ELEMENTS OF CHEMICAL REACTION ENGINEERING

SEVENTH EDITION

H. SCOTT FOGLER
BRYAN R. GOLDSMITH | ERANDA NIKOLLA
NIRALA SINGH

INTERNATIONAL SERIES IN THE
PHYSICAL AND CHEMICAL ENGINEERING SCIENCES

Elements of Chemical Reaction Engineering

Seventh Edition

H. SCOTT FOGLER
Ame and Catherine Vennema Professor of Chemical Engineering
and the Arthur F. Thurnau Professor

Bryan R. Goldsmith
Associate Professor of Chemical Engineering

Eranda Nikolla
Professor of Chemical Engineering

Nirala Singh
Associate Professor of Chemical Engineering

The University of Michigan, Ann Arbor

Pearson

Hoboken, New Jersey

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Dedicated to

Janet Meadors Fogler

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

—H.S.F.

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Introduction

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

A. Who Is the Intended Audience?

This book was written with today's students in mind. It provides instantaneous access to information; does not waste time on extraneous details; cuts right to the point; uses more bullets to make information easier to access; and includes new, novel problems on chemical reaction engineering (e.g., solar energy and electrochemical reactor engineering). The interaction between the text and Web site (*http://www.umich.edu/~elements/7e/*) breaks new ground and provides one of the most comprehensive active learning resources available. With the advent of sliders in both Wolfram and Python, students can explore the reactions and the reactor in which they occur, by carrying out simulation experiments and then writing a set of conclusions to describe what they found.

This book and interactive Web site are intended for use as both an undergraduate-level and a graduate-level text in chemical reaction engineering. The undergraduate course/courses usually focus on Chapters 1–13; the graduate course material includes topics such as diffusion limitations, effectiveness factors (discussed in Chapters 14 and 15), nonideal reactors, residence time distribution, and electrochemical reactors (discussed in Chapters 16–19) along with the additional material and Professional Reference Shelf (PRS) on the Web site.

This edition continues our emphasis on chemical reactor safety by ending each chapter, including the new Chapter 19, with a safety lesson called *And Now…* A Word From Our Sponsor-Safety (AWFOS–S). These lessons can also be found on the Web site at *http://umich.edu/~safeche/*.

B. What Are the Goals of This Book?

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

Chemical reaction engineering (CRE) is a great subject that is fun to learn and is the heart of chemical engineering. We have tried to provide a little Michigan humor as we go. Take a look at the humorous YouTube videos (e.g., "Black Widow" or "Chemical Engineering Gone Wrong") that illustrate certain principles in the text. These videos were made by chemical engineering students at the universities of Alabama and Michigan. In addition, Prof. Fogler found that students enjoy the Interactive Computer Games (ICGs) that, along with the videos, are linked from the CRE homepage (*http://www.umich.edu/~elements/7e/index.html*).

B.2 To Develop a Fundamental Understanding of Reaction Engineering

The second goal of this book is to help the reader clearly understand the fundamentals of CRE. This goal is achieved by presenting a structure that allows the reader to solve reaction engineering problems through reasoning rather than through memorization and recall of numerous equations and the restrictions and conditions under which each equation applies.

B.3 To Enhance Thinking Skills

A third goal of this text is to enhance critical thinking skills and creative thinking skills. For example, see Thoughts on Problem Solving (*http://www.umich.edu/~elements/7e/probsolv/index.htm*).

C. What Is the Structure of CRE?

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

The strategy behind the presentation of material is to build continually on a few basic ideas in CRE to solve a wide variety of problems. The building blocks of CRE and the primary algorithm allow us to solve isothermal CRE problems through logic rather than memorization. We start with the Mole Balance Building Block (Chapter 1) and then place the other blocks one at a time on top of the others until we reach the Evaluate Block (Chapter 5), by which time we can solve a multitude of isothermal CRE problems. As we study each block, we need to make sure we understand everything in that block and be sure not to cut corners by leaving anything out so we don't wind up with a stack of cylindrical blocks. An animation of what happens to such a stack is shown at the end of Lecture 1 notes (*http://www.umich.edu/%7Eelements/7e/lectures/umich.html*).

For nonisothermal reactions, we replace the "Combine" building block in Figure I-1 with the "Energy Balance" building block because nonisothermal reactions almost always require a computer-generated solution. Consequently,

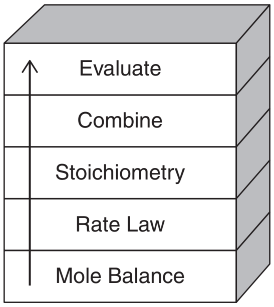


Figure I-1 Building blocks.

we don't need the "Combine" block because the computer combines everything for us. From these pillars and building blocks, we construct our CRE algorithm:

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

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

Margin Notes

The selection and order of topics and chapters are shown in Figure P-3 on the Web site (*http://www.umich.edu/~elements/7e/toc/Preface-Complete.pdf*). There are notes in the margins, which are meant to serve two purposes. First, they act as guides or commentary as one reads through the material. Second, they identify key equations and relationships that are used to solve CRE problems.

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

The interactive companion Web site material has been updated and is a novel, and integral part of this book. The main purposes of the Web site are to serve as an interactive part of the text with enrichment resources. The home page for the CRE Web site (*http://www.umich.edu/~elements/7e/index.html*) is shown in Figure I-2. For discussion of how to use the Web site and text interactively, see Appendix I.

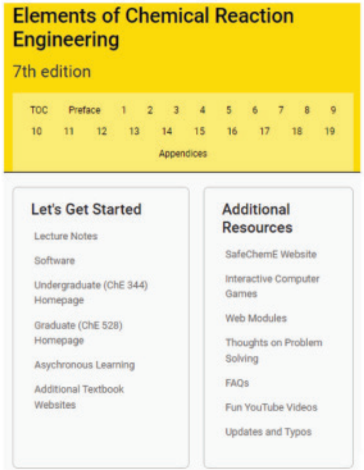


Figure I-2 Screen shot of the book's companion Web site (*http://www.umich.edu/~elements/7e/index.html*).

The objectives of the Web site are fourfold:

(1) To facilitate the interactive learning of CRE by using the companion Web site and Wolfram and Python sliders to explore Living Example Problems to gain a deep understanding of the reaction and the reactors in which they take place.

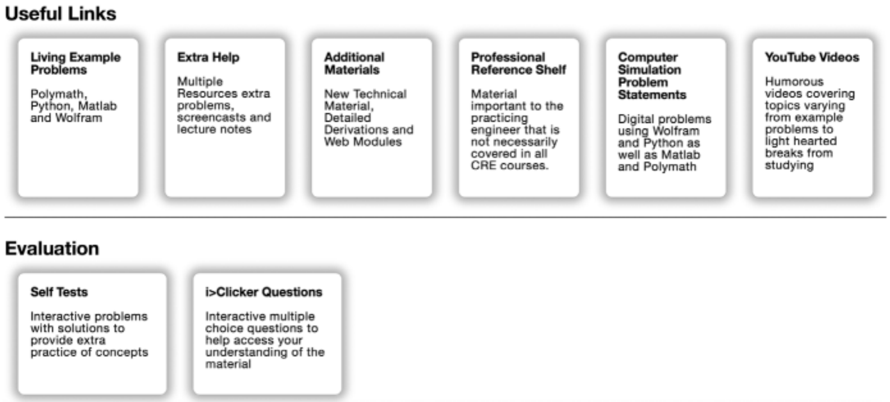
(2) To provide additional technical material in the extended material and in the Professional Reference Shelf.

(3) To provide tutorial information and self-assessment exercises such as the i>clicker questions.

(4) To make the learning of CRE fun through the use of interactive games, LEP simulations, and computer experiments, which allow one to use Inquiry-Based Learning (IBL) to explore the concepts of CRE.

D.1 How to Use the Web Site

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



Useful Links

Living Example Problems
Polymath, Python, Matlab and Wolfram

Extra Help
Multiple Resources extra problems, screencasts and lecture notes

Additional Materials
New Technical Material, Detailed Derivations and Web Modules

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

Computer Simulation Problem Statements
Digital problems using Wolfram and Python as well as Matlab and Polymath

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

Evaluation

Self Tests
Interactive problems with solutions to provide extra practice of concepts

i>Clicker Questions
Interactive multiple choice questions to help access your understanding of the material

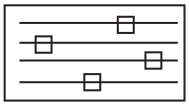
Figure I-3 Access to useful links
(*http://www.umich.edu/~elements/7e/01chap/obj.html#/*).

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

Figure I-4 Useful links.

