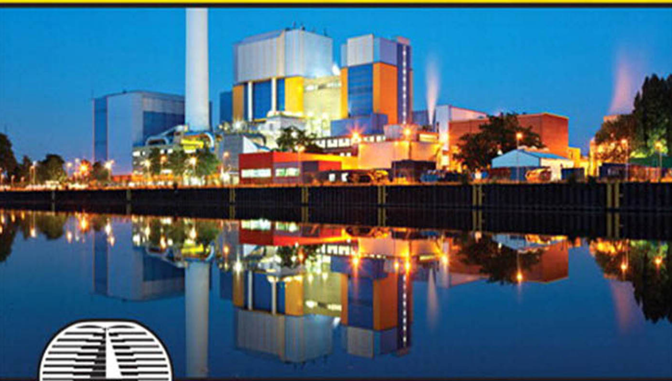
DVD-ROM INCLUDED

PRENTICE HALL

ESSENTIALS OF CHEMICAL REACTION ENGINEERING

H. SCOTT FOGLER



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Essentials of Chemical Reaction Engineering

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ESSENTIALS OF CHEMICAL REACTION ENGINEERING
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Essentials of Chemical Reaction Engineering

H. SCOTT FOGLER

Ame and Catherine Vennema Professor of Chemical Engineering
and the Arthur F. Thurnau Professor
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Dedicated to

Janet Meadors Fogler

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

Contents

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Preface

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

A. The Audience

This book for undergraduates 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., "What's wrong with this solution?"). It gives more emphasis to *safety* (Chapters 12 and 13) and *alternative energy sources: solar* (Chapters 3, 8, and 10) and *biofuel production* (Chapter 9). It also contains interactive computer games, as well as a little more Michigan humor here and there. A draft version of this book was printed, class tested at the University of Michigan and other leading universities, and further revised, taking into account the suggestions of more than 200 students. As a result, much of the material was revised and reworked based on that feedback.

B. The Goals

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

CRE is a great subject and the heart of chemical engineering. It is one of two core courses that is unique to chemical engineering.

B.2. To Develop a Fundamental Understanding of Reaction Engineering

The second goal of this book is to enable the reader to develop a clear understanding of the fundamentals of chemical reaction engineering (CRE). This goal will be 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. The algorithms presented in the text for reactor design provide this framework, and the homework problems will give practice using the algorithms. The conventional home problems at the end of each chapter are designed to reinforce the principles in the chapter. These problems are about equally divided between those that can be solved with a calculator and those that require a personal computer and a numerical software package, such as Polymath, AspenTech, or COMSOL.

To give a reference point as to the level of understanding of CRE required in the profession, a number of reaction engineering problems from the California Board of Registration for Civil and Professional Engineers—Chemical Engineering Examinations (PECEE) are included in the text.[1] Typically, these problems should each require approximately 30 minutes to solve.

Finally, the DVD-ROM should greatly facilitate learning the fundamentals of CRE because it includes summary notes of the chapters, PowerPoint slides of class lecture notes, added examples, expanded derivations, and self tests. A complete description of these *learning resources* is given in Appendix H.

B.3. To Enhance Critical Thinking Skills

A third goal is to enhance critical thinking skills. A number of home problems have been included that are designed for this purpose. Socratic questioning is at the heart of critical thinking, and a number of homework problems draw from R. W. Paul's six types of Socratic questions,[2] shown in Table P-1.

TABLE P-1 SIX TYPES OF SOCRATIC QUESTIONS USED IN CRITICAL THINKING

(1) *Questions for clarification:* Why do you say that? How does this relate to our discussion?

"Are you going to include diffusion in your mole balance equations?"

(2) *Questions that probe assumptions:* What could we assume instead? How can you verify or disprove that assumption?

"Why are you neglecting radial diffusion and including only axial diffusion?"

(3) *Questions that probe reasons and evidence:* What would be an example?

"Do you think that diffusion is responsible for the lower conversion?"

(4) *Questions about viewpoints and perspectives:* What would be an alternative?

"With all the bends in the pipe, from an industrial/practical perspective, do you think diffusion and dispersion will be large enough to affect the conversion?"

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[1] The permission for use of these problems, which, incidentally, may be obtained from the Documents Section, California Board of Registration for Civil and Professional Engineers—Chemical Engineering, 1004 6th Street, Sacramento, CA 95814, is gratefully acknowledged. (Note: These problems have been copyrighted by the California Board of Registration and may not be reproduced without its permission.)

[2] R. W. Paul, *Critical Thinking* (Santa Rosa, Cal.: Foundation for Critical Thinking, 1992).

TABLE P-1 SIX TYPES OF SOCRATIC QUESTIONS USED IN CRITICAL THINKING (CONTINUED)

(5) *Questions that probe implications and consequences:* What generalizations can you make? What are the consequences of that assumption?

"How would our results be affected if we neglected diffusion?"

(6) *Questions about the question:* What was the point of this question? Why do you think I asked this question?

"Why do you think diffusion is important?"

Scheffer and Rubenfeld[3,4] expand on the practice of critical thinking skills discussed by R. W. Paul by using the activities, statements, and questions shown in Table P-2. The reader should try to practice using some or all of these actions every day, as well as asking the critical thinking questions in Table P-1.

TABLE P-2 CRITICAL THINKING ACTIONS[5]

Analyzing: separating or breaking a whole into parts to discover their nature, function, and relationships
"I studied it piece by piece."
"I sorted things out."

Applying Standards: judging according to established personal, professional, or social rules or criteria
"I judged it according to…."

Discriminating: recognizing differences and similarities among things or situations and distinguishing carefully as to category or rank
"I rank ordered the various…."
"I grouped things together."

Information Seeking: searching for evidence, facts, or knowledge by identifying relevant sources and gathering objective, subjective, historical, and current data from those sources
"I knew I needed to look up/study…."
"I kept searching for data."

Logical Reasoning: drawing inferences or conclusions that are supported in or justified by evidence
"I deduced from the information that…."
"My rationale for the conclusion was…."

Predicting: envisioning a plan and its consequences
"I envisioned the outcome would be…."
"I was prepared for…."

Transforming Knowledge: changing or converting the condition, nature, form, or function of concepts among contexts
"I improved on the basics by…."
"I wondered if that would fit the situation of …."

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[3] Courtesy of B. K. Scheffer and M. G. Rubenfeld, "A Consensus Statement on Critical Thinking in Nursing," *Journal of Nursing Education,* 39, 352–59 (2000).

[4] Courtesy of B. K. Scheffer and M. G. Rubenfeld, "Critical Thinking: What Is It and How Do We Teach It?" *Current Issues in Nursing* (2001).

[5] R. W. Paul, *Critical Thinking* (Santa Rosa, Cal.: Foundation for Critical Thinking, 1992); B. K. Scheffer and M. G. Rubenfeld, "A Consensus Statement on Critical Thinking in Nursing," *Journal of Nursing Education,* 39, 352–59 (2000).

I have found that the best way to develop and practice critical thinking skills is to use Tables P-1 and P-2 to help students write a question on any assigned homework problem and then to explain why the question involves critical thinking.

More information on critical thinking can be found on the DVD-ROM in the section on *Problem Solving*.

B.4. To Enhance Creative Thinking Skills

The fourth goal of this book is to help enhance creative thinking skills. This goal will be achieved by using a number of problems that are open-ended to various degrees. Here the students can practice their creative skills by exploring the example problems, as outlined at the beginning of the home problems of each chapter, and by making up and solving an original problem. Problem P5-1 gives some guidelines for developing original problems. A number of techniques that can aid the students in practicing and enhancing their creativity can be found in Fogler and LeBlanc[6] and its companion Web site, *www.engin.umich.edu/scps*, and in the *Thoughts on Problem Solving* section on the DVD-ROM and on the Web sites *www.umich.edu/~essen* and *www.essentialsofCRE.com*. We will use these techniques, such as Osborn's checklist and de Bono's lateral thinking (which involves considering other people's views and responding to random stimulation) to answer add-on questions such as those in Table P-3.

TABLE P-3 PRACTICING CREATIVE THINKING

(1) Brainstorm ideas to ask another question or suggest another calculation that can be made for this homework problem.

(2) Brainstorm ways you could work this homework problem incorrectly.

(3) Brainstorm ways to make this problem easier or more difficult or more exciting.

(4) Brainstorm a list of things you learned from working this homework problem and what you think the point of the problem is.

(5) Brainstorm the reasons why your calculations overpredicted the conversion that was measured when the reactor was put on stream. Assume you made no numerical errors on your calculations.

(6) "What if…" questions: The "What if…" questions are particularly effective when used with the *Living Example Problems,* where one varies the parameters to explore the problem and to carry out a sensitivity analysis. For example*, what if someone suggested that you should double the catalyst particle diameter, what would you say?*

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. One problem whose solution exemplifies this goal is the Manufacture of Styrene, Problem P12-24$_C$. This problem is particularly interesting because two reactions are endothermic and one is exothermic.

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[6] H. S. Fogler and S. E. LeBlanc, *Strategies for Creative Problem Solving, Second Edition* (Upper Saddle River, N.J.: Prentice Hall, 2006).

(1) Ethylbenzene → Styrene + Hydrogen: *Endothermic*
(2) Ethylbenzene → Benzene + Ethylene: *Endothermic*
(3) Ethylbenzene + Hydrogen → Toluene + Methane: *Exothermic*

To summarize Section B, it is the author's experience that both critical and creative thinking skills can be enhanced by using Tables P-1, P-2, and P-3 to extend any of the homework problems at the end of every chapter.

C. The Structure

The strategy behind the presentation of material is to build continually on a few basic ideas in chemical reaction engineering to solve a wide variety of problems. These ideas, referred to as the *Pillars of Chemical Reaction Engineering*, are the foundation on which different applications rest. The pillars holding up the application of chemical reaction engineering are shown in Figure P-1.

