reactions, 594, 711
- Energy (work), 1000
- Energy balance, 543, 559, 580, 597, 599, 604–605, 612–613, 619, 620, 626, 627, 629, 958–960
 - on batch reactors, 684–685
 - adiabatic operation of batch reactor, 686–693
 - batch reactor with interrupted isothermal operation, 693–700
 - on common reactors, 547–549
 - on the coolant, 595, 596
 - dissecting the enthalpies, 553–554
 - equations, 551–557
 - evaluating the work term, 544–546
 - first law of thermodynamics, 543–544
 - heat of reaction, 551–553
 - overview of, 546–551
- PFR, 592–594

- steady-state molar flow rates, 551–553
- on well-mixed open system, 544
- Energy flux, 958, 959
- Engineering control, 144
- Enthalpy, 546, 553–554
 - of formation, 553, 554–555
- Enzymatic reactions, 425
 - batch reactor, 389–391
 - bioreactors, 399
 - catalyzes, 378
 - competitive inhibition, 392–394
 - enzyme–substrate complex, 378–380
 - inhibition of, 391–392
 - mechanisms, 380–382
 - Michaelis–Menten equation, 383–388
 - noncompetitive inhibition (mixed inhibition), 396–398
 - principles of enzyme kinetics, 377
 - property of, 378
 - reaction coordinate for enzyme catalysis, 377, 378
 - reversible inhibition, 392
 - substrate inhibition, 398–399
 - therapeutic proteins, 377
 - TV advertisements, 392
 - uncompetitive inhibition, 394–396
- Enzyme–substrate complex
 - active catalytic sites, 379
 - active intermediate, 381

chymotrypsin, 379
classes of, 380
definition, 378
and ionic intermediates, 369
models for, 379, 380
pseudo-steady-state hypothesis, 392
type of interactions, 379
EO. *See* Ethylene oxide
Equal-area graphical differentiation, 992–993
Equal molar counter diffusion (EMCD), 745
Equalmolar feed, 122
Equilibrium constant, 568–569
Equilibrium conversion, 255–256, 563, 566–571
 from thermodynamics, 569
Equimolar counter diffusion (EMCD), 796
Ergun equation, 156, 187, 189, 194
Esterification reactions, 249
Ethane, 208, 209
Ethyl acetate, 707
Ethylbenzene, 349
Ethylene, 181, 203, 209
Ethylene glycol (EG), 164, 173, 174
 concentration of, 166
 production of, 208
 safety of, 178
Ethylene oxide (EO), 164, 173, 202, 209, 310
Ethylidyne chemisorbed on platinum, 445

Ethynylation, 825

Exothermic reaction, 90, 556, 566–567, 711

interstage cooling for, 573–575

Exothermic reactions, 60, 234, 594

Exponential growth phase, 404

Exponential integral, 895

External-age distribution, 859, 860

External area per unit reactor volume, 822

External mass transfer, 816

External mass transfer–limited reactions, 823, 824

Extinction temperature, 635

ExxonMobil's Torrance California refinery's electrostatic precipitator unit, 519–522

F

Falsified kinetics, 809–811

Faujasite-type zeolite, 444

Faulty pressure relief valve, 144

FCC. *See* Fluid catalytic cracking

$F(t)$ curve, 854

Fed batch, 399

Feed stream, 51, 52

Femtosecond spectroscopy, 369

Fick's first law, 741, 743–744, 750

Fick's law, 942

diffusion of, 933

Fires

- triangle. *See* Fire triangle
- ways to prevent, 350–351
- ways to protect from, 351
- Fire triangle, 349
 - fuel, 350
 - ignition source, 350
 - oxygen, 350
- First law of thermodynamics, 543–544
- First-order liquid-phase reaction, 542
- First-order ordinary differential equations, 994
- First-order rate law, 81, 752–753
- First-order reaction, 274, 800–801, 804, 808, 811, 828, 889
 - active intermediates, 372–373
 - in CSTR, 168–169
 - differential equation for, 801–802
 - ideal CSTR, 893–896
 - ideal PFR, 893–896
 - laminar-flow reactor, 893–896
 - micromixing, 897
 - reaction rate, 889
 - segregation model, 892–893
 - tanks-in-series vs. segregation, 912
- Five-point quadrature formula, 996
- Fixed coordinate system, 742–743
- Flammability limit, 350
- Flash point, 350
- Flow, reaction, and axial dispersion, 937–939. *See also*
 - Dispersion coefficient (D_a)