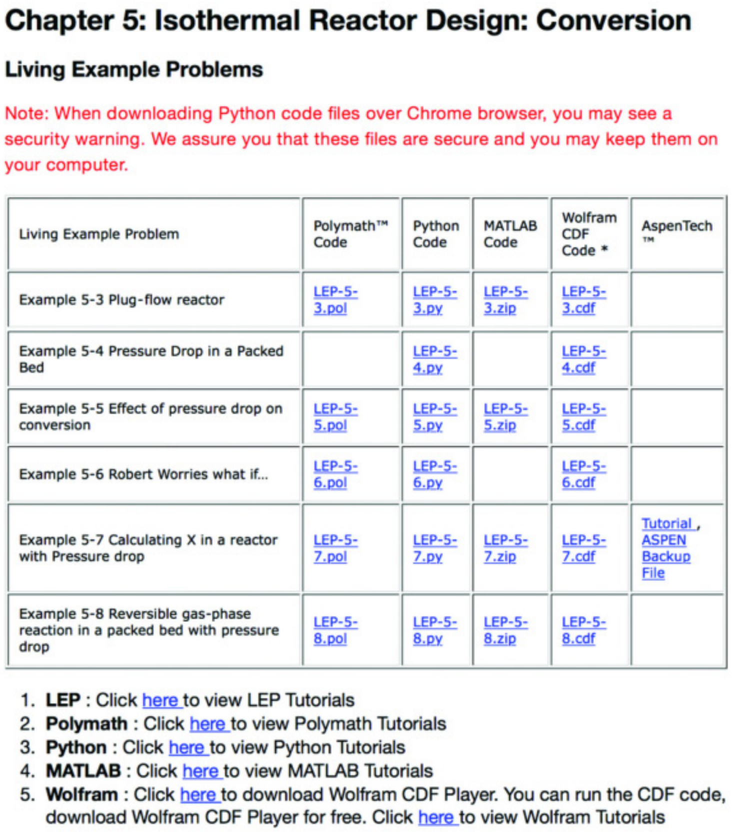
The *Living Example Problems* (LEPs), *including COMSOL*, have all numerical Example Problems programmed and ready for use with the click of a button. The *Extra Help* includes interactive notes, screen casts, and techniques that facilitate learning and studying. The *Additional Material* and *Professional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

D.2 Living Example Problems (LEPs)



What are LEPs? LEPs are **L**iving **E**xample **P**roblems that are really simulations that can be used to carry out experiments on the reactor and the reactions occurring inside the reactor. Here, rather than being stuck with the parameter values the authors give, the LEPs allow you to change the value of a parameter and see its effect on the reactor's operation. LEPs have been unique to this book since their invention and inclusion in the Third Edition of this title, published in 1999. However, Wolfram and Python have allowed us to take LEPs to a new level, resulting in a minor paradigm shift. The LEPs use simulation software, which can be downloaded directly onto one's own computer in order to "play with" the key variables and assumptions. Using the LEPs to explore the problem and asking "What if…?" questions provide students with the opportunity to practice critical and creative thinking skills. In this edition, there are more than 80 interactive simulations (LEPs) provided on the Web site. It is the authors' strong belief that using the LEP sliders will develop an intuitive feel for Chemical Reaction Engineering (CRE).

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



Chapter 5: Isothermal Reactor Design: Conversion

Living Example Problems

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

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

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

Figure I-5 Living Example Problems (LEPs).

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

It has been shown that students using **inquiry-based learning (IBL)** have a much greater understanding of information than students educated by traditional methods.[1,2] The learning was enhanced when it came to questions that required interpretation such as, “Why did the temperature profile go through a minimum?” Each chapter has a section on Computer Simulations and Experiments that will guide students in practicing **IBL**. Students have commented that the Wolfram slider LEPs are an efficient way to study the operation of a chemical reactor. For example, one can carry out a simulation experiment on the reactor (e.g., LEP 13-2) to investigate what conditions would lead to unsafe operation.

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[1] Adbi, A. “The Effect of Inquiry-based Learning Method on Students’ Academic Achievement in Science Course,” *Universal J. Educ. Res.*, 2(1), 37–41 (2014).

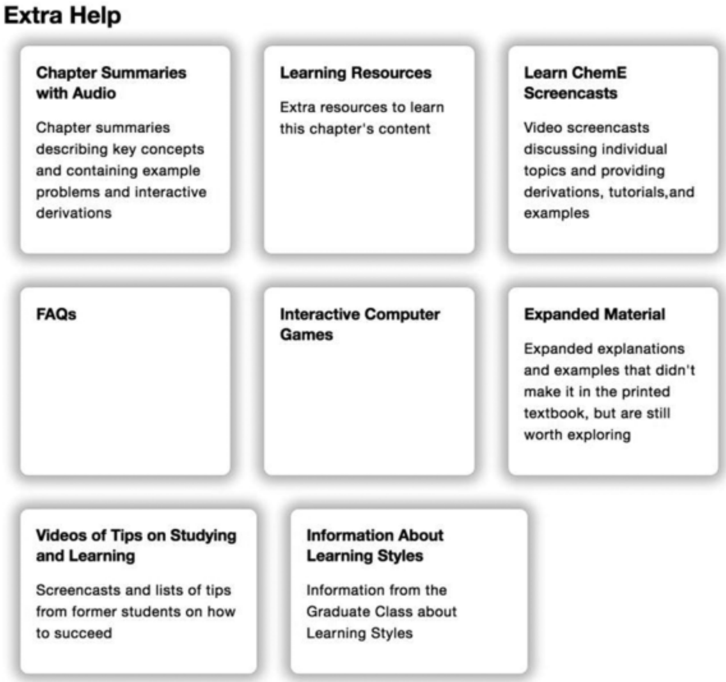
[2] Documentation of the advantages of IBL can be found at *Studies in Higher Education*, 38(9), 1239–1258 (2013), *https://www.tandfonline.com/doi/abs/10.1080/03075079.2011.616584*.

Note the tutorials listed just below the screen shot of the Living Example Problems in Figure I-5. There are 11 Polymath tutorials, and one LEP tutorial for each Polymath, Wolfram, Python, and MATLAB in later chapters. There are also six COMSOL tutorials. To access the LEP software you want to use—that is, Polymath, Wolfram, Python, or MATLAB—just click on the appropriate hot button, and then load and run the LEPs in the software you have chosen. Homework problems using the LEPs have been added to each chapter that requires the use of Wolfram, Python, and Polymath. The use of the LEP sliders will allow students to vary the reaction and reactor parameters to get a thorough understanding of the Computer Simulation Problems.

D.3 Extra Help

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

The *Learning Resources* give an overview of the material in each chapter through the Interactive *Summary Notes*. These notes include on-demand derivations of key equations, audio explanations, additional resources such as *Interactive Computer Games (ICGs)*, computer simulations and experiments, Web modules of novel applications of CRE, solved problems, study aids, *Frequently Asked Questions (FAQs)*, Microsoft PowerPoint lecture slides, and links to *LearnChemE videos*. The Web modules consist of a number of examples that apply key CRE concepts to both standard and nonstandard reaction engineering problems (e.g., glow sticks, the use of wetlands to degrade toxic chemicals, and pharmacokinetics of death from a cobra bite). The Web modules can be loaded directly from the CRE Web site (*http://www.umich.edu/~elements/7e/web_mod/index.html*). These resources are described in Appendix I.



Extra Help

Chapter Summaries with Audio
Chapter summaries describing key concepts and containing example problems and interactive derivations

Learning Resources
Extra resources to learn this chapter's content

Learn ChemE Screencasts
Video screencasts discussing individual topics and providing derivations, tutorials,and examples

FAQs

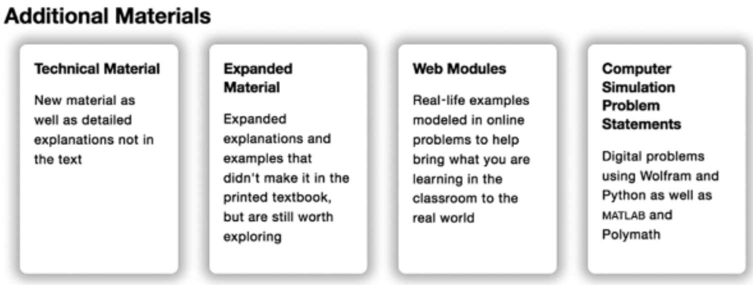
Interactive Computer Games

Expanded Material
Expanded explanations and examples that didn't make it in the printed textbook, but are still worth exploring

Videos of Tips on Studying and Learning
Screencasts and lists of tips from former students on how to succeed

Information About Learning Styles
Information from the Graduate Class about Learning Styles

Figure I-6 Screen shot of Extra Help.



Additional Materials

Technical Material

New material as well as detailed explanations not in the text

Expanded Material

Expanded explanations and examples that didn't make it in the printed textbook, but are still worth exploring

Web Modules

Real-life examples modeled in online problems to help bring what you are learning in the classroom to the real world

Computer Simulation Problem Statements

Digital problems using Wolfram and Python as well as MATLAB and Polymath

Figure I-7 Screen shot of Additional Materials.

D.4 Additional Material

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

D.5 Professional Reference Shelf

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

D.6 Computer Simulations, Experiments, and Problems

As discussed in section D.2, these problems help guide students to understand how the parameters and operating conditions affect the reaction and the reactors. These problems are in the printed version of the second edition of *Essentials of Chemical Reaction Engineering* and the seventh edition of *Elements of Chemical Reaction Engineering*.

D.7 YouTube Videos

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

D.8 COMSOL

The COMSOL Multiphysics software is a partial differential equation solver that is used with Chapters 13 and 18 to view both axial and radial temperature and concentration profiles. For users of this text, COMSOL has provided a special Web site that includes a step-by-step tutorial, along with examples. See Figure 18-15 on page 974 and also *https://www.comsol.com/books/elements-of-chemical-reaction-engineering-5th/models*. Further details are given in the Living Example Problems on the Web site.

E. Why Do We Assign Homework Problems?

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

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

It is recommended that students first work through *Computer Simulation Problems* that use MATLAB, Python, and Wolfram before going on to other problems. These example problems are a key resource. The subscript letter (A, B, C, or D) after each problem number denotes the difficulty of the problem (i.e., A = easy; D = difficult). The A- and B-level problems should be worked before tackling the more challenging homework problems in a given chapter.

F. Are There Other Web Site Resources?

CRE Web Site (***http://www.umich.edu/~elements/7e/index.html***). A complete description of all the educational resources and ways to use them can be found in Appendix I.