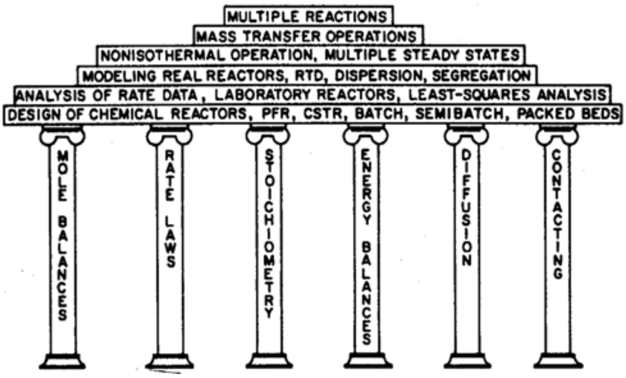

Figure P-1 Pillars of Chemical Reaction Engineering.

From these pillars we construct our CRE algorithm:

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

With a few restrictions, the contents of this book can be studied in virtually any order after students have mastered the first six chapters. A flow diagram showing the possible paths can be seen in Figure P-2.

The reader will observe that although metric units are used primarily in this text (e.g., kmol/m^3, J/mol), a variety of other units are also employed (e.g., lb$_m$/ft^3, Btu). *This choice is intentional!* We believe that whereas most papers published today use the metric system, a significant amount of reaction engineering data exists in the older literature in English units. Because engineers will be faced with extracting information and reaction rate data from older literature as well as from the current literature, they should be equally at ease with both English and metric units.

The notes in the margins are meant to serve two purposes. First, they act as guides or commentary as one reads through the material. Second, they identify

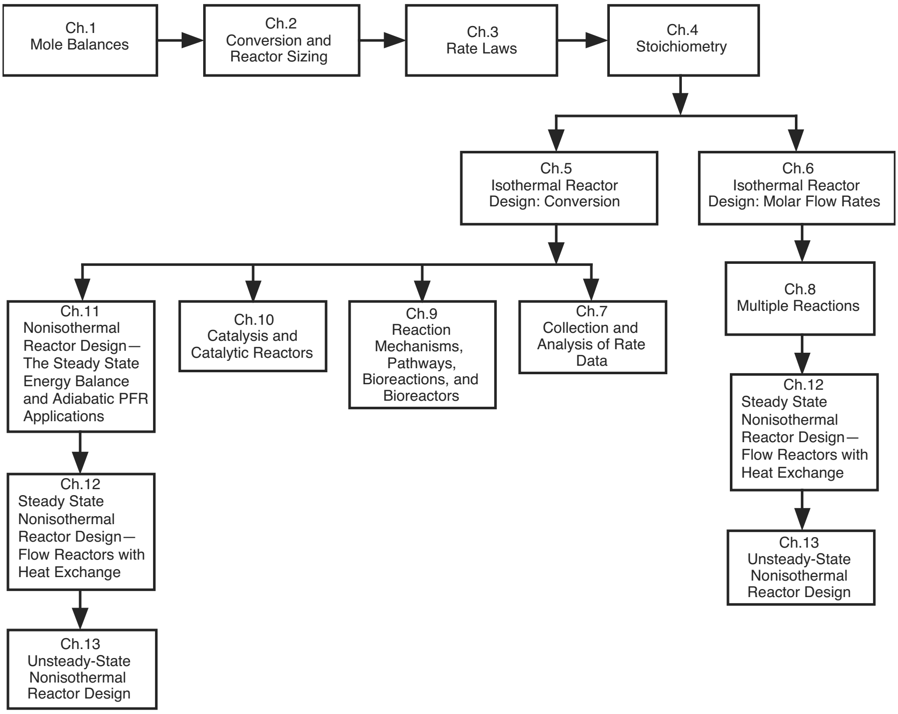

Figure P-2 Sequences for studying the text.

key equations and relationships that are used to solve chemical reaction engineering problems.

D. The Components of the DVD-ROM

The interactive DVD-ROM is a novel and unique part of this book. The main purposes of the DVD-ROM are to serve as an enrichment resource and as a professional reference shelf. The home page for the DVD-ROM and the CRE Web site (*www.umich.edu/~essen*) is shown in Figure P-3; also see the Web site *www.essentialsofCRE.com*.

The objectives of the DVD-ROM are fourfold: (1) to facilitate the learning of CRE by using the DVD-ROM to actively address the *Felder/Solomon Inventory of Learning Styles*[7] discussed in Appendix H; (2) to provide additional technical material; (3) to provide tutorial information and self-assessment exercises; and (4) to make the learning of CRE fun by using interactive games. The following components are listed at the end of most chapters and can be accessed from each chapter in the DVD-ROM.

- **Learning Resources**

  The Learning Resources give an overview of the material in each chapter and provide extra explanations, examples, and applications to reinforce the

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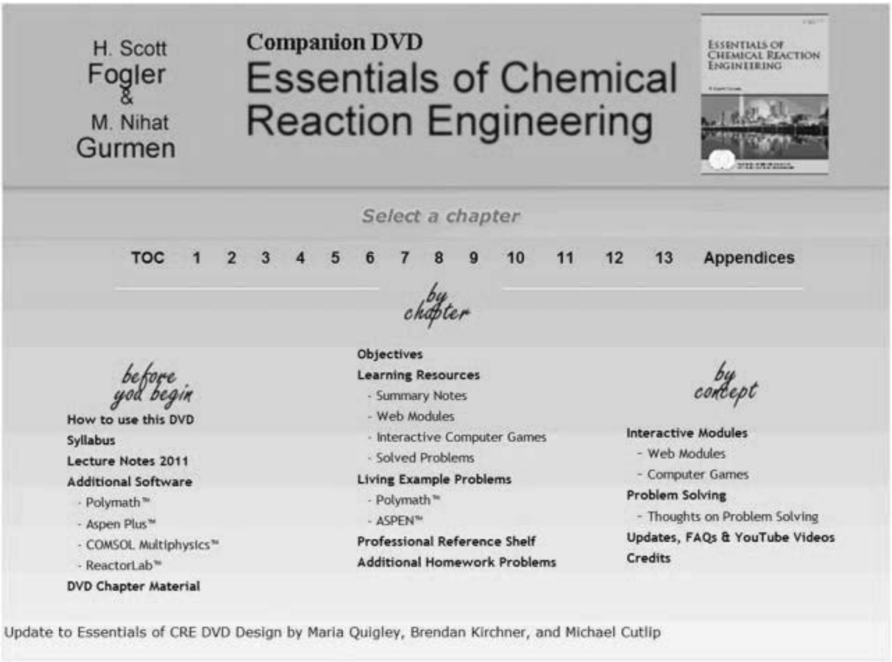
[7] *http://www.ncsu.edu/felder-public/ILSdir/styles.htm*



H. Scott
Fogler
&
M. Nihat
Gurmen

Companion DVD
Essentials of Chemical
Reaction Engineering

Select a chapter

TOC 1 2 3 4 5 6 7 8 9 10 11 12 13 Appendices

by chapter

before you begin
- How to use this DVD
- Syllabus
- Lecture Notes 2011
- Additional Software
  - Polymath™
  - Aspen Plus™
  - COMSOL Multiphysics™
  - ReactorLab™
- DVD Chapter Material

- Objectives
- Learning Resources
  - Summary Notes
  - Web Modules
  - Interactive Computer Games
  - Solved Problems
- Living Example Problems
  - Polymath™
  - ASPEN™
- Professional Reference Shelf
- Additional Homework Problems

by concept
- Interactive Modules
  - Web Modules
  - Computer Games
- Problem Solving
  - Thoughts on Problem Solving
- Updates, FAQs & YouTube Videos
- Credits

Update to Essentials of CRE DVD Design by Maria Quigley, Brendan Kirchner, and Michael Cutlip

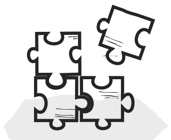
Figure P-3 Screen shot of Web site (*www.umich.edu/~essen*) and DVD-ROM home page.

basic concepts of chemical reaction engineering and are discussed further in Appendix E. The learning resources on the DVD-ROM include the following:

1. *Summary Notes*
   The *Summary Notes* give an overview of each chapter and provide on-demand additional examples, derivations, and audio comments, as well as self tests to assess each reader's understanding of the material. We have included links to comical **YouTube Videos** made by students in Professor Alan Lane's 2008 chemical reaction engineering class at the University of Alabama. Specifically, check out *Fogler Zone (you've got a friend in Fogler)* (Chapter 1), *The Black Widow* murder mystery and *Baking a Potato* by Bob the Builder and Friends (Chapter 3), *CRF Reactor Video*, Crimson Reactor Firm's video of a "semi batch" reactor with Diet Coke and Mentos (Chapter 4), learn a new dance and song, *CSTR* to the tune of *YMCA*, and a rap song and *Find Your Rhythm*, an *Ice Ice Baby* remix (Chapter 5).
2. *Web Modules*
   The Web Modules, which apply key concepts to both standard and nonstandard reaction engineering problems (e.g., the use of wetlands to degrade toxic chemicals, and death from a cobra bite), can be loaded directly from the DVD-ROM. Additional Web Modules are expected to be added to the Web site (*www.umich.edu/~essen*) over the next several years.
3. *Interactive Computer Games (ICGs)*
   Students have found the Interactive Computer Games to be both fun and extremely useful to review the important chapter concepts and then apply them to real problems in a unique and entertaining fashion.

- 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 the reader plays these interactive games, they will be asked a number of questions related to the corresponding material in the textbook. The computer will keep track of all the correct answers and at the end of the game will display a coded *performance number* that reflects how well the reader mastered the material in the text. Instructors will have a manual to decode the performance number.