isothermal laminar flow reactors, 941–949

Flow reactors, 125

continuous-flow systems, 39

continuous stirred-tank reactor, 40

first-order dependence, 42

function of conversion, 42

gas systems, 39

infinite reactor volume, 43

laboratory-bench or pilot-plant reaction system, 66

liquid systems, 39

molar flow rate, 39

packed-bed reactor, 41–42

rate of reaction, 42

reactor design and staging, 43–45

in series. *See* Series

sizing, 43, 46–51. *See also* Sizing

tubular flow reactor, 40–41

zero-order reactions, 43

Flow systems, 140–141, 146, 551

concentrations, 126

flow reactor, 125

gas-phase concentrations. *See* Gas-phase reactions

liquid-phase concentrations, 126–127

stoichiometric table, 125

Fluctuations, 935

Fluid catalytic cracking (FCC), 519, 520

Fluidized bed reactors, 20, 85, 826, 831

“Fluidized” CSTR, 480, 489

Fluid Péclet number (Pe_f), 935

Fluid–solid reactions, 443

Fluid velocity, 748

Force, 1000

Fouled pellet, 759

Fouling or coking, deactivation, 502–503

Fourier’s law, 743, 958

Fraction of molecular collisions

 Boltzmann distribution, 96

 energy distribution, 94

 rate of reaction, 95

 velocities, 93–94

Free-radical mechanism, 83

Free radicals, 369

Free-stream liquid velocity, 757

Frössling correlation, 751, 757–758

Fuel, 350, 351

Function of conversion, 132–134, 136

Fundamentals of Industrial Catalytic Processes (Farrauto and Bartholomew), 506

G

GAMES, 92

Gas–carbon interface, 761

Gas catalytic system, 498

Gas-hourly space velocities, 65

Gasoline, 571, 572

Gas-phase diffusivity, 774

Gas-phase flow systems, 118

Gas-phase reactions, 14, 38, 47, 146, 147, 156, 160, 230

algorithm for, 233

concentration of reacting species, 185

flow reactors with volumetric flow rate, 127–131

generic power-law rate law, 232

hydrodemethylation of toluene, 135

microreactor, 235–239

molar flow rates, 135, 230, 231, 234

mole balance, 135, 232

in packed beds, 156

partial pressures, 135

plug-flow reactor, 232, 238, 258–259

in plug-flow reactor, 180

pressure-drop equation, 232

in SO_2 , 132–134

SO_2 oxidation, 135–138

stoichiometric tables, 127

stoichiometry for, 186

synthesis of ammonia, 127

thermodynamic relationships, 1003–1005

in tubular reactors, 178

volumetric flow rate, 127

Gas–solid catalyzed reactions, 7, 85, 118, 243

Gas–solid heterogeneous reactions, 270

Gas–solid interactions, 445–446

Gas systems, 39

Gas velocity, 767

Gas volumetric flow rate, 65

General mole balance equation (GMBE), 8–10, 13, 15

Generic power-law rate law, 232

Germanium epitaxial film, 490

GHS. *See* Globally Harmonized System

Gibbs free energy, 1005

Globally Harmonized System (GHS), 104

Globules, 889, 890, 900

Glyceryl stearate, 123, 124

GMBE. *See* General mole balance equation

Gourmet foods, 1022

Gram of catalyst (g-cat), 136

Graphical differentiation method, 278

Graphical User Interface, 103

Gravitational conversion factor, 1001

Guassian 16, 92

H

“Hall of Fame” reaction, 76

Hand calculation, 905–906

Hanes–Wolf plot, 385, 412–413

Harriott, P., 768

Hazard, 210, 212

Hazardous chemicals used, 723

Head-space mole balance, 718–719

Heat capacity of solution, 684

Heat effects, 756

Heat exchange

algorithm to flow reactors, 594–595

PFR energy balance, 592–594

tubular reactor, 592

Heat exchanger, 234, 687, 693

batch and semibatch reactors with. *See* Batch and semibatch reactors

in batch reactor, 691–693

energy balance on, 685

heat load on, 573–574

Heat of reaction, 552, 555–556

Heat transfer coefficient, 961

Heat transfer correlation, 780

Heat-transfer fluid

co-current flow, 595–597

countercurrent flow, 597–598

Hemostasis, 333

Heterogeneous catalytic reaction, 443, 448

Heterogeneous reactions, 7, 76, 85–86

catalyst particles, 85

“fluidized” catalytic beds, 85

gas–solid catalyzed reactions, 85

hydrodemethylation of toluene, 85, 86

Langmuir-Hinshelwood kinetics, 85

weight of catalyst, 85

HFCS. *See* High-fructose corn syrup
High-fructose corn syrup (HFCS), 378
Hilder's approximation, 895
Holding time or mean residence time, 63
Homogeneous reactions, 76, 82–83
Homogeneous systems, diffusion and reactions in, 792
Hydrodemethylation, 85, 86
Hydrodenitrogenation, 825
Hydrodesulfurization, 825
Hydrodesulfurization reactor design, 1022
Hydrodynamic boundary layer, 748
Hydroformation, 825
Hydrogen, 572, 715, 716
 dependence of, 482
 and nitrogen, 462
 and toluene, 480
Hydrogenation, 825
 ethylene to ethane, 494–496
Hydrolysis, 248
Hypothetical stagnant film, 748, 749

I

Ideal CSTR, 893–896, 968
Ideal gas constant, 999
Ideal gas law, 39, 774
Ideal PFR, 893–896, 898
Ideal plug-flow reactor, 846

Ideal reactors, 878, 919

batch and plug-flow reactors, 860–861

laminar-flow reactor, 863–865

real CSTR, 874

real tubular reactors, 973

simple diagnostics and troubleshooting, 870–875

single-CSTR RTD, 861–863

Ignition–extinction curve

description, 634–635

locally stable steady-state values, 636

multiple steady-state temperatures, 635

points of intersection, 634

steady-state temperatures, 634

temperature, 635

unstable steady-state temperatures, 635–636

Ignition point, 634

Ignition source, 350

Ignition temperature, 635

Incident, 210, 212

Independent reactions, 310

Induced fit model, 379, 380

Industrial disasters, 25

Industrial reactors, 24, 57, 63

Inert membrane reactor with catalyst pellets on the feed side
(IMRCF), 239, 240, 243

Inert tracers

Aris–Taylor dispersion, 933

balances, 933–935

- boundary conditions, 935
- dispersion model, 933
- plug flow, 933
- Infinite reactor volume, 43
- Initiating event, 210, 212
- Inquiry Based Learning (IBL), xxiv
- Instantaneous selectivity, 311–313, 316, 322, 352
- Instantaneous yield, 312
- Integral method
 - analysis of rate data, 273
 - batch reactor mole balance and rate law equation, 273
 - CRE data analysis, 275–277
 - reaction-rate law, 275
- Integral relationships, residence time distribution, 853–854
- Integrals
 - in chemical reactor design, 991–992
 - numerical evaluation of, 995–997
- Integrating factor for series reactions, 994
- Interactive computer games (ICGs), 1028
- Interactive web modules, 1028
- Internal-age distribution $I(\alpha)$, 859–860, 919
- Internal diffusion, 793
 - limited reactions, 806–807
- Internal effectiveness factor, 791, 802, 803, 813–815, 821, 828
 - internal-diffusion-limited reactions, 806–807
 - isothermal first-order catalytic reactions, 802–806
 - Thiele modulus, 804

- with volume change with reaction, 806
- Weisz–Prater criterion for internal diffusion limitations, 807–809
- Internal mass transfer, 793
- International Union of Pure and Applied Chemistry (IUPAC), 1015
- IQMol, 92
- Irreversible isomerization, 793
- Irreversible liquid-phase reaction, 252
- Irreversible reactions, 43, 76
- Irreversible surface-reaction-limited rate laws, 478
- Isobutane, 560
- Isohexanes, 57
- Isomerization, 5, 817
 - of butane, 59
- Isothermal first-order catalytic reactions, 802–806
- Isothermal gas-phase isomerization, 43
- Isothermal laminar flow reactors. *See also* Laminar flow dispersion coefficient. *See* Dispersion coefficient (D_a)
Péclet number, 941–943
- Isothermal multiple reactions, 349
- Isothermal operation, 696–697
- Isothermal reaction, 58
 - design algorithm for conversion, 157
 - design algorithm for mole balances, 231
 - with radial and axial dispersion in LFR, 954–956
- Isothermal reactors
 - design algorithm for conversion, 157

design structure for, [156–160](#)

dispersion, PFR, CSTR and tanks-in-series models, [949–951](#)

inert tracers in. *See* [Inert tracers](#)

Isothermal semibatch reactor, [252–255](#)

Isotherms, [453](#)