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

What Entertainment Is on the Web Site?

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

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

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

As you play these interactive games, you will be asked a number of questions related to the corresponding material in the textbook. The ICG keeps track of all the correct answers and at the end of the game displays a coded performance number that reflects how well you mastered the material in the text. Instructors have a manual to decode the performance number.

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

A third goal of this book is to enhance critical and creative thinking skills. How does one enhance their critical thinking skills? Answer: By learning how to ask critical thinking questions and taking critical thinking actions of the type given on the Web site.

The goal to enhance creative thinking skills is achieved by using a number of problems that are open-ended to various degrees. With these, students can practice their *creative skills* by exploring the example problems, as outlined at the beginning of the homework problems of each chapter and by making up and solving an original problem.

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

(1) Ethylbenzene → Styrene + Hydrogen: Endothermic

(2) Ethylbenzene → Benzene + Ethylene: Endothermic

(3) Ethylbenzene + Hydrogen → Toluene + Methane: Exothermic

The student could get further practice in critical and creative thinking skills by adding any of the following exercises to any of the end-of-chapter homework problems:

(x) How could you make this problem easier? More difficult?

(y) Critique your answer by writing a critical thinking question.

(z) Describe two ways you could work this problem incorrectly.

H. What's New in This Edition?

This edition retains all the strengths of the previous editions of *Elements of Chemical Reaction Engineering* by using algorithms that allow students to learn chemical reaction engineering through logic rather than memorization. Major changes include an expanded molecular modeling section in Chapter 3, notable revisions to the catalysis section in Chapter 10, and an entirely new Chapter 19 on electrochemical reactor design. Chapter 19 introduces electrochemistry concepts and applies the principles of chemical reaction engineering from earlier chapters to electrochemical reactors with numerous examples and problems for students to practice. The Web site was completely revamped to improve accessibility and usability, while keeping its relationship with the textbook (e.g., using Wolfram, Python, MATLAB, and Polymath to explore reactors and reactions).

I. Tribute to H. Scott Fogler

We dedicate the seventh edition of *Elements of Chemical Reaction Engineering* to the late H. Scott Fogler. He was deeply passionate about this book, having authored the first six editions over the course of more than 30 years. Scott had an enormous impact on the chemical engineering discipline. Scott joined the Chemical Engineering faculty as an assistant professor at the University of Michigan (UofM) in 1965 and stayed until his passing in 2021. Within two decades of joining UofM, Scott was already so accomplished that he received an endowed chair. Scott made tremendous research advancements and leadership contributions over his career, but it was clear his true passion was teaching. He wanted to teach students the tools and creative skills they would use throughout their careers to make a difference in the world. We are honored to continue in his footsteps and his rich legacy to bring you the next edition of this book.

J. How Do We Say Thank You?

H. Scott Fogler

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

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

Michael B. Cutlip, coauthor of Polymath, not only gave suggestions and a critical reading of the first edition, but also, most importantly, provided continuous support and encouragement throughout the course of this project. Professor Chau-Chyun Chen provided two AspenTech examples. Ed Fontes at COMSOL Multiphysics not only provided encouragement, but also provided a COMSOL Web site containing a tutorial with CRE examples. Julie Nahil, senior content producer at Pearson for all of my book projects, has been fantastic throughout. She provided encouragement, attention to detail, and a great sense of humor, which were greatly appreciated. Indian Institute of Technology (IIT)—Guwahati chemical engineering graduate Mayur Tikmani was amazing in helping to get this text to the compositor in time. He provided all of the Wolfram coding for the LEP examples; when necessary, checked and corrected all the Polymath, Wolfram, Python, and MATLAB tutorials on the CRE Web site; and also helped proofread all the chapters. A number of summer interns have helped with preparation of the additional material for the book, especially the Safety Web site, as well as related material. Kaushik Nagaraj developed and provided the MATLAB coding for the simulations in Section 3.4 while Jakub Wlodarczyk (Warsaw University of Technology, Poland) checked all of the i>clicker questions and solutions. Students from Indian Institute of Technology, Bombay, who contributed to AWFOS-S at the end of each chapter include Kaushik Nagaraj, Triesha Singh, Reshma Kalyan Sundaram, Kshitiz Parihar, Manan Agarwal, Kushal Mittal, and Sahil Kulkarni. Vaibav Jain from IIT Delhi worked on the Solutions Manual. From the University of Michigan, Kara Steshetz, Alec Driesenga, Maeve Gillis, and Lydia Peters also worked on the Safety material.

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"Should I mention Jofostan here?" Jan also helped me learn that creativity involves knowing what to leave out. Without her enormous help and support the project would never have been possible.

May 2020

Bryan R. Goldsmith

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Eranda Nikolla

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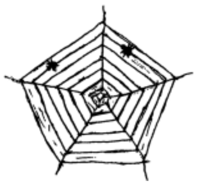
Nirala Singh

I would like to say thank you to my family, especially my parents, and my teachers for showing me the value of education.



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

www.umich.edu/~elements/7e/index.html

About the Authors

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

Professor Fogler's research interests included flow and reaction in porous media, wax and asphaltene deposition, asphaltene flocculation kinetics, gelation kinetics, colloidal phenomena, and catalyzed dissolution. He was research advisor to 49 PhD students and had more than 250 refereed publications in these areas. Fogler chaired ASEE's Chemical Engineering Division, served as director of the AIChE, and earned the Warren K. Lewis Award from AIChE for contributions to chemical engineering education. He also received the Chemical Manufacturers Association's National Catalyst Award, and the 2010 Malcom E. Pruitt Award from the Council for Chemical Research (CCR), and the 2019 Van Antwerpen Award from AIChE. He was the recipient of 12 named lectureships and was associate editor of *Energy & Fuels*. On April 15, 2016, Scott received a *doctor honoris causa* degree from the Universitat Rovira i Virgili, Tarragona, Spain.

Bryan R. Goldsmith is an Associate Professor of Chemical Engineering at the University of Michigan, Ann Arbor. He received his BS from the University of California Riverside and his PhD from the University of California in Santa Barbara. Prof. Goldsmith's overarching research goals are to use first-principles computational modeling and data science tools to understand and design catalysts and materials for sustainable chemical conversion, pollution reduction, and energy generation/storage. He has been advisor to 12 PhD students, 7 postdoctoral fellows, and 22 undergraduates, and has more than 50 refereed publications. Goldsmith received the AIChE 35 Under 35 Award in the category of energy and environment and received the NSF CAREER award.

He is currently serving as past-President of the Michigan Catalysis Society and as an advisory board member of the *Journal of Catalysis and Chem Catalysis*.

Eranda Nikolla is a Professor of Chemical Engineering at the University of Michigan, Ann Arbor. Her research interests focus on the development of heterogeneous catalysts and electrocatalysts for sustainable chemical conversion and energy generation/storage processes. Her impact to catalytic science has been recognized through the National Science Foundation CAREER Award, the Department of Energy Early Career Research Award, Camille Dreyfus Teacher-Scholar Award, the Young Scientist Award from the International Congress on Catalysis, the 2019 ACS Women Chemists Committee (WCC) Rising Star Award, the 2021 Michigan Catalysis Society Parravano Award for Excellence in Catalysis Research and Development, the 2022 ACS Catalysis Lectureship for the Advancement of Catalytic Science, and the 2023 Inaugural Maria Flytzani-Stephanopoulos Award for Creativity in Catalysis. She has served as the President of the Michigan Catalysis Society (MCS) and the Chair of the Catalysis and Reaction Engineering (CRE) Division of the American Institute of Chemical Engineering (AIChE). She is currently the Chair of the Catalysis Science and Technology (CATL) Division of the American Chemical Society (ACS), Director-at-large of The North American Catalysis Society (NACS), and the Division Representative for the Michigan Catalysis Society (MCS). She also serves as an editor for the *Journal of Catalysis* and is an editorial advisory board member for a number of journals including the *Journal of the American Chemical Society* (*JACS*) and *ACS Energy Letters*.

Nirala Singh is an Associate Professor of Chemical Engineering at the University of Michigan, Ann Arbor. He received his BS from the University of Michigan where he took undergraduate chemical reactor engineering when Prof. Fogler was editing a new edition of his book and received a draft copy for the course. He received his PhD from the University of California, Santa Barbara. Prof. Singh's research is in the area of catalysis and electrocatalysis for energy storage, sustainable fuels and chemical production, and wastewater remediation. He has advised 17 PhD students, 6 postdoctoral fellows, and >20 masters and undergraduate researchers. He has published more than 50 refereed articles. Singh is an NSF CAREER awardee and served as President of the Michigan Catalysis Society and officer of the American Chemical Society CATL division.

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.