Solved Problems

4. *Solved Problems*
   A number of solved problems are presented along with problem-solving heuristics. Problem-solving strategies and additional worked example problems are available in the *Problem Solving* section of the DVD-ROM.

- **Example Problems and Living Example Problems**

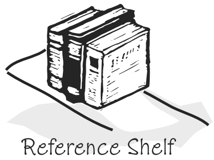
  The end of chapter problems numbered "2" (e.g., P3-2_A, P11-2_B) ask questions about the example problems in that chapter. **These problems are a key resource.** These number 2 problems should be worked before tackling the more challenging Home Problems in the chapter.

  The example problems that use an ODE solver (e.g., Polymath) are referred to as "*Living Example Problems*" because students can load the Polymath program directly onto their own computers in order to study the problem. Students are encouraged to change parameter values and to "play with" the key variables and assumptions. Using the *Living Example Problems* to explore the problem and asking "What if…" questions provide students with the opportunity to practice critical and creative thinking skills.


Living Example Problem

- **DVD Chapter Material**

  The DVD-ROM contains PDF files of the last five chapters from the fourth edition of the *Elements of Chemical Reaction Engineering*, which is mostly graduate material. These chapters, which were omitted from this book but are included on the DVD-ROM are: DVD Chapter 10, Catalyst Decay; DVD Chapter 11, External Diffusion Effects on Heterogeneous Reactions; DVD Chapter 12, Diffusion and Reaction; DVD Chapter 13, Distribution of Residence Times for Reactors; DVD Chapter 14, Models for Non Ideal Reactors; and a new chapter, DVD Chapter 15, Radial and Axial Temperature Variations in a Tubular Reactor.


Reference Shelf

- **Professional Reference Shelf**

  This section of the DVD-ROM contains

  1. Material from the fourth edition of *Elements of Chemical Reaction Engineering* that is not included in the printed text of this book is included on the DVD-ROM.

2. Material that 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.

- **Software Toolbox on the DVD-ROM**

  Polymath. The Polymath software includes an ordinary differential equation (ODE) solver, a nonlinear equation solver, and nonlinear regression. As with previous editions, Polymath is used to explore the example problems and to solve the home problems. Polymath tutorials with screen shots are given on the DVD-ROM *Summary Notes* in Chapter 1 and can also be accessed from the Home Page by going to *Living Example Problems* and then clicking on Polymath. Most chemical engineering departments in the United States have site licenses for Polymath. If your department does not have a site license and would like one, have your instructor e-mail the CACHE Corporation at cache@uts.cc.utexas.edu to learn how to obtain one.

  A special Polymath Web site (*www.polymath-software.com/fogler*) has been set up for this book by Polymath authors Cutlip and Shacham.

  AspenTech. AspenTech is a process flow sheet simulator used in most senior chemical engineering design courses. It is now routinely introduced in earlier chemical engineering courses, such as thermodynamics, separations, and now in chemical reaction engineering (CRE). See the AspenTech Web site, *www.aspentech.com*. Like Polymath, AspenTech site licenses are available in most chemical engineering departments in the United States. Four AspenTech simulation examples specific to CRE are provided on the DVD-ROM with step-by-step tutorial screen shots.

  As with Polymath programs, the input parameters can be varied to learn how they change the temperature and concentration profiles.

  COMSOL.[8] The COMSOL Multiphysics software is a partial differential equation solver that is used with DVD Chapter 15 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 *www.comsol.com/ecre*.

  Further details of these three software packages can be found in **Appendix E**.

- **Other DVD-ROM Resources**

  FAQs. The Frequently Asked Questions (FAQs) are a compilation of questions collected over the years from undergraduate students taking reaction engineering.

  Visual Encyclopedia of Equipment. 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 (www.SimzLab.com). Developed by Professor Richard Herz at the University of California at San Diego, this interactive tool will allow students

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[8] The name *FEMLAB* was changed to *COMSOL Multiphysics* on July 1, 2005.

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.


Green engineering

Green Engineering Home Problems. Green engineering problems for virtually every chapter have been developed by Professor Robert Hesketh at Rowan University and Professor Martin Abraham at the University of Toledo and these problems can be found at *www.rowan.edu/greenengineering*. These problems also accompany the book by David Allen and David Shonnard, *Green Engineering: Environmentally Conscious Design of Chemical Processes* (Prentice Hall, 2002).

Further information on how to use the DVD-ROM can be found in **Appendix H**.

E. The Web

The Web site (*www.umich.edu/~essen* or *www.essentialsofCRE.com*) will be used to update the text and the DVD-ROM. It will identify typographical and other errors in the first and later printings of *Essentials of Chemical Reaction Engineering*. In the near future, additional material may be added to include more solved problems, as well as additional Web Modules.

F. What's New

A. Pedagogy. This book maintains all the strengths of the fourth edition of *Elements of Chemical Reaction Engineering* by using algorithms that allow students to learn chemical reaction engineering through logic *rather than* memorization. At the same time, it provides new resources that allow students to go beyond solving equations in order to get an intuitive feel and understanding of how reactors behave under different situations. This understanding is achieved through more than sixty interactive simulations provided on the DVD-ROM that is bound in the back of the book. The DVD-ROM has been greatly expanded to address the Felder/Solomon Inventory of Different Learning Styles[9] through interactive *Summary Notes* and new and updated Interactive Computer Games (ICGs). For example, the Global Learner can get an overview of the chapter material from the *Summary Notes*; the Sequential Learner can use all the Derive hot buttons; and the Active Learner can interact with the ICGs and use the Self Test hot buttons in the *Summary Notes*.

A new pedagogical concept is introduced in this text through expanded emphasis on the example problems. Here, the students simply load the *Living Example Problems* (LEPs) onto their computers and then explore the problems to obtain a deeper understanding of the implications and generalizations before working the home problems for that chapter. This exploration helps students get an innate feel of reactor behavior and operation, as well as develop and practice their creative thinking skills. To develop critical thinking skills, instructors can assign one of the new home problems on troubleshooting, as well as ask the students to expand home problems by asking a related question that involves critical thinking using Tables P-1 and P-2. Creative thinking skills can be enhanced by exploring the example problems and asking "What if. . ."

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[9] *http://www.ncsu.edu/felder-public/ILSdir/styles.htm*

questions, by using one or more of the brainstorming exercises in Table P-3 to extend any of the home problems, and by working the open-ended problems. For example, in the case study on safety, students can use the DVD-ROM to carry out a post-mortem analysis on the nitroaniline explosion in Example 13-2 to learn what would have happened if the cooling had failed for five minutes instead of ten minutes. To this end, a new feature in the text is an ***Analysis*** paragraph at the end of each example problem. Significant effort has been devoted to developing example and home problems that foster critical and creative thinking.

B. Content. The following areas have received an a increased emphasis in *Essentials* over previous CRE editions by including thorough Example Problems and Home Problems on the following:

Safety: Three industrial explosions are discussed and modeled.
(1) Ammonium Nitrate CSTR Explosion (Chapters 12 and 13)
(2) Nitroaniline Batch Reactor Runaway (Chapter 13)
(3) T2 Laboratories Batch Reactor Runaway (Chapter 13)
(4) Resources from SAChE and CCPS (Chapter 12)

Solar Energy: Three examples of solar energy conversion are discussed.
(1) Solar Chemical Reactions (Chapter 3)
(2) Solar Thermal Reactors (Chapter 8)
(3) Solar Catalytic Water Spilling (Chapter 10)

Alternative Fuels:
(1) Production of Algae for Biomass (Chapter 9)

AspenTech:
An AspenTech tutorial for chemical reaction engineering and four example problems are provided on the DVD-ROM. The example problems are
(1) Production of Ethylene from Ethane
(2) The Pyrolysis of Benzene
(3) Adiabatic Liquid Phase Isomerization of Normal Butane
(4) Adabatic Production of Acetic Anhydride

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

G. Acknowledgments

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 fourth edition of *Elements of Chemical Reaction Engineering* as well as this book, *Essentials of Chemical Reaction Engineering* (see Introduction, DVD-ROM). I give special recognition as follows.

First of all, I thank my colleague Dr. Nihat Gürmen, who coauthored the original CD-ROM and Web site. He has been a wonderful colleague to work with. I also would like to equally thank University of Michigan undergraduate student Maria Quigley. Maria has been working with me the last two-and-a-half years to convert the CD-ROM from the fourth edition of *Elements of*

Chemical Reaction Engineering to the DVD-ROM in *Essentials of Chemical Reaction Engineering*. She also collected, typed, and organized more than 100 written reviews, critiques, and suggestions from the students who class-tested this book. Brendan Kirchner joined Maria the last eight months of the DVD development. Their hard work and suggestions are greatly appreciated, as is Mike Cutlip's work to solve some critical issues as the DVD approached production.

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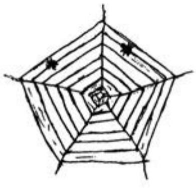
HSF
Ann Arbor



For updates on the DVD and new and exciting applications, see the **Web sites**:

www.umich.edu/~essen
or
www.essentialsofCRE.com

For typographical errors, click on Updates & FAQ on the Home page to find

www.engin.umich.edu/~essen/byconcept/updates/frames.htm

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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 and the 2009 President of the American Institute of Chemical Engineers. His research interests include flow and reaction in porous media, wax and asphaltene deposition, asphaltene flocculation kinetics, gellation kinetics, colloidal phenomena, and catalyzed dissolution. He has been research advisor to more than 40 Ph.D. students and has more than 200 refereed publications in these areas. Fogler has chaired ASEE's Chemical Engineering Division, served as director of the American Institute of Chemical Engineers, 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). He is the coauthor of the best-selling textbook *Strategies for Creative Problem Solving, Second Edition* (Prentice Hall, 2008).