J

Jeopardy Game, [148](#)

Jet Propulsion Laboratory, [1015](#)

Jofostan Central Research laboratories, [52](#)

Jofostanian trait, [766–768](#)

K

Karplus, Martin, [100](#)

Karplus's procedure, [100](#)

Kinematic viscosity, [754](#), [757](#), [768](#)

Kinetic expression, [78](#)

Kinetics, [930](#)

Knock intensity, [474](#)

Knudsen diffusion, [745](#)

Kunii, D., [768](#)

Kunii–Levenspiel model for fluidization, [826](#)

Köttlov, Dr. Prof. Sven, [31](#), [81](#), [116](#), [303](#), [344](#), [624](#), [709](#), [974](#)

L

Laboratory-bench reaction system, [66](#)

Laboratory bomb calorimeter reactor, [38](#)
Laboratory Safety, [297–298](#)
Lactobacillus, [410](#)
Lag phase, [403](#)
Laminar flow, [198–199](#), [200](#), [201](#)
 Aris–Taylor analysis, [953–954](#)
 microreactors, [234–235](#)
 in pipe, [943](#)
 radial diffusion, [942](#)
 velocity profile, [860](#)
Laminar-flow reactor (LFR), [178](#), [863–865](#)
 first-order reaction, [893–896](#)
 second-order reaction in, [897–900](#)
Langmuir-Hinshelwood kinetics, [85](#), [460](#), [464](#), [522](#)
Langmuir-Hinshelwood models, [270](#), [284](#)
Langmuir isotherm, [455](#), [458](#), [522](#)
LearnChemE videos, [1028](#)
Le Châtelier’s principle, [141](#), [1005](#)
Length, [1000](#)
LEPs. *See* [Living Example Problems](#)
Lessons learned, [211](#), [212](#)
Levenspiel, O., [768](#)
Levenspiel plot, [45](#), [48](#), [55](#), [56](#), [58](#), [62](#), [69](#), [135](#), [138](#), [142](#)
LFL. *See* [Lower flammability limit](#)
LFR. *See* [Laminar-flow reactor](#)
Life expectancy, [900](#), [901](#)
Limiting reactant, [118](#), [124–125](#)

Linear-least-squares technique, 284

Lineweaver–Burk plot, 385, 386, 388, 394–398, 425

Liquid-hourly space velocities, 65

Liquid phase

- mole balances, 230, 231, 232
- parameter values for system, 230
- semibatch reactor, 260
- volumetric flow rate, 230

Liquid-phase batch reactions, 122–123, 123–124

Liquid-phase reaction, 13, 38, 47, 156, 757–758, 897

- concentration of reactants, 185
- in plug-flow reactor, 179–180

Liquid systems, 39

Little batch reactors, 890, 892

Living Example Problems (LEPs), 141, 239, 605, 613, 940, 1010, 1027

Lock-and-key model, 379, 380

Lower flammability limit (LFL), 350

Lubricants, 1021

Luminescence, intensity of, 375, 376

M

mAb. *See* Monoclonal antibodies

Macrofluid, 889, 890

Macromixing, 889

Manganese chloride, 715

Manganese dimethylcyclopentadiene, 715, 716

- Marketable chemical products, 400
- Market Center Building (MCB), 626
- Mass, 1000
- Mass balances, 418
 - bioreactors, 413–415
- Mass transfer
 - boundary layer, 450
 - coefficient, 241, 242, 750–752
 - diffusion. *See* Diffusion
 - divided and undivided systems, 771–773
 - gas-phase velocity, 780
 - heat transfer correlation, 780
 - and limited reactions, 781
 - overenthusiastic engineers, 773–775
 - packed beds. *See* Packed-bed reactor
 - parameter sensitivity, 770–771
 - rate of, 780
 - and reaction in packed bed, 817–819
 - Sherwood and Schmidt numbers, 780
 - shrinking core model. *See* Shrinking core model
 - single particle. *See* Single particle
- MATLAB, 100, 214, 260, 287, 550, 1011
- Maximizing desired product, for one reactant, 316
 - maximizing the selectivity for Trambouze reaction, 318–322
 - reaction at low temperature, 318
 - reaction order of desired product, 316–317
 - reaction order of undesired product, 317

specific reaction rate of desired reaction, 317

Maximizing the selectivity

with respect to temperature, 320–322

for Trambouze reaction, 318–320

Maximum mixedness model, 920

conversion, 905–906

globules, 900

life expectancy, 900, 901

mole balance, 902

nonideal reactor, 903–904

plug-flow reactor, 900, 901

reactors, 900

volumetric flow rate, 901, 902

vs. segregation predictions, 909–910

Maxwell Boltzmann distribution, 93–94

MCB. *See* Market Center Building

McCabe, W. L., 768

MCMT. *See* Methylcyclopentadienyl manganese tricarbonyl

Mean conversion, 891–892

ideal PFR, ideal CSTR and laminar-flow reactor, 893–896

second-order reaction in LFR, 897–900

X_{seg} , calculations in real reactor, 896–897

Mean residence time, 854–855, 878, 945, 946, 948

Mears criterion, for external diffusion limitations, 816, 822–823, 829

Mechanism

active intermediates, 373–374

enzymatic reactions, 380–382

rules of thumb for development of, 374

Membrane reactors (MRs), 259

catalyst weight, 241, 243

catalytic membrane reactor, 239, 240

ceramic reactors, 240

dehydrogenation. *See* Dehydrogenation

Department of Energy, 242

description, 239

endothermic, 239

exothermic, 239

gas phase, 230

gas–solid catalytic reaction, 243

hydrogen molecule, 239

to improve selectivity in multiple reactions, 343–347

inert membrane reactor with catalyst pellets on the feed
side, 239, 240

mass transfer coefficient, 242

molar flow rate, 247

molar flux, 241

mole balances, 241, 243–244

numerical solution, 245

parameter evaluation, 245

Polymath program, 246

rate of diffusion, 243

rates, 244

reversible reaction, 239

stoichiometry, 244–245

thermodynamically limited, 239

transport and reaction, 242

transport coefficient, 244

types of, 239

use of, 247–248

Wolfram variables, 246

Membrane Reactor Technology, 242

Mercapto-propanal-L-praline, 392

Metal-oxide, semiconductor, field-effect transition
(MOSFET), 490

Methane (M)