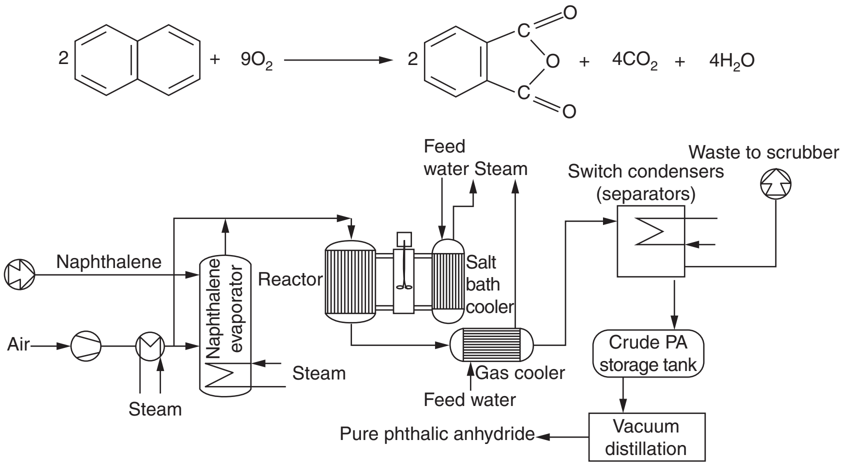
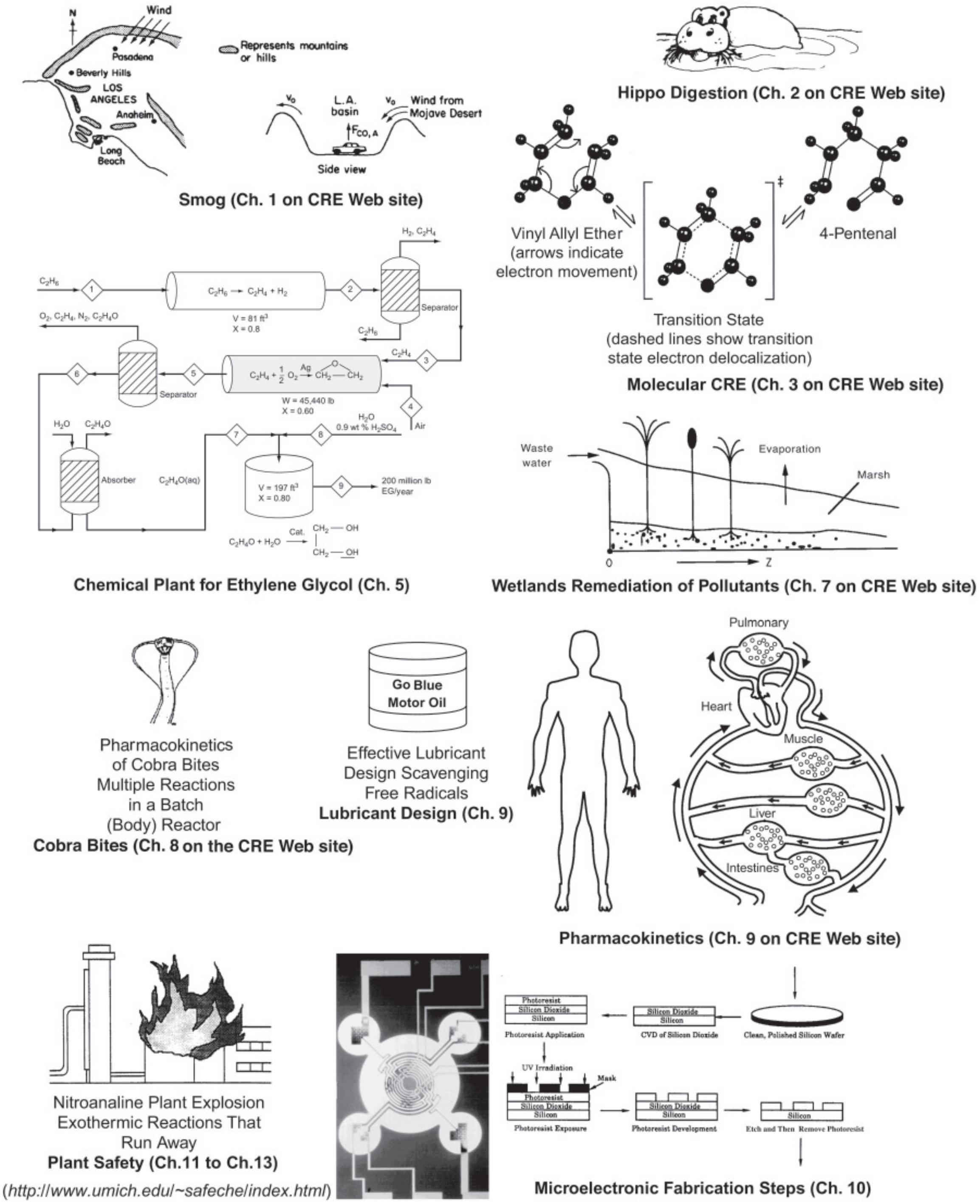


Figure 1-1 Manufacture of phthalic anhydride.

The chemical reaction engineering (**CRE**) principles learned here can also be applied in many areas, such as waste water treatment, microelectronics, nanoparticles fabrication, and pharmacokinetics of living systems, in addition to the more traditional areas of the manufacture of chemicals and pharmaceuticals. Some of the examples that illustrate the wide application of CRE principles in this book are shown in Figure 1-2. These examples, which can be found either in the text or as Web modules *(www.umich.edu/~elements/7e/index.html)*, include modeling smog in the Los Angeles (L.A.) basin (Chapter 1 Web module), the digestive system of a hippopotamus (Chapter 2 Web module), molecular CRE (Chapter 3 Web module), use of wetlands to degrade toxic chemicals (Chapter 6 on the CRE Web site), pharmacokinetics of cobra bites (Chapter 8 Web module), free-radical scavengers used in the design of motor oils (Chapter 9), enzyme kinetics (Chapter 9), drug delivery pharmacokinetics (Chapter 9 on the CRE Web site), and electrochemical reactors (Chapter 19). Also shown in Figure 1-2 are the manufacture of ethylene glycol (antifreeze), where three of the most common types of industrial reactors are used (Chapters 5 and 6). Other examples shown are heat effects, runaway reactions, and plant safety (Chapters 11–13); and increasing the octane number of gasoline (not shown in Figure 1-2) and the manufacture of computer chips (Chapter 10).



Smog (Ch. 1 on CRE Web site)

Hippo Digestion (Ch. 2 on CRE Web site)

Molecular CRE (Ch. 3 on CRE Web site)

Chemical Plant for Ethylene Glycol (Ch. 5)

Wetlands Remediation of Pollutants (Ch. 7 on CRE Web site)

Pharmacokinetics of Cobra Bites
Multiple Reactions in a Batch (Body) Reactor
Cobra Bites (Ch. 8 on the CRE Web site)

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

Pharmacokinetics (Ch. 9 on CRE Web site)

Nitroanaline Plant Explosion
Exothermic Reactions That Run Away
Plant Safety (Ch.11 to Ch.13)
(*http://www.umich.edu/~safeche/index.html*)

Microelectronic Fabrication Steps (Ch. 10)

Figure 1-2 The wide world of CRE applications.

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

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

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

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

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

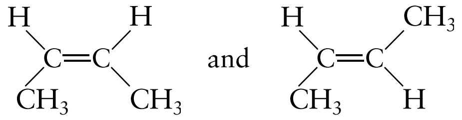
1.1 The Rate of Reaction, $-r_A$

Identity of chemical species
– Kind
– Number
– Configuration

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


para-xylene

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



cis-2-butene *trans*-2-butene

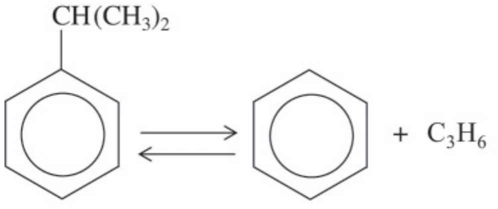
As a consequence of the different configurations, these two isomers display different chemical and physical properties. Therefore, we consider them as two different species, even though each has the same number of atoms of each element.

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.

Definition of *Rate of Reaction*

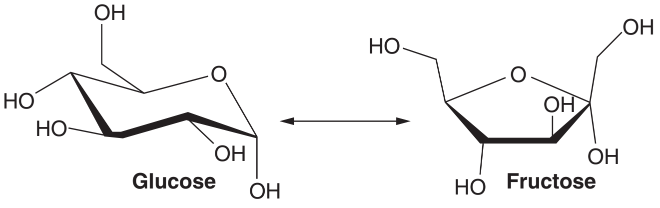
There are three basic ways a species may lose its chemical identity: decomposition, combination, and isomerization. In *decomposition*, the molecule loses its identity by being broken down into smaller molecules, atoms, or atom fragments. For example, if benzene and propylene are formed from a cumene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



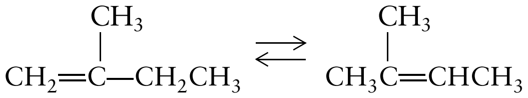
Cumene Benzene Propylene

A species can lose its identity by
- Decomposition
- Combination
- Isomerization

the cumene molecule has lost its identity (i.e., disappeared) by breaking its bonds to form these molecules. A second way that a molecule may lose its chemical identity is through *combination* with another molecule or atom. In the above reaction, the propylene molecule would lose its chemical identity if the reaction were carried out in the reverse direction, so that it combined with benzene to form cumene. The third way a species may lose its chemical identity is through isomerization, such as the reaction of 2-methyl-1-butene to 2-methyl-2-butene and glucose to fructose (largest biocatalytic process in the world for the production of high-fructose corn syrups).



In these reactions, the molecule loses its identity though a chance in configuration while the nature and number of atoms in the chemical structure remain the same.



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

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 different ways by referring it to different chemical species in the reaction. To illustrate, consider the reaction of chlorobenzene with chloral in the presence of fuming sulfuric acid to produce the banned insecticide DDT (dichlorodiphenyl trichloroethane) and water.

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

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

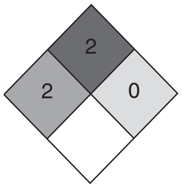
$$A + 2B \longrightarrow C + D$$

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).