Mole Balances 1

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

How is a chemical engineer different from other engineers?

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.

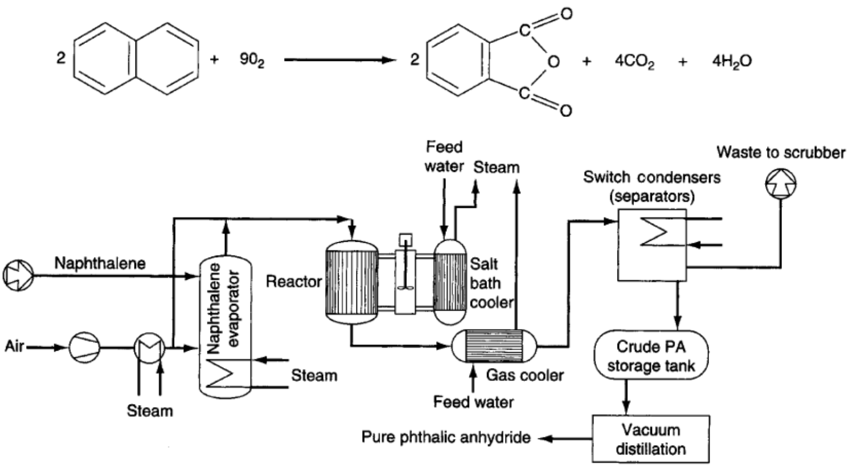
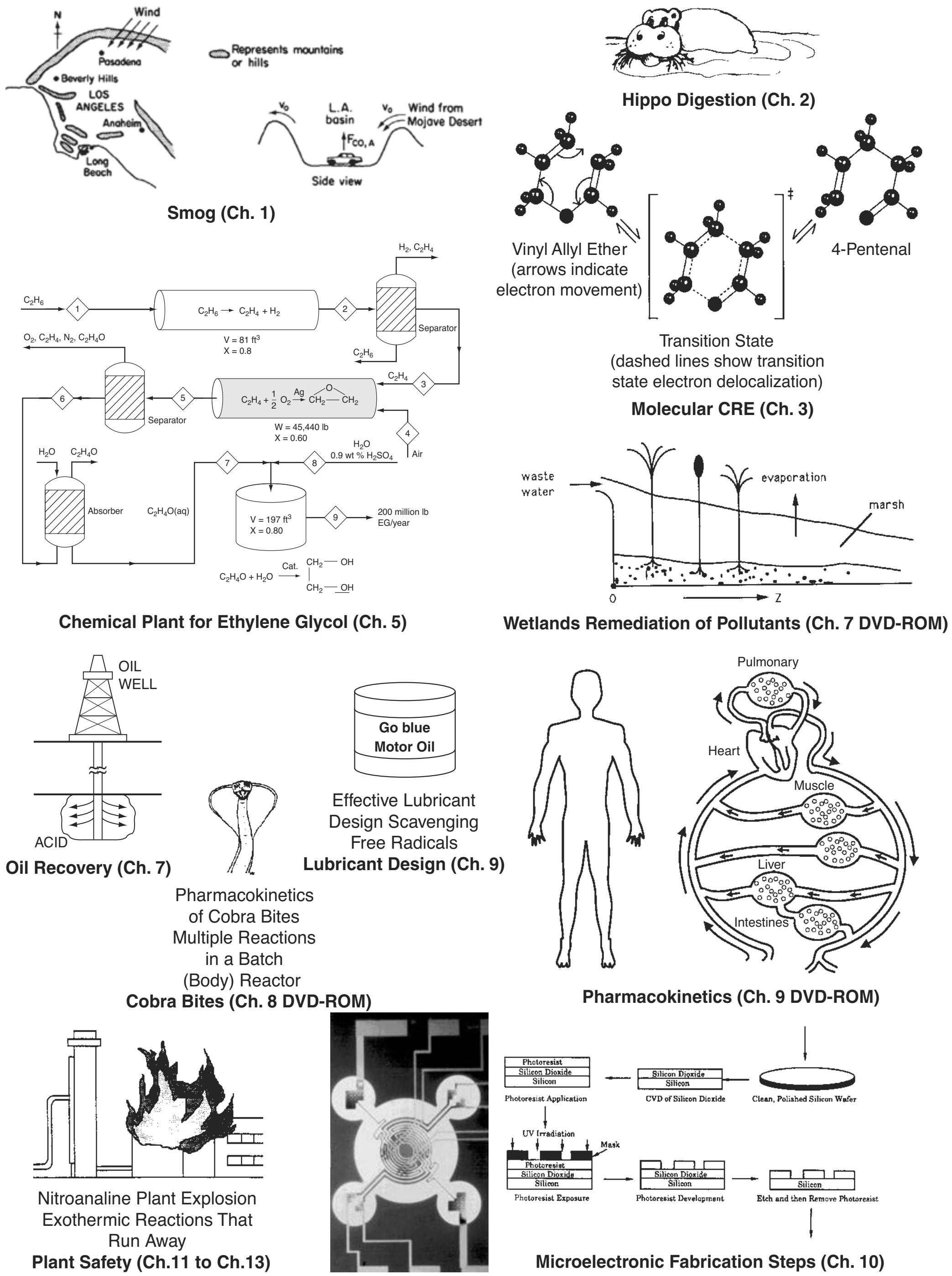


Figure 1-1 Manufacture of phthalic anhydride.

The Chemical Reaction Engineering (**CRE**) principles learned here can also be applied in many areas, such as waste treatment, microelectronics, nanoparticles, and 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 include modeling smog in the L.A. basin (Chapter 1), the digestive system of a hippopotamus (Chapter 2 DVD-ROM), and molecular CRE (Chapter 3). 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 DVD-ROM). 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 DVD-ROM); heat effects, runaway reactions, and plant safety (Chapters 11 through 13); increasing the octane number of gasoline and the manufacture of computer chips (Chapter 10).



Smog (Ch. 1)

Hippo Digestion (Ch. 2)

Molecular CRE (Ch. 3)

Chemical Plant for Ethylene Glycol (Ch. 5)

Wetlands Remediation of Pollutants (Ch. 7 DVD-ROM)

Oil Recovery (Ch. 7)

Pharmacokinetics of Cobra Bites Multiple Reactions in a Batch (Body) Reactor
Cobra Bites (Ch. 8 DVD-ROM)

Effective Lubricant Design Scavenging Free Radicals
Lubricant Design (Ch. 9)

Pharmacokinetics (Ch. 9 DVD-ROM)

Nitroanaline Plant Explosion Exothermic Reactions That Run Away
Plant Safety (Ch.11 to Ch.13)

Microelectronic Fabrication Steps (Ch. 10)

Figure 1-2 The wide world of CRE applications.

Overview—Chapter 1. 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 the reader 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 rate mechanisms and reactor design, it is necessary to account for the various chemical species entering and leaving a reaction 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, and/or remaining within the reaction system volume. After defining the rate of reaction, $-r_A$, we show how the general balance equation may be used to develop a preliminary form of the design equations of the most common industrial reactors:

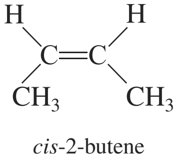
- Batch (BR)
- Continuous-stirred tank (CSTR)
- Tubular (PFR)
- Packed bed (PBR)

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 are given at the end of the chapter.

1.1 The Rate of Reaction, $-r_A$

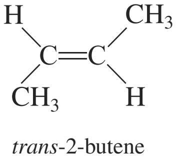
p-xylene

The rate of reaction tells us how fast a 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 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.



cis-2-butene

and



trans-2-butene

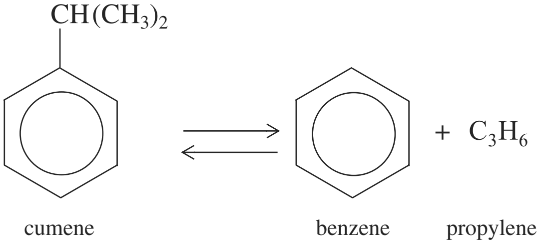
As a consequence of the different configurations, these two isomers display different chemical and physical properties. Therefore, we consider them as two different species, even though each has the same number of atoms of each element.

When has a chemical reaction taken place?

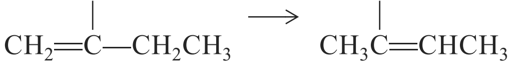
We say that a *chemical reaction* has taken place when a detectable number of molecules of one or more species have lost their identity and assumed a new form by a change in the kind or number of atoms in the compound and/or by a change in structure or configuration of these atoms. In this classical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

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 species identity is through *combination* with another molecule or atom. In the above reaction, the propylene molecule would lose its species 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 identity is through *isomerization,* such as the reaction



$$CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}CH_2CH_3 \longrightarrow CH_3\overset{\overset{CH_3}{|}}{C}{=}CHCH_3$$

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 several ways. To illustrate, consider the reaction of chlorobenzene and chloral to produce the banned insecticide DDT (dichlorodiphenyl-trichloroethane) in the presence of fuming sulfuric acid.

$$\mathrm{CCl_3CHO + 2C_6H_5Cl \longrightarrow (C_6H_4Cl)_2CHCCl_3 + H_2O}$$

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

$$\mathrm{A + 2B \longrightarrow C + D}$$

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

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 (mol/dm^3·s).

Example 1–1

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

$$A + 2B \longrightarrow C + D$$

Write the rates of disappearance and formation (i.e., generation) for each species in this reaction.