and benzene, 480

dependence of, 481

Methanol poisoning, 1024

Methanol synthesis, 1022

Methyl amine, 252, 254

Methyl bromide, 252, 254

Methylcyclopentadiene (MCP), 715

Methylcyclopentadiene dimer, 716

Methylcyclopentadienyl manganese tricarbonyl (MCMT),
715, 716, 723

Michaelis constant, 383, 384, 386, 393–394

Michaelis–Menten equation

affinity constant, 383

parameters V_{\max} and K_M , 383–388

rate of reaction, 383

single-enzyme molecule, 383

substrate concentration, 383

Microelectronic fabrication

- chemical vapor deposition, 490–493
- fabrication of, 490
- semiconductors, 490
- surface reactions, 490
- Microfluid, 889, 890
- Micromixing, 889
- Microplant, 234, 235
- Microreaction systems, 234
- Microreactor
 - advantage of, 234
 - exothermic reactions, 234
 - gas-phase reaction, 235–239
 - heat exchanger, 234
 - microplant, 234, 235
 - surface-area-to-volume ratio, 234
 - use, 234
- Microsoft Excel, 1011–1012
- Mitigating action, 143, 144
- Mixed inhibition. *See* Noncompetitive inhibition
- Mixing, in nonideal reactors, 845
- Mixing, RTD, 888–890
- Model discrimination, 493–496
- Modifications to CRE algorithm, for multiple reactions, 314–315
- Molal enthalpy, 553
- Molar feed rate, 247
- Molar flow, 740, 744, 746, 756, 764
- Molar flow rate, 28, 39, 44, 53, 128, 129, 230, 237, 247, 552

heat effects in PFRs and PBRs, 600, 656
membrane reactors. *See* Membrane reactors
microreactor. *See* Microreactor
semibatch reactors. *See* Semibatch reactors
species j , 129
of tracer, 934

Molar flux, 241, 742–743, 744, 780, 956–958

Molar rate of mass transfer, 812

Mole balance, 38, 63, 68, 161, 174, 194, 241, 243–244, 259,
315, 320, 326–327, 330–331, 335, 600, 604, 612, 625–634,
639, 643, 646, 688, 695, 703, 708, 712, 775, 796, 817, 894,
898, 902, 960

batch reactor, 270

constant-volume batch reactor, 273, 287

CRE algorithm, 280–281

differential PBR, 270

on ethylene oxide, 164

gas phase, 232–234

liquid phase, 230–232

for multiple reactions, 314

on O_2 , 762

power-law model, 270–271

and rate law equation, 271, 273

on reactor, 53

on second reactor, 177

semibatch reactor, 249–253

on species, 27, 37, 236, 593

straight-through transport reactors, 515, 516

- zero-order reaction, 273
- Mole balance (design equation), 185, 542
- Molecular adsorption, 453, 454–456
- Molecular diffusion, 933, 942
- Molecularity, 76
- Molecular Modeling in Chemical Reaction Engineering*, 92
- Molecular properties, 1025
- Molecular sieves, 443
- Molecular simulations
 - historical perspective, 100–101
 - stochastic modeling of reactions, 101–103
- Molecular trajectories, 103, 109
- Monoclonal antibodies (mAb), 400
- Monod equation, 400, 405, 406, 410, 412, 418, 424, 436
- Monte Carlo simulation, 100
- MOSFET. *See* Metal-oxide, semiconductor, field-effect transition
- Moving-bed reactors
 - catalytic cracking, 512–514
 - commercial use, 510
 - Damköhler number, 514–514
 - mole balance, 511
 - rate of reaction, 511
 - reactant feed stream, 510–511
 - regenerated catalyst, 510
- MRs. *See* Membrane reactors
- MSS. *See* Multiple steady states
- Multiphase reactors, 824–825

slurry reactors, 825–826

trickle bed reactors, 826

Multiple gas-phase reactions, in PBR, 335–339

Multiple reactions, 727, 920

algorithm for, 313–314, 352–353

conversion, 313

definitions, 310–313

maximum mixedness model, 913

modifications to CRE algorithm for, 314–315

mole balances for, 314

RTD and complex reactions, 913–917

segregation model, 912–913

selectivity, 311–312

in semibatch reactor, 711–714

types, 310–311

yield, 312–313

Multiple steady states (MSS)

concept of, 630

energy balance and mole balance, 630, 631

heat-generated term, $G(T)$, 633–634

heat-removed term, $R(T)$, 632

ignition–extinction curve, 634–637

ODE solver, 631

Multitude of equations, 158

N

National Fire Protection Agency (NFPA) Diamond, 66–67

National Fire Protection Association (NFPA), 104

National Institute of Standards and Technology (NIST), 1015

National Oceanic and Atmospheric Administration (NOAA),
654

Net rates of formation, 77

NFPA. *See* National Fire Protection Association

NFPA Diamond. *See* National Fire Protection Agency
Diamond

Nicotinamide phosphoribosyltransferase, 396

Nitric oxide (NO), 819–821

Nitrogen, 97

Nitrous oxide (NO) gas, 235

N-methyl-2-pyrrolidone (NMP), 898

NMP. *See* *N*-methyl-2-pyrrolidone

NOAA. *See* National Oceanic and Atmospheric
Administration

Nomenclature, 1017–1019

Non-adiabatic CSTR, 622, 632

Non-coalescent globules, 889

Noncompetitive inhibition

- definition, 392, 396
- Lineweaver–Burk plot, 397, 398
- rate law for, 396
- reversible reaction paths, 396
- steps, 397
- trends and relationships, 398

Nonelementary rate laws

- apparent first-order reactions, 83–85

- heterogeneous reactions, 85–86
- homogeneous reactions, 82–83
- Nonelementary reaction, 80
- Nonenzymatic lipoprotein, 333
- Nonideal reactors, 844, 845, 879, 903–904, 910
 - balance equations, 937–938
 - closed-closed system, 938–939
 - conflicting goals, 930
 - CSTRs and PFRs, 972–973
 - developing models, 930–932
 - dispersion and reaction, 952–954
 - guidelines, 931
 - inert tracers. *See* Inert tracers
 - isothermal laminar flow reactors. *See* Isothermal laminar flow reactors
 - kinetics, 930
 - laminar-flow reactor, 954–956
 - mixing, 888–890
 - modeling, 888
 - one-parameter models, 932
 - pharmacokinetic modeling, 973–974
 - tanks-in-series model vs. dispersion model, 951–952
 - tubular reactor. *See* Tubular reactor
 - two-parameter models, 932–933
- Nonisothermal exothermic reactions, 51
- Nonisothermal multiple reactions, 349, 711–723
- Nonlinear regression
 - concentration–time data, 287–288