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

NFPA Diamond



DDT
See Section 2.7

Example 1–1 Rates of Disappearance and Formation

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

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

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

Solution

(a) *Chloral [A]:* 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 = $-r_B = -2r_A$ = 20 mol/m^3·s
Rate of formation of B = r_B = –20 mol/m^3·s

$-r_A$ = 10 mol A/m^3·s†
r_A = –10 mol A/m^3·s
Equation (3-1) page 77
Then

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

$r_B = 2(r_A)$ = –20 mol B/m^3·s
$-r_B$ = 20 mol B/m^3·s
$r_C = -r_A$ = 10 mol C/m^3·s
$r_D = -r_A$ = 10 mol D/m^3·s

---

† Tutorial Video: *https://www.youtube.com/watch?v=6mAqX31RRJU*

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

$-r_A = 10$ mol A/m^3·s
$r_A = -10$ mol A/m^3·s
$-r_B = 20$ mol B/m^3·s
$r_B = -20$ mol B/m^3·s
$r_C = 10$ mol C/m^3·s

Analysis: The purpose of this example is to better understand the convention for the rate of reaction. The symbol r_j is the rate of formation (generation) of species *j*. If species *j* is a reactant, the numerical value of r_j will be a negative number. If species *j* is a product, then r_j will be a positive number. The rate of reaction, $-r_A$, is the rate of disappearance of reactant A and must be a positive number. A mnemonic relationship to help remember how to obtain relative rates of reaction of A to B, and so on, is given by Equation (3-1) on page 79.

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

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

What is $-r'_A$?

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

Definition of r_j

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

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

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

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

What is $-r_A$ a function of?

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

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

$$A \longrightarrow \text{Products}$$

may be a linear function of concentration,

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

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

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

or

The rate law is an algebraic equation.

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

The convention

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, or specific reaction rate, 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.

1.2 The General Mole Balance Equation (GMBE)

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

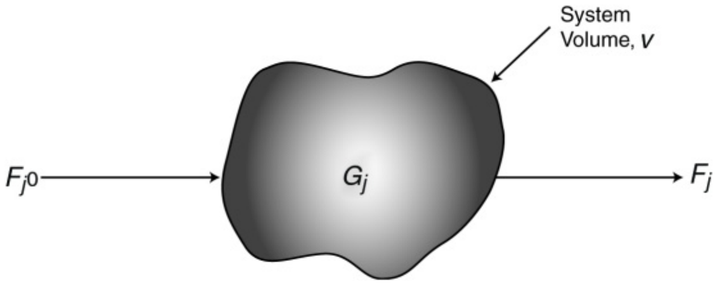


Figure 1-3 Mole balance on species j in a system volume, V.

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[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).

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

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

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

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

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

$$G_j = r_j \cdot V$$

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

Now suppose that the rate of formation of species *j* for the reaction varies with position in the system volume. That is, it has a value r_{j1} at location 1, which is surrounded by a small volume, ΔV_1, within which the rate is uniform; similarly, the reaction rate has a value r_{j2} at location 2 and an associated volume, ΔV_2, and so on (Figure 1-4).

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

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

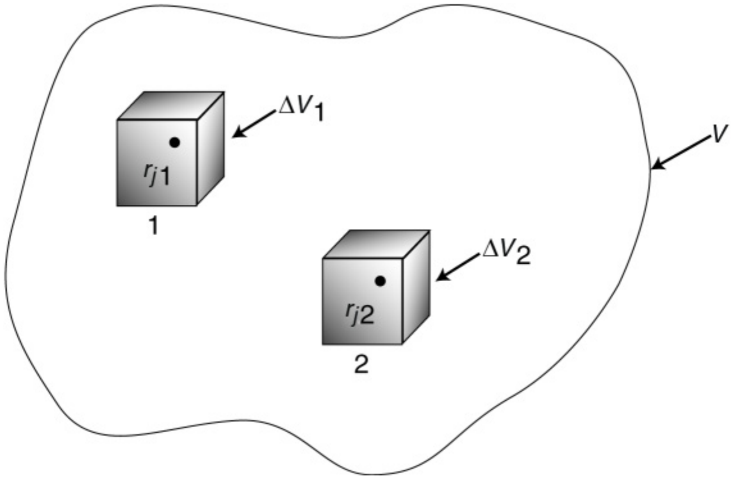


Figure 1-4 Dividing up the system volume, V.

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

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

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

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

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

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.

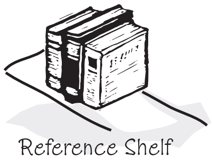
This is a basic equation for chemical reaction engineering.

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

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), reactor volume, or catalyst weight (continuous-flow) necessary to convert a specified amount of the reactants into products.

1.3 Batch Reactors (BRs)

When is a batch reactor used?



A batch reactor is used for small-scale operation, for testing new processes that have not been fully developed, for the manufacture of expensive products, and for processes that are difficult to convert to continuous operations. The reactor can be charged (i.e., filled) through the holes at the top (see Figure 1-5(a)). The batch reactor has the advantage of high conversions that can be obtained by leaving the reactant in the reactor for long periods of time, but it also has the disadvantages of high labor costs per batch, the variability of products from batch to batch, and the difficulty of large-scale production (see Industrial Reactor Photos in *Professional Reference Shelf* [*PRS*] (*http://www.umich.edu/~elements/7e/01chap/prof-reactors.html*) on the CRE Web site, *www.umich.edu/~elements/7e/index.html*). Also see *https://encyclopedia.che.engin.umich.edu/reactors/*.

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

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

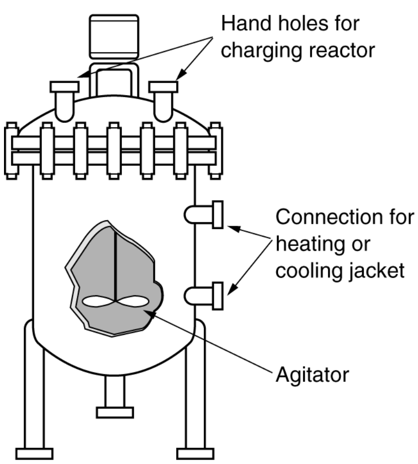


Figure 1-5(a) Simple homogeneous batch reactor (BR). [Excerpted by special permission from *Chem. Eng.*, *63*(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

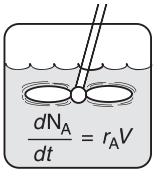
Figure 1-5(b) Batch reactor mixing patterns. Further descriptions and photos of the batch reactors can be found in both the *Visual Encyclopedia of Equipment* and in the *Professional Reference Shelf* on the CRE Web site.

Also see *https://encyclopedia.che.engin.umich.edu/batch/*.

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

Perfect mixing

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



Batch Reactor

Let's consider the isomerization of species A in a 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.

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

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

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.

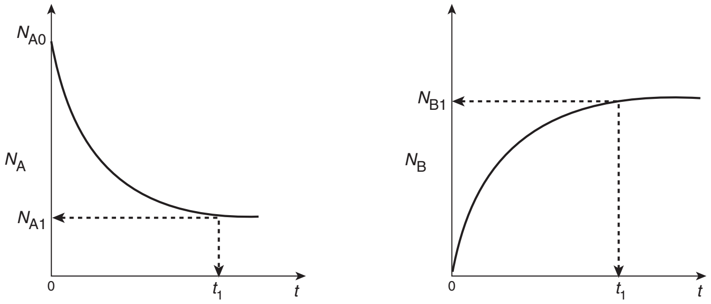
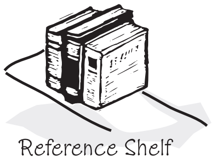


Figure 1-6 Moles of A vs. time (left) and moles of B vs. time (right) for A reacting to form B in a batch reactor.

1.4 Continuous-Flow Reactors



Continuous-flow reactors are almost always operated at steady state. We will consider three types: the *continuous-stirred tank reactor* (CSTR), the *plug-flow reactor* (PFR), and the *packed-bed reactor* (PBR). Detailed physical descriptions of these reactors can be found in both the *Professional Reference Shelf* (*PRS*) (*http://www.umich.edu/~elements/7e/01chap/prof.html*) of Chapter 1 and in the *Visual Encyclopedia of Equipment* (*https://encyclopedia.che.engin.umich.edu/cstr/*), and on the CRE Web site.

1.4.1 Continuous-Stirred Tank Reactor (CSTR)

What is a CSTR used for?

A type of reactor commonly used in industrial processing is the stirred tank operated continuously (Figure 1-7). It is referred to as the *continuous-stirred tank reactor* (CSTR) or *vat*, or *backmix reactor*, and is primarily used for *liquid-phase reactions*. It is normally operated **at steady state** and is assumed to be **perfectly mixed**; consequently, there is no time dependence or position dependence of the temperature, concentration, or reaction rate inside the CSTR. That is, every variable is the same at every point inside the reactor. Because the temperature and concentration are identical everywhere within the reaction vessel, they are the same at the *exit point* as they are elsewhere in the tank. Thus, the temperature and concentration in the exit stream are modeled as being the same as those inside the reactor. In systems where mixing is highly *nonideal*, the well-mixed model is inadequate, and we must resort to other modeling techniques, such as residence time distributions, to obtain meaningful results. This topic of nonideal mixing is discussed in Chapters 16 and 17, while nonideal flow reactors are discussed in Chapter 18.