Solution

(a) *Chloral[A]:* The rate of reaction of chloral [A] ($-r_A$) is given as 10 mol/m^3·s
Rate of disappearance of A = $-r_A$ = 10 mol/m^3·s
Rate of formation of A = r_A = –10 mol/m^3·s

(b) *Chlorobenzene[B]:* For every mole of chloral that disappears two moles of chlorobenzene [B] also disappear.
Rate of disappearance of B = $-r_B$ = 20 mol/m^3·s
Rate of formation of B = r_B = –20 mol/m^3·s

(c) *DDT[C]:* For every mole of chloral that disappears one mole of DDT[C] appears.
Rate of formation of C = r_C = 10 mol/m^3·s
Rate of disappearance of C = $-r_C$ = –10 mol/m^3·s

(d) *Water[D]:* Same relationship to chloral as the relationship to DDT.
Rate of formation of D = r_D = 10 mol/m^3·s
Rate of disappearance of D = $-r_D$ = –10 mol/m^3·s

$A + 2B \rightarrow C + D$

The convention

$-r_A = 10$ mol A/m$^3\cdot$s
$r_A = -10$ mol A/m$^3\cdot$s
$-r_B = 20$ mol B/m$^3\cdot$s
$r_B = -20$ mol B/m$^3\cdot$s
$r_C = 10$ mol C/m$^3\cdot$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, etc., is given by equation (3-1) on page 75.

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* (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.

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

We can say four things about the reaction rate r_j. The reaction rate law for r_j is

- **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.

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

$$A \longrightarrow products$$

may be a linear function of concentration,

$$-r_A = kC_A \tag{1-1}$$

or, as shown in Chapter 3, it may be some other algebraic function of concentration, such as

---

[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).

$$-r_A = kC_A^2 \tag{1-2}$$

or

The rate law is an algebraic equation.

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

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

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).

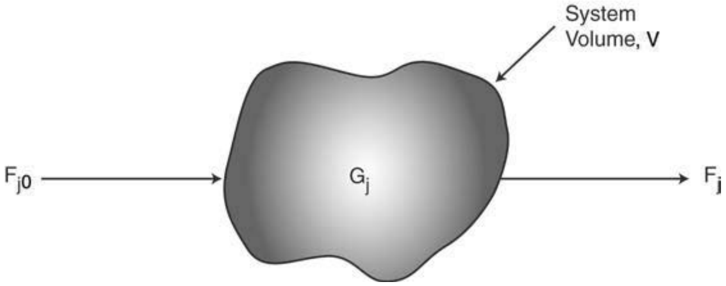


Figure 1-3 Mole balance on species j in a system volume, V.

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

$$\begin{bmatrix}\text{Rate of flow}\\ \text{of } j \text{ into}\\ \text{the system}\\ \text{(moles/time)}\end{bmatrix} - \begin{bmatrix}\text{Rate of flow}\\ \text{of } j \text{ out of}\\ \text{the system}\\ \text{(moles/time)}\end{bmatrix} + \begin{bmatrix}\text{Rate of generation}\\ \text{of } j \text{ by chemical}\\ \text{reaction within}\\ \text{the system}\\ \text{(moles/time)}\end{bmatrix} = \begin{bmatrix}\text{Rate of}\\ \text{accumulation}\\ \text{of } j \text{ within}\\ \text{the system}\\ \text{(moles/time)}\end{bmatrix}$$

Mole balance

$$\textbf{In} - \textbf{Out} + \textbf{Generation} = \textbf{Accumulation}$$

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

where N_j represents the number of moles of species j in the system at time t. 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, is just the product of the reaction volume, V, and the rate of formation of species j, r_j.

$$G_j = r_j \cdot V$$

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

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 r_{j2} at location 2 and an associated volume, ΔV_2, and so on (Figure 1-4).

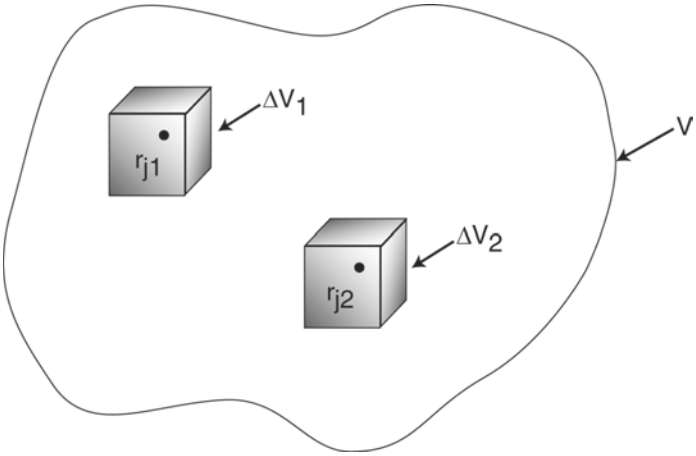


Figure 1-4 Dividing up the system volume, V.

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)

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

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.

This is a basic equation for chemical reaction engineering.

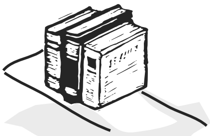
$$\boxed{F_{j0} - F_j + \int^V r_j \, dV = \frac{dN_j}{dt}} \tag{1-4}$$

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) or reactor volume (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 *Professional Reference Shelf* [*PRS*] on the DVD-ROM and Web).


Reference Shelf

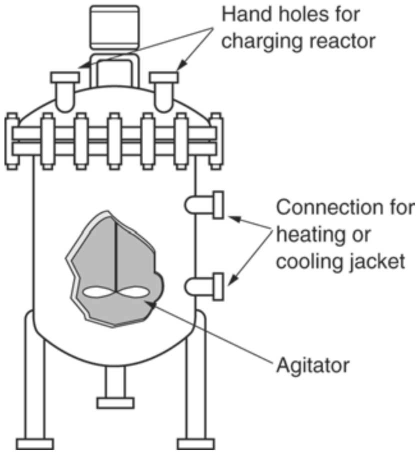


Figure 1-5(a) Simple batch homogeneous reactor. [Excerpted by special permission from *Chem. Eng., 63*(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

Figure 1-5(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 DVD-ROM.

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

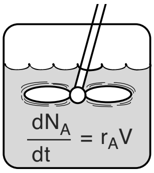
$$\frac{dN_j}{dt} = \int^V r_j \, dV$$

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 mole balance in the form

Perfect mixing

$$\boxed{\frac{dN_j}{dt} = r_j V} \tag{1-5}$$

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



Batch Reactor

$$A \longrightarrow B$$

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.

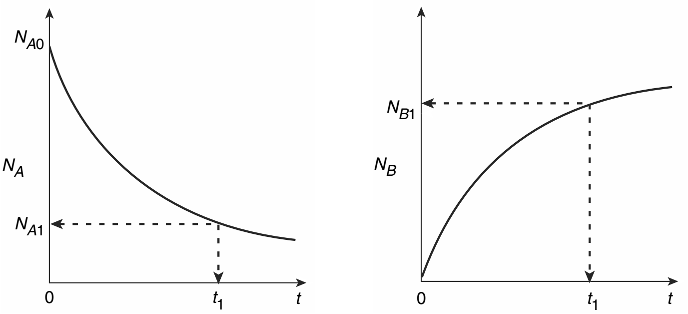


Figure 1-6 Mole-time trajectories.

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,

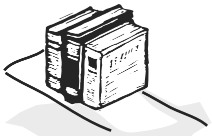
$$dt = \frac{dN_A}{r_A V}$$

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

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

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*) for Chapter 1 and in the *Visual Encyclopedia of Equipment* on the DVD-ROM.

1.4.1 Continuous-Stirred Tank Reactor (CSTR)

What is a CSTR used for?

A type of reactor used commonly 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 used primarily for liquid

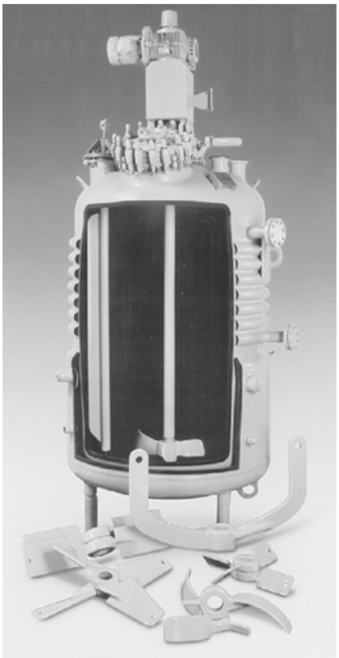


Figure 1-7(a) CSTR/batch reactor. [Courtesy of Pfaudler, Inc.]

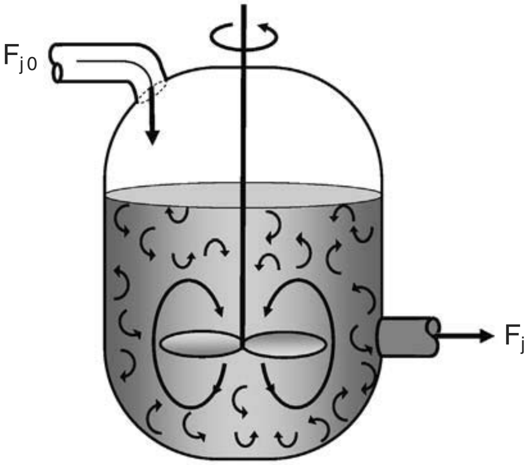


Figure 1-7(b) CSTR mixing patterns. Also see the *Visual Encyclopedia of Equipment* on the DVD-ROM.

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 DVD-ROM Chapters DVD13 and DVD14, on the DVD-ROM included with this text, and in Chapters 13 and 14 in the fourth edition of *The Elements of Chemical Reaction Engineering* (*ECRE*).