- data point, 284–285
- linear-least-squares technique, 284
- minimum sum of squares, 285, 286
- model discrimination, 290
- model parameters k , K_B , and K_T , 484–486
- parameter values, 284, 286–287
- Polymath, 284, 495
- reaction order and specific reaction rate, 285, 286
- techniques, 348
- Nonreactive trajectory, 100
- Nonseparable kinetics, 497
- Normal butane, adiabatic liquid-phase isomerization of, 560–566
- Normalized RTD function $E(Q)$, 859
- Notre Dame Radiation Laboratory, 1015
- Numerical differentiation formulas, 278–279
- Numerical evaluation of integrals, 995–997
- O**
 - Observed rate of reaction, 803
 - Occupation Safety and Health Administration (OSHA), 104
 - Octane, 571
 - Octane number of gasoline, 474–475
 - ODEs. *See* Ordinary differential equations
 - ODE solver. *See* Ordinary differential equation solver
 - Ogle, R. A., 763
 - One-parameter models, 888, 932

continuous stirred-tank reactor, 932
in T-I-S model. *See* Tanks-in-series (T-I-S) model
tubular reactors, 932
O-nitrochlorobenzene (ONCB), 693–695
Open-ended problems, 1021–1024
Open-open vessel boundary conditions, 935, 947–949
Optimum feed temperature, 575–579
Ordinary differential equations (ODEs), 23, 24, 631, 652, 937
Ordinary differential equation (ODE) solver, 214–215
Organometallic catalyst, 57
OSHA. *See* Occupation Safety and Health Administration
Ostwald ripening, 498
Overall effectiveness factor, 811–815, 822, 828
Overall selectivity, 312
Overall yield, 312, 352
Oxidation, 825
Oxidizing agent, 350
Oxygen, 350
Oxygen diffusion, 759

P

Packed-bed reactor (PBR), 18–19, 56, 137, 764, 844, 888
 complex gas-phase reactions in, 335–339
 deactivation process, 505
 decay laws, 506–507
 dispersion coefficient, 944, 947
 flow, 944

flow reactors, 41–42
with heat exchange, 547
Jofostanian trait, 766–768
mass transfer–limited reactions, 763–766
movement of activity front, 505
poisoning by reactants or products, 506
reactor design, 480
space satellite, 768–770
in terms of conversion, 547
in terms of molar flow rates, 548
Parabolic velocity profile, 941
Parallel reactions, 310
 maximizing desired product for one reactant, 316–322
 reactor selection and operating conditions, 322–325
 selectivity, 316
Parameter sensitivity, 770–771
Partial differential equation (PDE), 742, 943, 956
Partial pressures, 135, 147
PBR. *See* Packed-bed reactor
PDE. *See* Partial differential equation
Peach bottom nuclear reactor, 1021
Peclet–Bodenstein number, 952
Péclet number (Pe_r), 935, 939–945, 948, 952
Penicillium chrysogenum, 404
Perfectly mixed CSTR, 317
Personal protective equipment (PPE), 143
PFR. *See* Plug-flow reactor

PFR/CSTR series RTD, 866–869

PFR/PBR design

 endothermic reaction, 610–619

 exothermic reaction, 603–610

 gas-phase reactions with heat effects, 598–603

Phosgene, 82–83

Phthalic anhydride, 2

Physical adsorption, 445

Pilot-plant reaction system, 66

Platinum on alumina, 476

Plug-flow reactor (PFR), 15, 17, 232, 258–259, 317, 900, 901

 algorithm, 561–563

 complex reactions, 645–652

 and CSTR, 42, 43, 51–52, 55–56

 Damkohler numbers, 895

 design equation, 41

 energy balance, 592–594

 gas-phase reactions in, 180

 with heat exchange, 547

 isothermal reactors, 865–867

 liquid-phase reactions in, 179–180

 multiple reactions, 637–639

 multiple reactions in, 548

 nonideal reactors, 885–887

 packed-bed reactors, 41

 parallel reactions, 639–641

 RTD function, 893, 919

- segregation model for a continuous-flow system, 891
- sequencing of reactors, 61–62
- in series, 56, 57–58
- series reactions, 638–639
- sizing, 47–50
- Tanks-in-series (T-I-S) model, 865–867
- in terms of conversion, 547
- in terms of molar flow rates, 548
- two-parameter model, 889
- zero-order parameter models, 889
- Point of no return, 698
- Poisoning
 - deactivation, 503–504
 - in feed, 504–505
 - reactants or products, 506
- Polanyi-Semenov equation, 99
- Polymath program, 23, 24, 48, 138, 139, 140, 145, 160, 185, 201, 205–208, 214, 215, 230, 238, 245, 246, 254, 563, 577, 605, 608, 609, 613, 690–691, 698, 706, 721, 850, 856, 857, 896, 904, 916, 940, 950, 963, 967, 1009–1010
 - adiabatic operation, 614, 651
 - co-current exchange, 616, 648–649
 - constant T_a , 615, 651
 - countercurrent exchange, 618, 650
- Living Example Problems, 1010
- nonlinear regression, 284
- and output for semibatch reactor, 709
- for startup of CSTR, 714

- tutorials, 1010
- Polynomial, 850, 851, 896, 897, 903, 907–909, 913–916
- Porous catalysts, 443
- Potential energy surfaces
 - bond distortions, hydrogen atom and an ethane molecule, 93
 - col or saddle point, 90–91
 - 3D plot of, 90–91
 - energy barrier E_B , 92
 - equilibrium position, 92
 - exothermic reaction, 90
 - GAMES, 92
 - Guassian 16, 92
 - IQMol, 92
 - Molecular Modeling in Chemical Reaction Engineering*, 92
 - Q-Chem, 92
 - Spartan software, 92
 - transition state, 92
- Power law models, 79–82, 270, 275, 300, 449, 496, 508, 910
- PPE. *See* Personal protective equipment
- Practical stability limit, 702, 704–706
- Pressure, 1000
- Pressure drop
 - analytical solution for reaction with, 194–197
 - calculating X in reactor with, 202–208
 - effect on conversion profile, 196–197
 - in packed bed, 187–193
 - in pipes, 191–193

- and rate law, 185–186
- in reactors, 185
- second-order gas-phase reaction in PBR, 194–195
- Pressure-drop equation, 232, 595
- Pressure-drop parameter, 190, 198–201, 237, 486
- Pressure equilibrium constant, 136
- Probability function of reaction, 101
- Processed data, 276, 279, 282
- Process safety, 25
- Process safety triangle
 - application, 423–424
 - example of, 424
 - levels of, 422–423
- Product-inhibited reactions, 51
- Professional Reference Shelf, 1028
- Promoters, 444
- Propylene, 5
- Propylene glycol, 702
 - adiabatic CSTR, 623–628
- Propylene oxide, 702, 704, 705
- Pseudo-steady-state hypothesis (PSSH)
 - azomethane, 370–372
 - enzyme–substrate complex, 392
 - Polymath solution, 377
 - rate law, 370, 478
 - theory of active intermediates, 369–370
- PSSH. *See* Pseudo-steady-state hypothesis