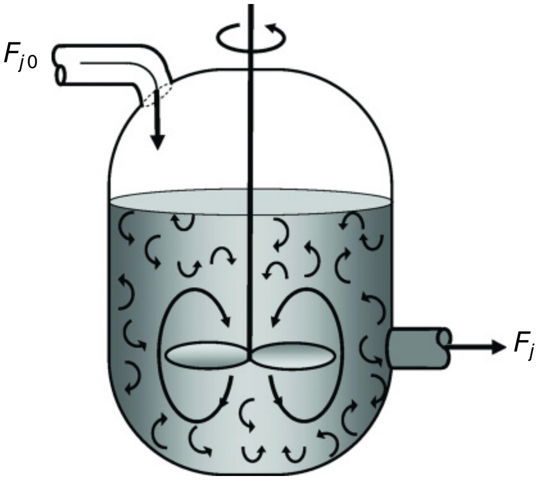


Figure 1-7 CSTR mixing patterns.

Also see *https://encyclopedia.che.engin.umich.edu/cstr/*.

When the general mole balance equation

GMBE

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

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

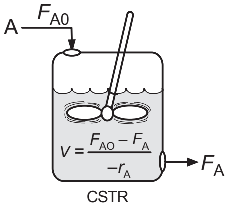
$$\frac{dN_j}{dt} = 0$$

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, which is sometimes called *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 molar flow rate of species j from F_{j0} to the exit molar flow rate F_j, when species j is disappearing at a rate of $-r_j$. We note that the CSTR is modeled such that the conditions in the exit stream (e.g., concentration and temperature) **are identical** to those in the tank. The molar flow rate F_j is just the product of the concentration of species j and the volumetric flow rate υ

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

Applying Equation (1-8) at the entrance of the reactor, one obtains the inlet flow rate is equal to the inlet concentration (C_{j0}) multiplied by the inlet volumetric flow rate (υ_0).

$$F_{j0} = C_{j0} \cdot \upsilon_0$$

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

$$\boxed{V = \frac{\upsilon_0 C_{A0} - \upsilon C_A}{-r_A}} \tag{1-9}$$

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 (cf. Equation 3-2), will *also* vary axially. For the purposes of the material presented here, we consider systems in which the flow field may be modeled by that of a plug-flow profile (e.g., uniform radial velocity in turbulent flow), as shown in Figure 1-9. That is, there is no radial variation in reaction rate, and the reactor is referred to as a *plug-flow reactor* (PFR). (The laminar-flow reactor (LFR) is discussed in Chapters 16–18, along with a discussion of nonideal reactors.)

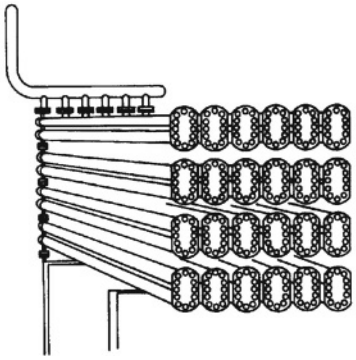


Figure 1-8(a) Tubular reactor schematic. Longitudinal tubular reactor. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

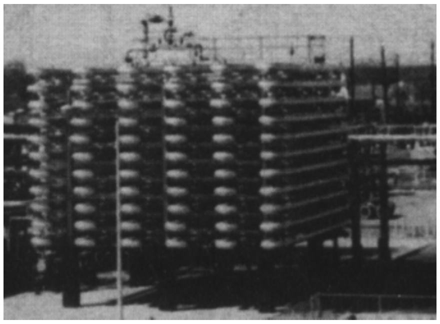


Figure 1-8(b) Tubular reactor photo. Tubular reactor for production of Dimersol G. (Photo courtesy of Editions Techniq Institut Français du Pétrole.)

Also see *https://encyclopedia.che.engin.umich.edu/pfr/*.

Also see PRS and *Visual Encyclopedia of Equipment*.

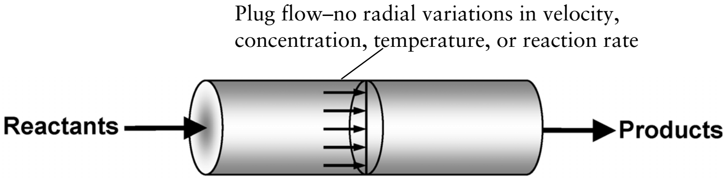


Figure 1-9 Plug-flow tubular reactor.

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

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

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

In − Out + Generation = Accumulation

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

Dividing Equation (1-10) by ΔV and rearranging

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

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

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

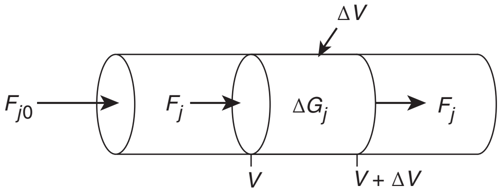
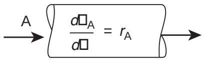


Figure 1-10 Mole balance on species j in volume ΔV.

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



Tubular reactor

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

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

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

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 or perhaps one of his followers.

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

Let's 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 as shown in Figure 1-12(a) while F_B increases as the reactor volume V increases, as shown in Figure 1-12(b).

Picasso's
reactor

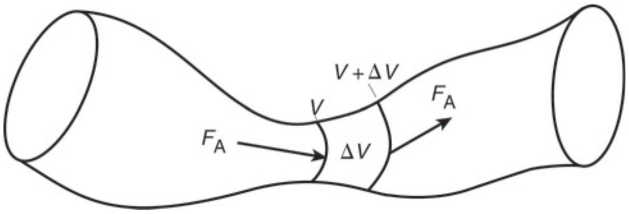


Figure 1-11 Pablo Picasso's reactor.

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

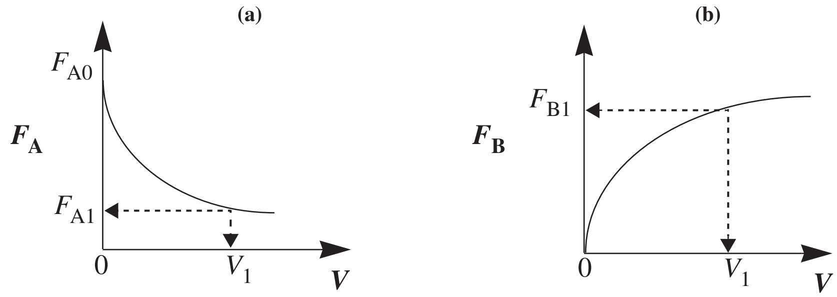


Figure 1-12 Profiles of molar flow rates of a reactant, A (left), and product, B (right), in a PFR.

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

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

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

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

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 Figure 10-5). The greater the mass of a given catalyst, the greater the reactive surface area. Consequently, the reaction rate is based on mass of solid catalyst, *W*, rather than on reactor volume, *V*. For a fluid–solid heterogeneous system, the rate of reaction of a species A, $-r'_A$, is defined as

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

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

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

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

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

In the three idealized types of reactors just discussed (the perfectly mixed batch reactor [BR], the plug-flow tubular reactor [PFR]), and the perfectly mixed continuous-stirred tank reactor [CSTR]), the design equations (i.e., mole balances) were developed based on reactor volume. The derivation of the design equation for a packed-bed catalytic reactor (PBR) will be carried out in a manner analogous to the development of the tubular design equation. To accomplish this derivation, we simply replace the volume coordinate, *V*, in Equation (1-10) with the catalyst mass (i.e., weight) coordinate *W* (Figure 1-14).

PBR
Mole Balance

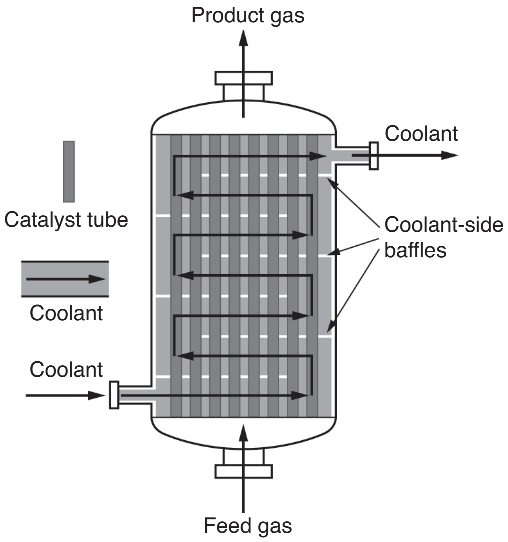


Figure 1-13 Longitudinal catalytic packed-bed reactor. Also see *https://encyclopedia.che.engin.umich.edu/packed-bed-reactors/*.

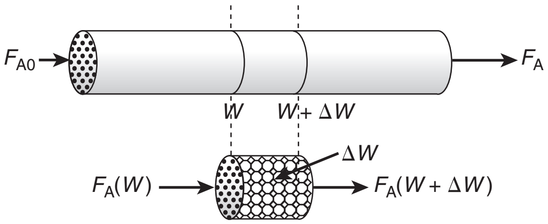


Figure 1-14 Packed-bed reactor schematic.

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

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

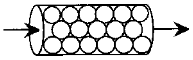
The dimensions of the generation term in Equation (1-14) are

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

which are, as expected, the same dimensions of the molar flow rate F_A. After dividing Equation (1-14) by ΔW and taking the limit as $\Delta W \to 0$, 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 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 molar flow rate F_A.

1.4.4 Well-Mixed "Fluidized" Catalytic Bed Reactor

For particular catalytic gas-phase systems, fluidized catalytic bed reactors are also in common use. This reactor design is characterized by the flow of the reacting medium through a bed of solid catalyst pellets at high enough velocities to suspend, or fluidize, the solid catalyst pellets and cause it to behave like a well-mixed CSTR as shown in Figure 1-15.