When the general mole balance equation

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

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

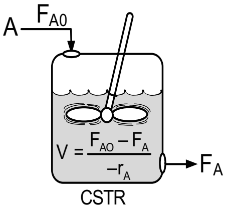
$$\frac{dN_j}{dt} = 0$$

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

The ideal CSTR is assumed to be perfectly mixed.

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

it takes the familiar form known as the *design equation* for a CSTR:



$$\boxed{V = \frac{F_{j0} - F_j}{-r_j}} \tag{1-7}$$

The CSTR design equation gives the reactor volume V necessary to reduce the entering flow rate of species j from F_{j0} to the exit 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:

$$\boxed{\begin{array}{c} F_j = C_j \cdot v \\ \frac{\text{moles}}{\text{time}} = \frac{\text{moles}}{\text{volume}} \cdot \frac{\text{volume}}{\text{time}} \end{array}} \tag{1-8}$$

Similarly, for the entrance molar flow rate we have $F_{j0} = C_{j0} \cdot v_0$. Consequently, we can substitute for F_{j0} and F_j into Equation (1-7) to write a balance on species A as

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

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

1.4.2 Tubular Reactor

When is a tubular reactor most often used?

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.

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, will also vary axially. For the purposes of the material presented here, we consider systems in which the flow

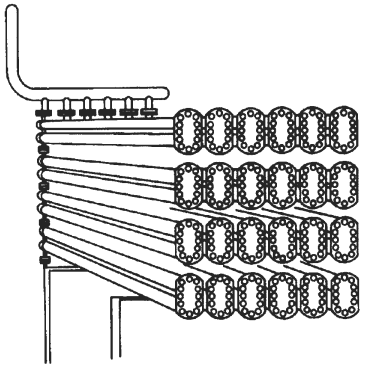


Figure 1-8(a) Tubular reactor schematic. Longitudinal tubular reactor. [Excerpted by special permission from *Chem. Eng., 63*(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

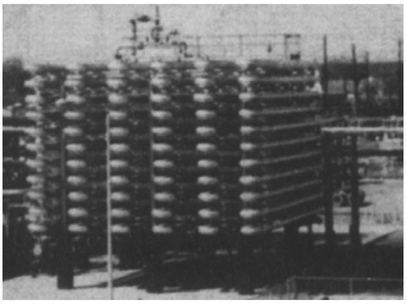


Figure 1-8(b) Tubular reactor photo. Tubular reactor for production of Dimersol G. [Photo Courtesy of Editions Techniq Institut français du pétrole].

field may be modeled by that of a plug flow profile (e.g., uniform 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 is discussed on the DVD-ROM in Chapter DVD13 and in Chapter 13 of the fourth edition of *ECRE*.)

Also see PRS and *Visual Encyclopedia of Equipment*.

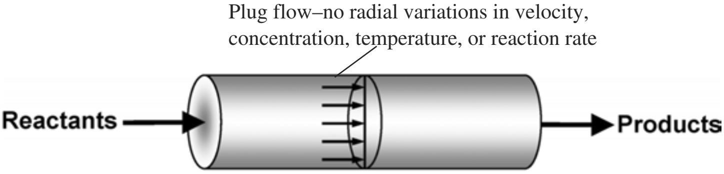


Figure 1-9 Plug-flow tubular reactor.

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

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

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

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

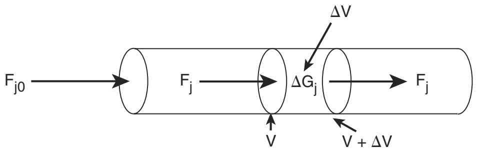


Figure 1-10 Mole balance on species *j* in volume ΔV.

$$\begin{bmatrix}\text{Molar flow}\\ \text{rate of species } j\\ \textit{In} \text{ at V}\\ \textit{moles/time}\end{bmatrix} - \begin{bmatrix}\text{Molar flow}\\ \text{rate of species } j\\ \textit{Out} \text{ at } (V+\Delta V)\\ \textit{moles/time}\end{bmatrix} + \begin{bmatrix}\text{Molar rate of}\\ \textit{Generation}\\ \text{of species } j\\ \text{within } \Delta V\\ \textit{moles/time}\end{bmatrix} = \begin{bmatrix}\text{Molar rate of}\\ \textit{Accumulation}\\ \text{of species } j\\ \text{within } \Delta V\\ \textit{moles/time}\end{bmatrix}$$

In – **Out** + **Generation** = **Accumulation**

$$F_j\big|_{\mathrm{V}} - F_j\big|_{\mathrm{V}+\Delta \mathrm{V}} + r_j\Delta V = 0 \tag{1-10}$$

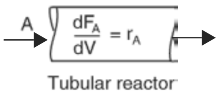
Dividing by ΔV and rearranging

$$\left[\frac{F_j\big|_{\mathrm{V}+\Delta \mathrm{V}} - F_j\big|_{\mathrm{V}}}{\Delta V}\right] = r_j$$

the term in brackets resembles the definition of a derivative

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

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



$$\boxed{\frac{dF_j}{dV} = r_j} \tag{1-11}$$

We could have made the cylindrical reactor on which we carried out our mole balance an irregular shape reactor, such as the one shown in Figure 1-11 for reactant species A.

Picasso's reactor

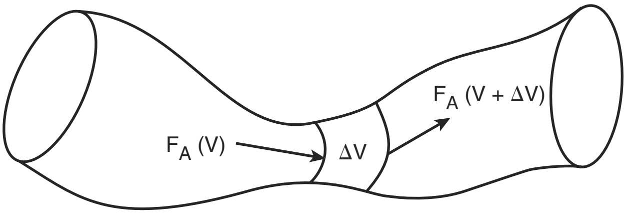


Figure 1-11 Pablo Picasso's reactor.

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

$$\boxed{\frac{dF_A}{dV} = r_A} \tag{1-12}$$

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.

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.

Again consider the isomerization A → 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, while F_B increases as the reactor volume V increases, as shown in Figure 1-12.

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

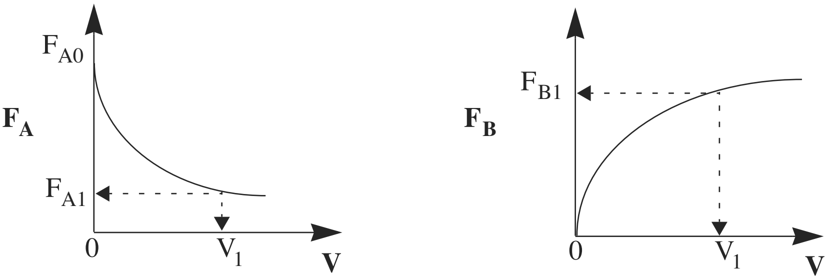


Figure 1-12 Profiles of molar flow rates in a PFR.

We now ask what is the reactor volume V_1 necessary to reduce the entering molar flow rate of A from F_{A0} to 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 $F_A = F_{A1}$.

$$V_1 = \int_{F_{A0}}^{F_{A1}} \frac{dF_A}{r_A} = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r_A} \tag{1-13}$$

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 Chapter 10). 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 is defined as

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

The mass of solid catalyst is used because the amount of catalyst is what is important to the rate of product formation. 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.

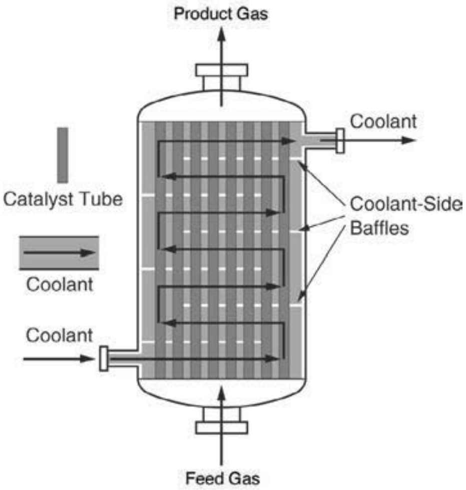


Figure 1-13 Longitudinal catalytic packed-bed reactor. [From Cropley, American Institute of Chemical Engineers, *86*(2), 34 (1990). Reproduced with permission of the American Institute of Chemical Engineers, Copyright © 1990 AIChE. All rights reserved.]

PBR
Mole Balance

In the three idealized types of reactors just discussed (the perfectly mixed batch reactor, 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 in Equation (1-10) with the catalyst mass (i.e., weight) coordinate *W* (Figure 1-14).

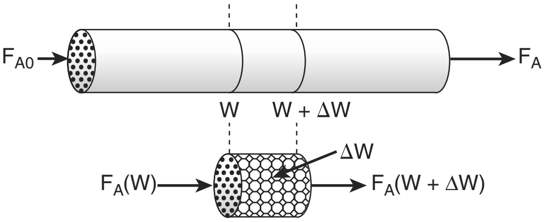


Figure 1-14 Packed-bed reactor schematic.

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

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

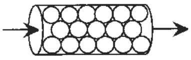
The dimensions of the generation term in Equation (1-14) are

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

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

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

$$\boxed{\frac{dF_A}{dW} = r'_A} \tag{1-15}$$



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

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

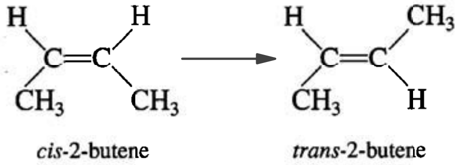
$$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A} = \int_{F_A}^{F_{A0}} \frac{dF_A}{-r'_A} \tag{1-16}$$

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

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 It?

Consider the liquid phase *cis – trans* isomerization of 2–butene



which we will write symbolically as

$$A \longrightarrow B$$

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, i.e., $v = v_0$.

1. Sketch the concentration profile.
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 necessary to reduce the exiting concentration to 10% of the entering concentration when the volumetric flow rate is 10 dm^3/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 as we move. 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 Figure 1-12 plot, the concentration of A as a function of reactor volume, as shown in Figure E1-2.1.