Pulse input experiment, residence time distribution, 847–852

Python, xxiv, 23, 95, 185, 193, 197, 205, 215, 246, 260, 339, 417, 519, 613, 614, 699, 705, 706, 775, 1010–1011, 1028

Q

Q-Chem, 92

QSSA. *See* Quasi-steady state assumption

Quadrature formula, 48

Quasi-steady state assumption (QSSA), 760

Questions Before Reading (QBR), 29, 70, 109, 148, 217, 262, 301, 355, 429, 526, 658, 729, 733, 734, 782, 832, 880, 920, 979

R

Rapid reaction, 754

Rate constant, 78

Rate data

- analysis of, 270–271

- AWFOS–S7 Laboratory Safety, 297–298

- experimental planning, 297

- graphical differentiation method, 278

- integral method, 273–277

- method of excess, 272–273

- methods, 269, 277–278

- nonlinear regression. *See* Nonlinear regression

- numerical method, 278–279

- rate law, 280–284

- rate-law parameters, 279

reaction-rate data, differential reactors, 290–292

Rate law, 76, 78, 103–104, 141–142, 147, 161, 174, 186, 195, 316, 326, 336, 340, 345, 348, 371, 376, 389, 404–407, 415, 449, 486, 542, 598–600, 604, 612, 625, 629, 640, 643, 646, 688, 695, 703, 708, 712, 797, 893, 894, 960, 968

azomethane, 370

for competitive inhibition, 393

determining, 280–284

energy needed for crossing the barriers, 78

for ethylene oxide hydrolysis, 165

experimental data, 481–482

law of mass action, 78

molecular simulations, 100–103

Monod growth, 426

for noncompetitive inhibition, 396

nonelementary. *See* Nonelementary rate laws

parameters. *See* Rate-law parameters

potential energy surfaces, 78

power law models. *See* Elementary rate law

pseudo-steady-state hypothesis, 371, 478

rate of reaction, 78

reaction-rate constant. *See* Reaction-rate constant

reactor sizing and design, 103–104

reversible reactions. *See* Reversible reactions

rules of thumb, 374

synthesizing, 463–466

temperature dependence of, 479

for uncompetitive inhibition, 395

urea decomposition, 389

Rate-law equation, partial pressure, 137

Rate-law parameters, 288–289

- concentration–time data, 287
- homogeneous reactions, 272
- nonlinear regression, 284
- rate law and, 270–271, 293, 299

Rate-limiting step (RLS), 523

- adsorption of cumene, 463, 466–469
- decomposition of cumene, 463, 473–474
- initial reaction rate, 466
- Langmuir–Hinshelwood kinetic mechanism, 464
- rate of benzene desorption, 465
- reforming catalysts, 474–478
- surface reaction, 470–473
- surface reaction equilibrium constant, 465

Rate of accumulation, 9

Rate of adsorption, 454, 455, 456, 458, 461, 466, 523

Rate of benzene desorption, 465

Rate of change of energy, 1001

Rate of formation, 8

Rate of generation, 8, 9

Rate of product formation, 408

Rate of reaction, 4–8, 156

Rates of chemical reactions, 76

Rates of disappearance and formation, 6–7

Raw data, 275, 279, 292–297, 306

Reactants, [14](#)

Reacting species, [888](#)

moles of, [118](#), [119](#)

Reaction

at low temperature, [318](#)

in series. *See* [Series reactions](#)

Reaction energetics, [1025](#)

Reaction order, [107](#)

of desired product, [316–317](#)

of undesired product, [317](#)

Reaction rate, [14](#), [18](#)

Reaction-rate constant

activation energy. *See* [Activation energy](#)

Arrhenius plot. *See* [Arrhenius plot](#)

law of mass action, [89](#)

temperature, [89–90](#)

Reaction-rate data

differential reactors, [290–297](#)

Reaction-rate law, [7](#), [466](#), [467](#), [497](#), [500](#), [1015](#)

Reaction-rate parameters, [952](#)

Reaction yield, [312](#)

Reactive distillation, [249](#)

Reactive intermediates, [478](#)

Reactive trajectory, [100](#)

Reactor

mole balances, [718](#)

selection and operating conditions, [322–325](#)

sizing and design, 103–104

volume, 20–24

Reactor and conditions, to minimize unwanted products, 324–325

Reactor design, 1

catalytic reactor design, 486–489

chemical reaction engineers, 479

differential reactor, 480

experimental observations, 483–484

model parameters k , K_B , and K_T , 484–486

packed-bed reactor, 480

rate law. *See* Rate law

rate-law parameters, 484

Reactor Lab, 1013, 1028

Reactor staging, with interstage cooling or heating

endothermic reactions, 571–575

exothermic reactions, 571

Real CSTR model. *See also* Tubular reactor

bypassing and dead space, 965–966

CSTRs with interchange, 968–970

Real reactor, 845, 892

Real reactor volume, 932

Real tubular reactors, 973

Reciprocal rate, 43

Reforming catalysts

irreversible surface-reaction-limited rate laws, 478

isomerization, 476

octane number of gasoline, 474–475

- platinum on alumina, 476
- reaction mechanism and rate-limiting step, 477
- spectroscopic measurements, 478
- Relative rates of reaction, 76, 77–78, 118
- Residence time, 846
- Residence time distribution (RTD), 844, 845–846, 869, 875
 - characteristics of, 853
 - integral relationships, 853–854
 - mean residence time, 854–855
 - diagnostics and troubleshooting, 869–875
 - different nonideal reactor situations, 870
 - dimensionless residence time, 919
 - ideal reactor, 919
 - in ideal reactors. *See* Ideal reactors
 - internal-age distribution, 859–860, 919
 - measurement of, 846–847, 848
 - nonideal reactors, 888–890
 - normalized RTD function, 859
 - other moments of, 855–858
 - PFR/CSTR series, 866–869
 - pulse input experiment, 847–852
 - software packages. *See* Software packages
 - step tracer experiment, 852–853
 - tanks-in-series model. *See* Tanks-in-series (T-I-S) model
 - zero-adjustable-parameter models. *See* Zero-adjustable-parameter models
- Reversible inhibition, 392
- Reversible reactions, 76, 138, 239