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

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

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

$$\boxed{W = \frac{F_{A0} - F_A}{-r'_A}} \tag{1-18}$$

Looking Ahead

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

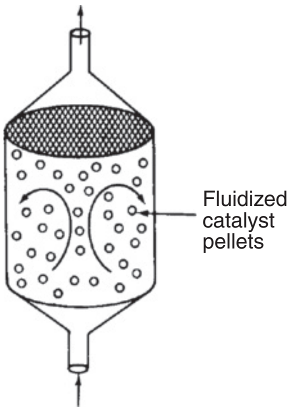
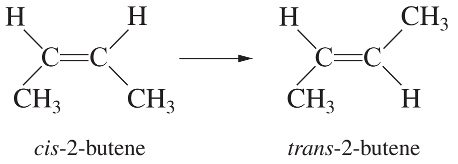


Figure 1-15 Well-mixed fluidized bed modeled as a CSTR.

Example 1–2 How Large Is the Reactor Volume?

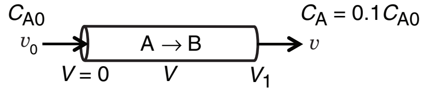
Let's consider the liquid-phase *cis–trans* isomerization of 2–butene



which we will write symbolically as

$$A \longrightarrow B$$

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, υ, is constant, that is, $\upsilon = \upsilon_0$.



1. Without solving any equations, sketch what you think the concentration profile (C_A as a function of V) would look like.
2. Derive an equation relating the reactor volume to the entering and exiting concentrations of A, the rate constant k, and the volumetric flow rate υ_0.
3. Determine the reactor volume, V_1, necessary to reduce the exiting concentration to 10% of the entering concentration, that is, $C_A = 0.1C_{A0}$, when the volumetric flow rate υ_0 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. Because the volumetric flow rate is constant, $\upsilon = \upsilon_0$, one can use Equation (1-8) to obtain the concentration of A, $C_A = F_A/\upsilon_0$, and then by comparison with the plot in Figure 1-12, obtain the concentration of A as a function of reactor volume, as shown in Figure E1-2.1.

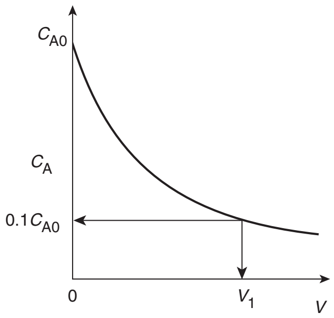


Figure E1-2.1 Concentration profile.

2. Derive an equation relating V, 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)

Mole Balance:

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

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

Rate Law:

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

Reactor sizing

Because the volumetric flow rate, υ, is constant ($\upsilon = \upsilon_0$), as it is for virtually 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

Combine:

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

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

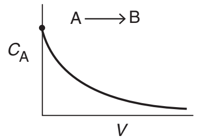
Solve:

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

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

Concentration profile

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



3. Calculate the volume V. We want to find the volume, V_1, at which $C_A = \frac{1}{10}C_{A0}$ when k = 0.23 min^{-1} and υ_0 = 10 dm^3/min.

Evaluate:

Substituting C_{A0}, C_A, υ_0, and k in Equation (E1-2.5), we have

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

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

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

$$C_A = 0.01C_{A0}$$

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

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

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

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

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

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

Polymath Formulation

Mole Balances
$$\frac{d(Ca)}{d(V)} = ra/\upsilon o \qquad \text{(E1-3.1)}$$

$$\frac{d(Cb)}{d(V)} = rb/\upsilon o \qquad \text{(E1-3.2)}$$

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

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

$$k = 0.23$$

$$\upsilon o = 10$$

A Polymath tutorial to solve the ordinary differential equations (ODEs) can be found on the Web sites, *http://www.umich.edu/~elements/7e/tutorials/ODE_Equation_Tutorial.pdf* and *http://www.umich.edu/~elements/7e/tutorials/Polymath_tutorials.html.*

TABLE E1-3.1 POLYMATH PROGRAM AND OUTPUT FOR ISOTHERMAL PFR

Differential equations

1 d(Cb)/d(V) = rb/vo

2 d(Ca)/d(V) = ra/vo

Explicit equations

1 vo = 10

2 k = 0.23

3 ra = –k*Ca

4 rb = –ra

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	Ca	10.	1.002588
2	Cb	0	8.997412
3	k	0.23	0.23
4	ra	–2.3	–0.2305953
5	rb	2.3	0.2305953
6	V	0	100.
7	vo	10.	10.

LEP Sliders

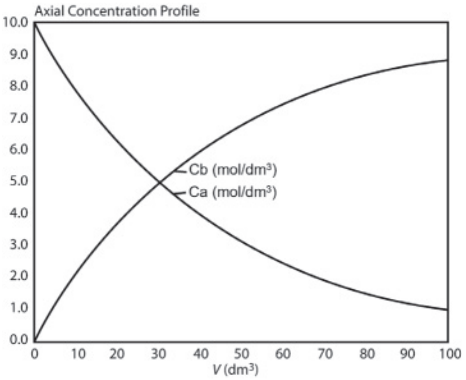


Figure E1-3.1 Axial concentration profiles for A and B.

The parameter values are $k = 0.23\ \text{min}^{-1}$, $\upsilon o = 10\ \text{dm}^3/\text{min}$, and $C_{A0} = 10\ \text{mole/dm}^3$. The initial and final values for the integration wrt the volume V are $V = 0$ and $V = 100\ \text{dm}^3$, respectively.

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

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

1.5 Industrial Reactors

Reference Shelf

Be sure to view the actual photographs of industrial reactors on the CRE Web site so you will know them when you run into them. There are also links to view reactors on different Web sites. The CRE Web site also includes a portion of the *Visual Encyclopedia of Equipment*, *encyclopedia.che.engin.umich.edu*, “Chemical Reactors” developed by

Dr. Susan Montgomery and her students at the University of Michigan. Also see *Professional Reference Shelf* on the CRE Web site for "Reactors for Liquid-Phase and Gas-Phase Reactions," along with photos of industrial reactors, and Expanded Material on the CRE Web site.[2]

https://encyclopedia.che.engin.umich.edu/reactors/

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

The CRE Web site describes industrial reactors, along with typical feed and operating conditions. In addition, two solved example problems for Chapter 1 can be found on the CRE Web site, *http://www.umich.edu/~elements/7e*.

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

A critical aspect of process safety is "anticipating" what could go wrong in a chemical process and ensuring it won't go wrong. Equipment and processes involving exothermic chemical reactions are some of the most at risk in a chemical plant. Consequently, each chapter will end with a segment "*And Now*… A Word From Our Sponsor–Safety" (AWFOS–S). In addition, to highlight process safety across the chemical engineering curriculum, a Web site (*http://umich.edu/~safeche/*) has been developed that features a safety module specific to every core chemical engineering lecture course plus lab safety. In this chapter, we define process safety along with a very brief discussion on why it is important to study process safety.

1.6.1 What Is Chemical Process Safety?

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

1.6.2 Why Study Process Safety?

Industrial disasters such as UCIL Bhopal, T2 Laboratories (Figure 1-16), BP Texas City, and Flixborough have collectively killed and injured thousands of people and caused billions of dollars in damage to chemical plants and nearby communities. Accidents such as these occur because chemical engineering processes are some of the most potentially dangerous due to extreme operating conditions and the use of explosive, reactive, and flammable materials. What surprises people is that most of these chemical engineering accidents, such as those listed in the Chemical Safety Board Videos on the companion Web site, (*http://umich.edu/~safeche/*) were preventable.

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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, Chap. 11.

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

They were the result of poor engineering decisions, made by people who lacked fundamental understanding of basic chemical engineering concepts and chemical engineering safety. Thus, knowing the fundamentals of chemical engineering and process safety may save your life and the lives of innocent people, and prevent the loss of millions of dollars of material and equipment.

Engineers have an ethical and professional obligation to work only in areas for which they are competent and qualified. The best way to prevent future industrial disasters is to understand how to effectively and safely design, operate, and troubleshoot chemical processes. To prepare a prevention plan, we must take the time and effort to understand chemical processes and chemical process safety. To help achieve this understanding, the last section of every chapter has a tutorial, AWFOS–S, that can help you prevent accidents.

A comparison of process safety and personal safety is very succinctly given on the Web site (*http://www.energysafetycanada.com/files/pdf/Personal_vs_Process_Safety_v3.pdf*).

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

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

- Mole Balance, Chapters 1 and 2
- Rate Law, Chapter 3
- Stoichiometry, Chapter 4
- Isothermal Reactor Design, Chapter 5
    Combine
    Evaluate
- Energy Balance, Chapters 11–13

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

A Word of Caution: *The falling CRE Tower.* *As we proceed through the next five chapters, we will see how these building blocks form a tower. Now, if one cuts corners when studying this material, the building blocks become cylinders and as a result the tower becomes unstable and all of the understanding of CRE falls apart.* See *http://www.umich.edu/~elements/7e/01chap/assets/player/KeynoteDHTMLPlayer.html#3*.