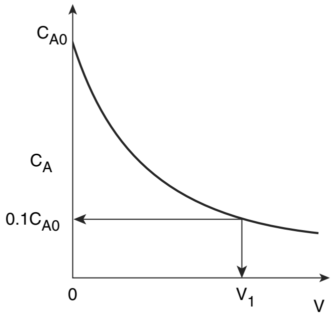


Figure E1-2.1 Concentration profile.

2. Derive an equation relating V, υ_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)

$$\frac{dF_A}{dV} = r_A \tag{1-12}$$

For a first-order reaction, the rate law (discussed in Chapter 3) is

$$-r_A = kC_A \tag{E1-2.1}$$

Reactor sizing

Because the volumetric flow rate, υ, is constant ($\upsilon = \upsilon_0$), as it is for most all liquid-phase reactions,

$$\frac{dF_A}{dV} = \frac{d(C_A\upsilon)}{dV} = \frac{d(C_A\upsilon_0)}{dV} = \upsilon_0\frac{dC_A}{dV} = r_A \tag{E1-2.2}$$

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

$$-\frac{\upsilon_0 dC_A}{dV} = -r_A = kC_A \tag{E1-2.3}$$

Separating the variables and rearranging gives

$$-\frac{\upsilon_0}{k}\left(\frac{dC_A}{C_A}\right) = dV$$

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

$$-\frac{\upsilon_0}{k}\int_{C_{A0}}^{C_A}\frac{dC_A}{C_A} = \int_0^V dV \tag{E1-2.4}$$

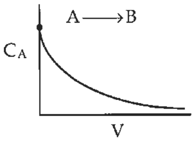
Carrying out the integration of Equation (E1-2.4) gives

$$\boxed{V = \frac{\upsilon_0}{k}\, ln\,\frac{C_{A0}}{C_A}} \tag{E1-2.5}$$

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

$$C_A = C_{A0}\exp\,(-kV/\upsilon_0)$$

Concentration
Profile



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

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

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

Let's calculate the volume to reduce the entering concentration to $C_A = 0.01\ C_{A0}$. Again using equation (E1-2.5)

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

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., $C_A = 0.01\ C_{A0}$).

We see that a reactor volume of 0.1 m^3 is necessary to convert 90% of species A entering into product B for the parameters given.

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 species A consumed and converted to product B, the larger must be the reactor volume *V*. 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).

1.5 Industrial Reactors[2]

When is a batch reactor used?

Be sure to view the actual photographs of industrial reactors on the DVD-ROM and on the Web site. There are also links to view reactors on different Web sites. The DVD-ROM also includes a portion of the *Visual Encyclopedia of Equipment*—"Chemical Reactors" developed by Dr. Susan Montgomery and her students at the University of Michigan. Also see *Professional Reference Shelf* on the DVD-ROM for "Reactors for Liquid Phase and Gas Phase Reactions."


Reference Shelf

In this chapter, and on the DVD-ROM, 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; for further elaboration, refer to the detailed discussion of industrial reactors given by Walas.[3]

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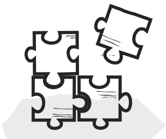
[2] *Chem. Eng., 63*(10), 211 (1956). See also *AIChE Modular Instruction Series E,* 5 (1984).

[3] S. M. Walas, *Reaction Kinetics for Chemical Engineers* (New York: McGraw-Hill, 1959), Chapter 11.



The DVD-ROM describes industrial reactors, along with typical feed and operating conditions. In addition, two solved example problems for Chapter 1 can be found on the DVD-ROM.

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

Mole Balance

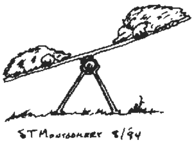
This algorithm and its corresponding building blocks will be developed and discussed in the following chapters:

- Mole Balance, Chapter 1
- Rate Law, Chapter 3
- Stoichiometry, Chapter 4
- Combine, Chapter 5
- Evaluate, Chapter 5
- Energy Balance, Chapters 11 through 13

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

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

$$F_{j0} - F_j + \int^V r_j \, dV = \frac{dN_j}{dt} \tag{S1-1}$$

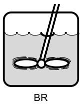
If, and only if, the contents of the reactor are well mixed, then the mole balance (Equation S1-1) on species A gives

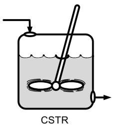
$$F_{A0} - F_A + r_A V = \frac{dN_A}{dt} \tag{S1-2}$$

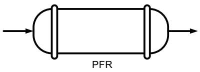
2. The kinetic rate law for r_j is:
   - The rate of formation of species j per unit volume (e.g., mol/s·dm^3)
   - Solely a function of the properties of reacting materials and reaction conditions (e.g., concentration [activities], temperature, pressure, catalyst, or solvent [if any]) and does not depend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

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 as follows.







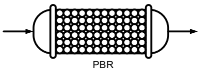
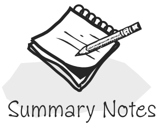


TABLE S.1. SUMMARY OF REACTOR MOLE BALANCES

Reactor	*Comment*	*Mole Balance Differential Form*	*Algebraic Form*	*Integral Form*
BR	No spatial variations	$\frac{dN_A}{dt} = r_A V$		$t_1 = \int_{N_{A1}}^{N_{A0}} \frac{dN_A}{-r_A V}$
CSTR	No spatial variations, steady state	—	$V = \frac{F_{A0} - F_A}{-r_A}$	—
PFR	Steady state	$\frac{dF_A}{dV} = r_A$		$V_1 = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r_A}$
PBR	Steady state	$\frac{dF_A}{dW} = r_A'$		$W_1 = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r_A'}$

DVD-ROM MATERIAL



- **Learning Resources**
  1. *Summary Notes*
  2. *Web Material*
     A. Problem-Solving Algorithm
     B. Getting Unstuck on a Problem
     This site on the Web and DVD-ROM gives tips on how to overcome mental barriers in problem solving.
     C. Smog in L.A. Web module includes a *Living Example Problem.*

B. Getting Unstuck

C. Smog in L.A.

Fotografiert von ©2002 Hank Good.

3. *Interactive Computer Games*
   A. Quiz Show I

Interactive
Computer Games

Mole Balance	Reactions	Rate Laws	Reactor Types
100		100	100
200	200	200	200
300	300	300	300
400	400	400	400
500	500	500	500

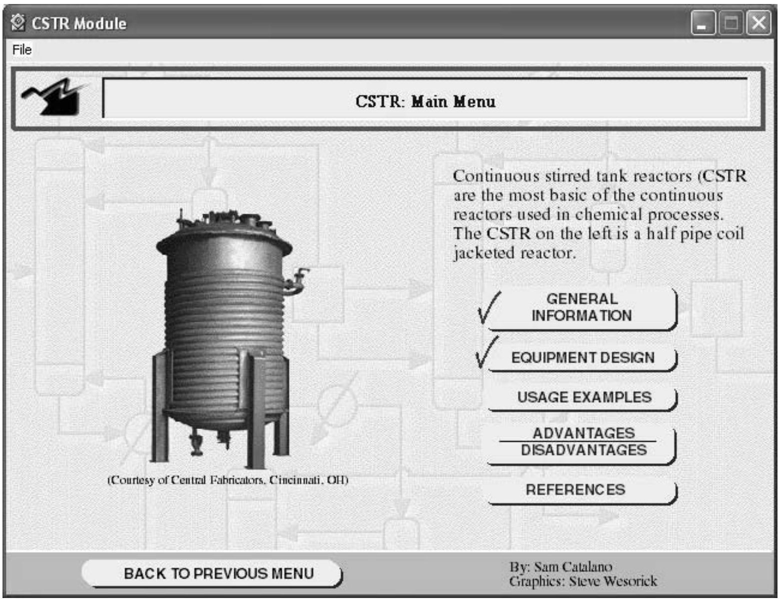
4. *Solved Problems*
   CDP1-A_B Batch Reactor Calculations: A Hint of Things to Come

- **FAQ [Frequently Asked Questions]**—In Updates/FAQ icon section
- **Professional Reference Shelf**
  R1.1 *Photos of Real Reactors*

Living Example Problem
Smog in L.A.

Reference Shelf

R1.2 *Reactor Section of the Visual Encyclopedia of Equipment*
This section of the DVD-ROM shows industrial equipment and discusses its operation. The reactor portion of this encyclopedia is included on the DVD-ROM accompanying this book.



Continuous stirred tank reactors (CSTR are the most basic of the continuous reactors used in chemical processes. The CSTR on the left is a half pipe coil jacketed reactor.

(Courtesy of Central Fabricators, Cincinnati, OH)

By: Sam Catalano
Graphics: Steve Wesorick

R1.3 *Industrial Reactors*
A. Liquid Phase
- Reactor sizes and costs
- Battery of stirred tanks
- Semibatch

B. Gas Phase
- Costs
- Fluidized bed schematic

R1.4 *Top Ten List of Chemical Products and Chemical Companies*

Homework Problems

QUESTIONS 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: A, least difficult; D, most difficult.

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

A = ● B = ■ C = ◆ D = ◆◆

In each of the questions and problems below, 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) to enhance the quality of your sentences.

P1-1$_A$ **(a)** Read through the Preface. Write a paragraph describing both the content goals and the intellectual goals of the course and text. Also describe what's on the DVD-ROM and how the DVD-ROM can be used with the text and course.

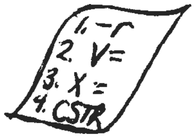
(b) List the areas in Figure 1-2 you are most looking forward to studying.

(c) Take a quick look at the Web Modules and list the ones that you feel are the most novel applications of CRE.

P1-2$_A$ **Revisit Example 1-1.**

(a) Rework this example using Equation 3-1 on page 75.