benzene (B), 86–87

endothermic reactions, 89

equilibrium constant K_C , 86, 88

formation of diphenyl, 87–88

rate laws, 86

thermodynamic relationship, 86

Reynolds (Re) number, 751, 754, 767, 786, 935, 943, 944,
754, 767

Rhizobium trifolii, 407

Ribonucleic acid (RNA), 401

RLS. *See* Rate-limiting step

RNA. *See* Ribonucleic acid

RTD. *See* Residence time distribution

Runaway reactions, 322, 700, 723, 724

safety in chemical plants with, 693–700

R.W. Paul's six types critical thinking questions, 827

S

Saccharomyces cerevisiae, 411, 415

SAChE program. *See* Safety and Chemical Engineering
Education program

SAChE Web site

chemical reactivity hazards, 654

membership, 655

runaway reactions, 654

rupture of a nitroaniline reactor, 654

Seveso accidental release case history, 654–655

Safety, 1024

Safety Analysis of the Incident algorithm, 210–213

Safety and Chemical Engineering Education (SACChE) program, 654–655

Safety disk rupture failure, 699–700

Safety statistics

- causes of batch reactor accidents, 653
- Chemical Engineering Curriculum Web Site, 652–653
- chemical reactivity, 654
- incidence of batch process accidents, 653
- nitroaniline explosion, 653
- Safety and Chemical Engineering Education, 654–655

Sapphire Energy, 400

Scavenger, 376

Schmidt (Sc) number, 751, 752, 754, 943, 944

Secondary nutrient, 409–410

Second-order ordinary differential equations, 995

Second-order rate laws, 81

Second-order reaction, 274, 276

- batch reactor equation, 903
- in CSTR, 169–170
- isothermal semibatch reactors, 252–255
- in laminar-flow reactor, 897–900

Second reactor, 574–575

Segregation model, 235, 919

- batch reactors, 891
- completely micromixed fluid, 890
- continuous-flow system, 891
- continuous stirred tank reactor, 890

first-order reaction, 892–893

fluid elements, 890

little batch reactors (globules), 890

mean conversion, 891–892. *See also* Mean conversion

multiple reactions. *See* Multiple reactions

physical insight, 892

RTD function, 891

vs. maximum mixedness predictions, 909–910

Seldom, 62

Selectivity

multiple reactions, 311–312

parallel reactions, 316

Semibatch operation, with heat exchanger, 707–710

Semibatch reactors, 259, 726

complex liquid-phase reactions in, 341–343

and CSTR, 248

energy balance on, 701

heat effects in, 707–710

mole balances, 249–252

multiple reactions in, 711–714

second-order reaction, 252–255

type of, 248

use, 249

Semiconductors, 490

Semi-log graphs, 997

Separable deactivation kinetics, 506

Separable kinetics, 497

Series

adiabatic liquid-phase isomerization, 59–61

conversion, 51

CSTRs, 52–56

CSTR vs. PFR, 57–58

feed stream, 52

plug flow reactor, 56

sequencing of reactors, 61–62

Series–parallel reactor system, 888

Series reactions, 310

in batch reactor, 325–329

in CSTR, 329–332

PFR, 332–333

Shell balance on catalyst pellet, 796

Shell-side pressure, 247

Sherwood number, 751, 756, 768

Shrinking core model

combustion time, single particle, 762–763

constant total molar concentration, 760

dust particles surface, 760

elemental carbon, 761

gas–carbon interface, 761

gas-phase species, 758

molar density of solid carbon, 761

mole balance on O_2 , 762

principles of, 759

quasi-steady state assumption, 762

solid combustible dust particles, 758

solid organic particles, 759–760

solid surface, 759–760

spherical dust particle, 761

time release of drugs, 758

Silica-alumina

cracking catalyst, 443

dehydrogenation catalyst, 444

Simpson's one-third rule, 995–996

Simpson's rule, 49, 60

Simpson's three-eighths rule, 996

Single continuous-stirred tank reactors, 168–171

Single-CSTR RTD, 861–863

Single particle

catalyst particle, 752–755

first order rate laws, 752–753

liquid phase reaction, 757–758

mass transfer of oxygen to carbon particle, 755–757

Single-site mechanism, 458

Sintering (aging)

deactivation, 498–500

Site balance, 453, 468

Sizing

CSTR, 46–47

CSTR vs. PFR sizes, 50–51

definition, 43

first-order dependence, 42

function of conversion, 42
infinite reactor volume, 43
irreversible reactions, 43
mole balance, 42
plug-flow reactor, 47–50
reactor design and staging, 43–45
reciprocal rate, 43
Slow reaction, 754–755
Slurry reactors, 825–826, 830
Smith, J. C., 768
Soap, 123
Sodium chloride, 715
Sodium hydroxide, 123, 124, 707
Sodium methylcyclopentadiene, 715, 726
Software packages, 997
 Aspen, 1013
 COMSOL, 1012
 MATLAB, 1011
 maximum mixedness model, 907
 Microsoft Excel, 1011–1012
 ODE solver program, 907
 Polymath, 1009–1010
 Python, 1011
 Reactor Lab, 1013
 segregation vs. maximum mixedness predictions, 909–910
 use, maximum mixedness model, 908–909
 Wolfram, 1010–1011

Solid catalyst, [18](#)

Solid combustible dust particles, [758](#)

Sonoluminescence, [375](#)

Space satellite, [768–770](#)

Space time (t), [62–64](#), [65](#), [69](#)

Space time tau, [63](#)

Space velocity (SV), [64–65](#), [69](#)

Spartan software, [92](#)

Specific reaction rate of desired reaction, [317](#)

Spherical catalyst pellets, diffusion and reactions in, [793](#)

- derivation of differential equation, [795–798](#)
- differential equation for first-order reaction, [801–802](#)
- effective diffusivity, [793–795](#)
- equation in dimensionless form, [798–801](#)

Spherical dust particle, [761](#)

Split-boundary-value problem, [939](#)

Stable steady-state temperatures, [637](#)

Standard temperature and pressure (STP), [65](#)

Startup of CSTR, [702–706](#)

Stationary phase, [404](#), [408–410](#)

Steady-state energy balance, [556](#)

Steady-state molar flow rates, [551–553](#)

Steady-state nonisothermal reactor design

- complex reactions, PFR, [645–652](#)
- CSTR with heat effects. *See* [CSTR, with heat effects](#)
- heat exchange. *See* [Heat exchange](#)
- heat-transfer fluid. *See* [Heat-transfer fluid](#)