(b) What does a negative number for the rate of formation of species (e.g., Species A) signify? What does a positive number signify? Explain.



(c) **Revisit Example 1-2.** Calculate the volume of a CSTR for the conditions used to figure the plug-flow reactor volume in Example 1-2. Which volume is larger, the PFR or the CSTR? Explain why. Suggest two ways to work this problem incorrectly.

(d) **Revisit Example 1-2.** Calculate the time to reduce the number of moles of A to 1% of its initial value in a constant-volume batch reactor for the same reaction and data in Example 1-2. Suggest two ways to work this problem incorrectly.

P1-3$_A$ Visit the Web site on Critical and Creative Thinking, *www.engin.umich.edu/~cre/probsolv/strategy/crit-n-creat.htm.*

(a) Write a paragraph describing what "critical thinking" is and how you can develop your critical thinking skills.

(b) Write a paragraph describing what "creative thinking" is and then list four things you will do during the next month that will increase your creative thinking skills.

= Hint on the Web

P1-4$_A$ Surf the DVD-ROM and the Web (*www.engin.umich.edu/~cre*). Go on a scavenger hunt using the summary notes for Chapter 1 on the DVD-ROM.

(a) Review the objectives for Chapter 1 in the Summary Notes on the DVD-ROM. Write a paragraph in which you describe how well you feel you met these objectives. Discuss any difficulties you encountered and three ways (e.g., meet with professor, classmates) you plan to address removing these difficulties.

(b) Look at the Chemical Reactor section of the *Visual Encyclopedia of Equipment* on the DVD-ROM. Write a paragraph describing what you learned.

(c) View the photos and schematics on the DVD-ROM under *Essentials of Chemical Reaction Engineering*—Chapter 1. Look at the QuickTime videos. Write a paragraph describing two or more of the reactors. What similarities and differences do you observe between the reactors on the Web (e.g., *www.loebequipment.com*), on the DVD-ROM, and in the text? How do the used reactor prices compare with those in Table 1-1?

ICG Quiz Show

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

P1-5$_A$ **(a)** Load the Interactive Computer Games (ICG) from the DVD-ROM or Web. Play this game and then record your performance number, which indicates your mastery of the material.

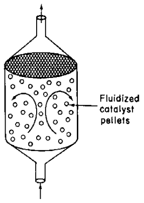
ICG Kinetics Challenge 1 Performance # ______________________________

(b) View the YouTube video (*www.youtube.com*) made by the chemical reaction engineering students at the University of Alabama, entitled *Fogler Zone (you've got a friend in Fogler)*. Type in "chemicalreactor" to narrow your search. You can also access it directly from a link in Chapter 1 *Summary Notes* on the Web site at *www.umich.edu/~essen*.

P1-6$_A$ Make a list of the five most important things you learned from this chapter.

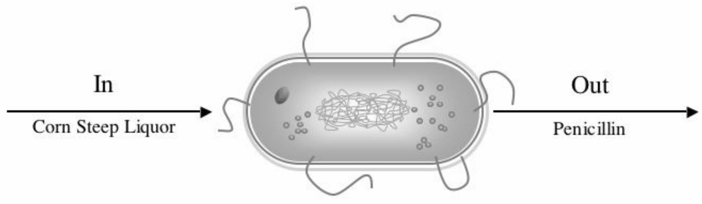
P1-7$_A$ What assumptions were made in the derivation of the design equation for:

(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 $-r'_A$. Is the reaction rate $-r_A$ an extensive quantity? Explain.



P1-8$_A$ Use the mole balance to derive an equation analogous to Equation (1-7) for a fluidized CSTR containing catalyst particles in terms of the catalyst weight, *W*, and other appropriate terms. [*Hint:* See margin figure.]

P1-9$_B$ We are going to consider the cell as a reactor. The nutrient corn steep liquor enters the cell of the microorganism *Penicillium chrysogenum* and is decomposed to form such products as amino acids, RNA, and DNA. Write an unsteady mass balance on (a) the corn steep liquor, (b) RNA, and (c) penicillin. Assume the cell is well mixed and that RNA remains inside the cell.



Penicillium chrysogenum

Hall of Fame

Web Hint

P1-10$_B$ Schematic diagrams of the Los Angeles basin are shown in Figure P1-12$_B$. The basin floor covers approximately 700 square miles ($2\times10^{10}\,ft^2$) and is almost completely surrounded by mountain ranges. If one assumes an inversion height in the basin of 2000 ft, the corresponding volume of air in the basin is $4\times10^{13}\,ft^3$. 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.

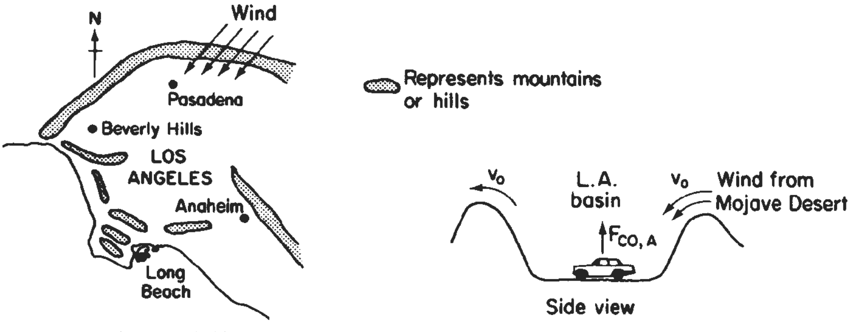


Figure P1-12$_B$ Schematic diagrams of the Los Angeles basin.

Living Example Problem

We shall perform an unsteady-state mole balance 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.

P1-11$_B$ The reaction

$$A \longrightarrow B$$

is to be carried out isothermally in a continuous-flow reactor. The entering volumetric flow rate v_0 is 10 dm^3/h. (*Note*: $F_A = C_A v$. For a constant volumetric flow rate $v = v_0$, then $F_A = C_A v_0$. Also, $C_{A0} = F_{A0}/v_0$ = ([5 mol/h]/[10 dm^3/h]) 0.5 mol/dm^3 .)

Calculate both the CSTR and PFR reactor 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:

(a) $-r_A = k$ with $k = 0.05 \dfrac{\text{mol}}{\text{h} \cdot \text{dm}^3}$ [*Ans.*: $V_{\text{CSTR}} = 99 \text{ dm}^3$]

(b) $-r_A = kC_A$ with $k = 0.0001 \text{ s}^{-1}$

(c) $-r_A = kC_A^2$ with $k = 300 \dfrac{\text{dm}^3}{\text{mol} \cdot \text{h}}$ [*Ans.*: $V_{\text{CSTR}} = 660 \text{ dm}^3$]

(d) 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 $C_{A0} = 0.5$ mol/dm^3.

P1-12$_B$ This problem focuses on using Polymath, an ordinary differential equation (ODE) solver, and also a non-linear 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 E** and on the DVD-ROM.

(a) There are initially 500 rabbits (x) and 200 foxes (y) on Farmer Oat's property. 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:

$$\frac{dx}{dt} = k_1 x - k_2 x \cdot y$$

$$\frac{dy}{dt} = k_3 x \cdot y - k_4 y$$

Constant for growth of rabbits $k_1 = 0.02 \ day^{-1}$
Constant for death of rabbits k_2 = 0.00004/(day × no. of foxes)
Constant for growth of foxes after eating rabbits k_3 = 0.0004/(day × no. of rabbits)
Constant for death of foxes $k_4 = 0.04 \ day^{-1}$

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

Vary the parameters k_1, k_2, k_3, and k_4. Discuss which parameters can or cannot be larger than others. Write a paragraph describing what you find.

Polymath Tutorial on DVD-ROM

(b) Use Polymath or MATLAB to solve the following set of nonlinear algebraic equations:

$$x^3y - 4y^2 + 3x = 1$$

$$6y^2 - 9xy = 5$$

with initial guesses of $x = 2$, $y = 2$. Try to become familiar with the edit keys in Polymath and MATLAB. See the DVD-ROM for instructions.

Summary Notes

Screen shots on how to run Polymath are shown at the end of the Summary Notes for Chapter 1 on the DVD-ROM and on the Web

P1-13$_A$ **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 making 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

Web Hint

Enrico Fermi Problem

(a) **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. Etc. __________

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

(b) **EFP #2.** How many square meters of pizza were eaten by an undergraduate student body population of 20,000 during the Fall term 2010?

(c) **EFP #3.** How many bath tubs of water will the average person drink in a lifetime?

(d) **EFP #4.** Novel and Musical 24,601 = Jean _?_ _?_

P1-14$_A$ **What is wrong with this solution?** The irreversible liquid phase second order reaction $(-r_A = kC_A^2)$

$$2A \xrightarrow{k_1} B \qquad k_1 = 0.03\ \text{dm}^3/\text{mol}\cdot\text{s}$$

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_o, is constant at 3 dm³/s. What is the corresponding reactor volume?

<u>*Solution*</u>

1. Mole Balance

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

2. Rate Law (2nd order)

$$-r_A = kC_A^2$$

3. Combine

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

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

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

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

Solved Problems

NOTE TO INSTRUCTORS: Additional problems (cf. those from the preceding editions) can be found in the solutions manual and on its DVD-ROM. 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/~essen* but also

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

   MURPHY, REGINA M., *Introduction to Chemical Processes: Principles, Analysis, Synthesis,* New York, NY: McGraw-Hill Higher Education, 2007.

   HIMMELBLAU, D. M., and J. D. Riggs, *Basic Principles and Calculations in Chemical Engineering*, 7th ed. Upper Saddle River, N.J.: Prentice Hall, 2004, Chapters 2 and 6.

   SANDERS, R. J., *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.

   CRYNES, B. L., 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

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

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