- multiple reactions, CSTR, 642–645
- multiple steady states. *See* Multiple steady states
- parallel reactions in PFR, 639–641
- PFR/PBR design. *See* PFR/PBR design
- plug-flow reactors, 637–639
- radial and axial temperature variations, 652
- Stepanek, J., 768
- Step tracer experiment, residence time distribution, 852–853
- Stereospecific catalysts, 400
- Stern–Volmer equation, 374–377
- Stirred reactors
 - ammonolysis, 248
 - chlorination, 248
 - CSTR, 248
 - hydrolysis, 248
 - semibatch reactors, 248
 - unsteady operation, 248
- Stochastic modeling of reactions, 101–103
- Stoichiometric coefficient
 - NOCl, 236
 - species j , 129
- Stoichiometric equations, 960
- Stoichiometric feed, 122
- Stoichiometric table, 146
 - batch system, 119, 120, 125
 - continuous-flow reactor, 140
 - conversion, 121, 147

flow system, 125

function of conversion, 117, 125, 127, 146

gas-phase reaction, 130

SO₂, 132

Stoichiometry, 106, 118, 158, 159, 161, 162, 165, 168, 175, 179, 180, 183, 186, 194, 203, 213, 232, 233, 237, 244, 253, 259, 315, 337, 341, 346, 353, 407–409, 416, 426, 486, 489, 500, 513, 518, 542, 559, 560, 561, 568, 599, 600, 612, 625, 640, 647, 688, 695, 703, 708, 713, 720

Stoichiometry (liquid phase), 542

Stoke's flow, 756

STP. *See* Standard temperature and pressure

Straight-through transport reactors (STTR)

- catalyst decays, 516–519
- mole balance, 515, 516
- moving-bed reactors, 515
- production of gasoline, 515
- rapid decay, 510
- and regeneration unit, 520

Streamlines, 941–942

Streptomyces aureofaciens, 421

STTR. *See* Straight-through transport reactors

Styrene, 349

Substrate (S), 378

Substrate inhibition, 398–399

Sugar/dust explosion, 778–780

Supported catalysts, 444

Surface-limited reaction, 463

Surface reaction, 447, 448, 449

equilibrium constant, 465

rate-limiting step, 470–473

SV. *See* Space velocity

Sven Köttlov Consulting Company, 626

Swiss Cheese Model, 143–144

System volume, 8

T

Tank reactor, with heat exchanger, 701

Tanks-in-series (T-I-S) model, 910, 911, 919

conversion, 912

nonideal reactors, 910

PFR and CSTR, 949–951

real reactor, 911–912

vs. dispersion model, 951–952

vs. segregation model, 912

Temperature, 1000

Temperature–concentration phase plane, 702

Temperature inactivation, 391

Temperature surface, 962

Temperature–time trajectory, 508–510, 524, 690, 694, 699

Terephthalic acid, 972

Termolecular, 76

TF. *See* Tissue factor

Therapeutic proteins, 377

Thermal denaturizing, 391

Thermodynamic equilibrium constant, 468, 470
Thermodynamic properties, of molecular species, 1025
Thermodynamics, 138
 first law of, 543–544
Thiele modulus, 798, 800–802, 804, 806–808, 821, 829
Thoenes–Kramers correlation, 769
T-I-S model. *See* Tanks-in-series model
Tissue Engineering, 840–841
Tissue factor (TF), 333–334
T2 Laboratories explosion, 715–723
 safety analysis of the incident, 723–725
TOF. *See* Turnover frequency
Toluene (T)
 dependence of, 481
 hydrodemethylation of, 480, 482, 486
 and hydrogen, 480
Tracer, 846
Tracer balance, 969
Tracer data, 931
Trambouze reactions, 318
Transient heat effects, 56
Transition-state
 molecule, 92
 theory, 109
Translational kinetic energy, 368–369
Transport law, 743
Trapezoidal rule, 995

Trial-and-error solution, 62

Trickle bed reactors, 825, 826

Tubular flow, 746

Tubular flow reactor, 40–41

Tubular reactor, 14–18, 178–179, 945

- axial and radial gradients, 962–963
- COMSOL program, 963
- differential cylindrical annulus, 956, 957
- dispersion and reaction in, 933, 939–941
- effect of e on conversion, 180–185
- energy balance, 958–960
- energy flux, 958
- gas-phase reactions in PFR, 180
- liquid-phase reactions in PFR, 179–180
- molar flux, 956–958
- one-parameter models, 932
- perfect operation of PFR (P) model, 873
- PFR with channeling (bypassing, BP) model, 873–874
- PFR with dead volume (DV) model, 874–875
- real CSTR. *See* Real CSTR model

Turbulent flow, 199, 200–201

Turnover frequency (TOF), 446

Two-parameter model, 888, 932–933

- with PFR and CSTR, 889

Two-parameter models, 888

U

UFL. *See* Upper flammability limit

Uncompetitive inhibition, 392, 394–396

Underground wet oxidation, 1022

Undesired reactions, 311

Unimolecular, 76

University of Cologne, 1015

University of Colorado, 1028

Unpacked laminar-flow tubular reactor, 932

Unstable steady-state temperatures, 635

Unsteady-state energy balance, 682–684

Unsteady-state mass balance, 426

Unsteady-state operation

 stirred reactors. *See* Stirred reactors

Unsteady-state tracer balance, 945

Unsupported catalysts, 444

Upper flammability limit (UFL), 350

Uranium (U), 76

V

van der Waals forces, 379, 445

van't Hoff's equation, 656, 1004

Variance, 855

Varying-density, 127

Velocity profile, 932

Vessel dispersion number, 935

Viscosity, 1000

Visual encyclopedia of equipment, 1013, 1028

Volume, 1000

of ideal gas, 999

Volumetric flow rate, 39, 62, 126, 127, 129, 130, 230, 898,
901, 902, 911, 932, 963, 972

W

Washout, bioreactors, 419–421

Water-gas shift reaction, 1006–1008

Weisz–Prater criterion, for internal diffusion limitations, 807–
809, 829

Who done it?, 113, 219, 222, 226

Wolfram, xxiv, 23, 95, 185, 193, 197, 205, 215, 246, 260, 339,
417, 519, 613, 614, 699, 705, 706, 940, 775, 1010–1011,
1028

Work, 1000

Y

Yield coefficients

bioreactors, 411–413

cells and substrate, 407

stoichiometric, 408, 409

Yield, multiple reactions, 312–313

Z

Zeolite catalysts, 443

Zero-adjustable-parameter models, 888

first-order reaction, 896

maximum mixedness. *See* Maximum mixedness model

second order reaction, 897

segregation. *See* Segregation model

Zero-order parameter models, 976

with PFR and CSTR, 889

Zero-order reactions, 43, 51, 274

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