SUMMARY

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

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

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

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

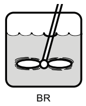
$$F_{A0} - F_A + r_A V = \frac{dN_A}{dt} \tag{S1-2}$$

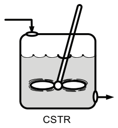
2. The kinetic rate law for r_j is
   - The rate of formation of species j per unit volume (e.g., mol/s·dm^3)
   - Solely a function of the properties of reacting materials and reaction conditions (e.g., concentration [activities], temperature, pressure, catalyst, or solvent [if any]) and does not depend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

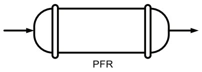
   For homogeneous catalytic systems, typical units of $-r_j$ may be gram moles per second per liter; for heterogeneous systems, typical units of r_j' may be gram moles per second per gram of catalyst. By convention, $-r_A$ is the rate of disappearance of species A and r_A is the rate of formation of species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

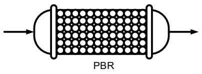
3. Mole balances on species A in four common reactors are shown in Table S1-1.

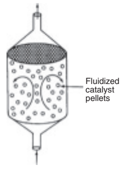
TABLE S1-1 SUMMARY OF REACTOR MOLE BALANCES











Reactor	*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	$\frac{dF_A}{dW} = r'_A$		$W_1 = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r'_A}$
Fluidized CSTR	Steady state	—	$W = \frac{F_{A0}-F_A}{-r'_A}$	—

CRE WEB SITE MATERIALS

(*http://www.umich.edu/~elements/7e/01chap/obj.html#/*)

Useful Links

Living Example Problems
Polymath, Python, Matlab and Wolfram

Extra Help
Multiple Resources extra problems, screencasts and lecture notes

Additional Materials
New Technical Material, Detailed Derivations and Web Modules

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

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

Evaluation

Self Tests
Interactive problems with solutions to provide extra practice of concepts

i>Clicker Questions
Interactive multiple choice questions to help access your understanding of the material

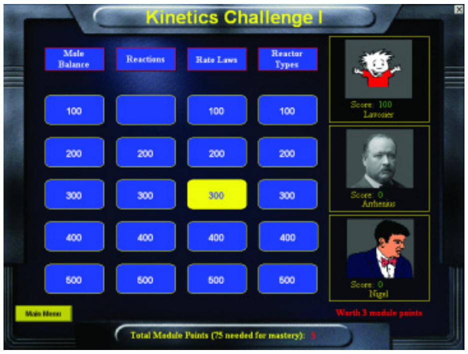
Getting Unstuck on a Problem

(*http://www.umich.edu/~elements/7e/01chap/iclicker_ch1_q1.html*)

Smog in L.A. Web Module

Photograph by Radoslaw Lecyk/Shutterstock (*http://www.umich.edu/~elements/7e/web_mod/la_basin/index.htm*) Living Example Problem: *http://www.umich.edu/~elements/7e/01chap/live.html*

Interactive Computer Games (*http://www.umich.edu/~elements/7e/icm/index.html*)
A. Quiz Show I (*http://www.umich.edu/~elements/7e/icm/kinchal1.html*)



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

QUESTIONS, SIMULATIONS, AND PROBLEMS

> I wish I had an answer for that, because I'm getting tired of answering that question.
>
> —Yogi Berra, New York Yankees
> *Sports Illustrated,* June 11, 1984

The subscript to each of the problem numbers indicates the level of difficulty, that is, A, least difficult; B, moderate difficulty; C, fairly difficult; D, (double black diamond), most difficult. A = ● B = ■ C = ◆ D = ◆◆ For example, P1-5_B means "1" is the Chapter number, "5" is the problem number, "$_B$" is the problem difficulty, in this case B means moderate difficulty.

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

Questions

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

Q1-2$_A$ Go to Chapter 1 **Evaluation** on the Web site. Click on **i>Clicker Questions** (*http://www.umich.edu/~elements/7e/01chap/iclicker_ch1_q1.html*) and view at least five i>clicker questions. Choose one that could be used as is, or a variation thereof, to be included on the next exam. You also could consider the opposite case: explaining why the question should *not* be on the next exam. In either case, explain your reasoning.

i>Clicker Questions

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

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

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

Q1-6$_A$ Go to Chapter 1 **Useful Links** (*http://www.umich.edu/~elements/7e/01chap/obj.html#/*) and click on Professional Reference Shelf to view the photos and schematics of real reactors. Write a paragraph describing two or more of the reactors. What similarities and differences do you observe between the reactors on the Web site, and in the text? How do the used reactor prices compare with those in Table 2-6?

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

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

Type of Reactor	Characteristics	Phases Present	Usage	Advantages	Disadvantages

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

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

Q1-11$_A$ Go to Chapter 1 **Extra Help** on the Web site and click on **LearnChemE ScreenCasts** (*http://www.umich.edu/~elements/7e/01chap/learn-cheme-videos.html*). Choose the **How to Study** screencast and list three ways that screencasts can help you learn the material.

Q1-12$_A$ Go to **Extra Help** then click on **Videos of Tips on Studying and Learning.** Go to Chapter 1 (*http://www.umich.edu/~elements/7e/01chap/obj.html#/video-tips/*).

(**a**) View one of the 5- to 6-minute video tutorials and list two of the most important points in the video. List two things you think this screencast did well.

(**b**) After viewing the three screencasts on How to Study (*http://www.learncheme.com/student-resources/how-to-study-resources*), describe the most efficient way to study. In video 3 How to Study, the author of this book has a very different view of one of the points suggested. What do you think it is?

(**c**) View the video 13 Study Tips**** (4 Stars) (*https://www.youtube.com/watch?v=eVlvxHJdql8&feature=youtu.be*). List four of the tips that you think might help your study habits.

(**d**) Rate each of the sites on video tips, (1) Not Helpful, (5) Very Helpful.

Computer Simulations and Experiments

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

P1-1_A (a) Revisit **Example 1-3**.

Wolfram and Python

(i) Describe how C_A and C_B change when you experiment with varying the volumetric flow rate, υ_0, and the specific reaction rate, k, and then write a conclusion about your experiments.

(ii) Click on the description of reversible reaction A $\rightleftarrows$ B to understand how the rate law becomes $-r_A = k\left[C_A - \frac{C_B}{K_e}\right]$. Set K_e at its minimum value and vary k and υ_0. Next, set K_e at its maximum value and vary k and υ_0. Write a couple sentences describing how varying k, υ_0, and K_e affect the concentration profiles. We will learn more about K_e in Section 3.2.

(iii) After reviewing *Generating Ideas and Solutions* on the Web site (*http://www.umich.edu/~elements/7e/toc/SCPS,3rdEdBook(Ch07).pdf*), choose one of the brainstorming techniques (e.g., lateral thinking) to suggest two questions that should be included in this problem.

Polymath

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

Problems

P1-2_B Schematic diagrams of the Los Angeles basin are shown in Figure P1-2_B. The basin floor covers approximately 700 square miles (2×10^{10} ft^2) and is almost completely surrounded by mountain ranges. If one assumes an inversion height in the basin of 2,000 ft, the corresponding volume of air in the basin is 4×10^{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.

Member
Hall of Fame

We shall perform an unsteady-state mole balance (Equation (1–4)) on CO as it is depleted from the basin area by a Santa Ana wind. Santa Ana winds are high-velocity winds that originate in the Mojave Desert just to the northeast of Los Angeles. Load the **Smog in Los Angeles Basin Web Module**. Use the data in the module to work parts 1–12 (a) through (h) given in the module. Load the **Living Example Polymath code** and explore the problem. For part (i), vary the parameters υ_0, a, and b, and write a paragraph describing what you find.

Photograph by Radoslaw Lecyk/Shutterstock

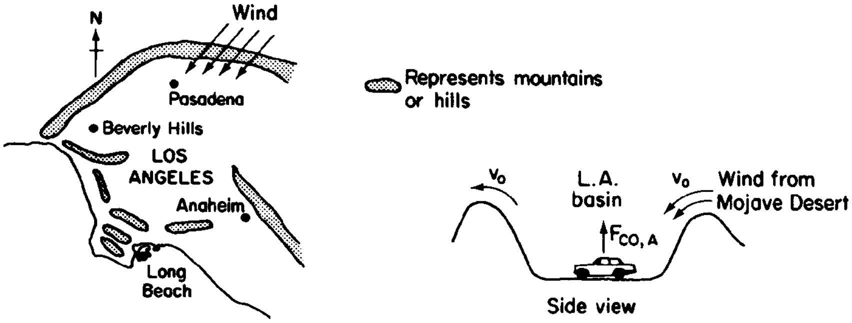


Figure P1-2_B Schematic diagrams of the Los Angeles basin.
(*http://www.umich.edu/~elements/7e/web_mod/la_basin/index.htm*)

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

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

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

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

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

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 for both sets of values. Explain why the curves look the way they do. **Polymath Tutorial** (*https://www.youtube.com/watch?v=nyJmt6cTiL4*)

(b) Using Wolfram and/or Python in the Chapter 1 LEP on the Web site, what parameters would you change to convert the foxes versus rabbits plot from an oval to a circle? Suggest reasons that could cause this shape change to occur.

(c) We will now consider the situation in which the rabbits contracted a deadly virus also called *rabbit measles (measlii)*. The death rate is $r_{\text{Death}} = k_D x$ with k_D = 0.005 day^{-1}. Now plot the fox and rabbit concentrations as a function of time and also plot the foxes versus rabbits. Describe, if *possible,* the minimum growth rate at which the death rate does not contribute to the net decrease in the total rabbit population.

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

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

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

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

Screenshots on how to run Polymath are shown at the end of Summary Notes for Chapter 1 or on the CRE Web site, *www.umich.edu/~elements/7e/software/polymath-tutorial.html.*

Interactive Computer Games

P1-4$_A$ Find the Interactive Computer Games (ICG) on the CRE Web site (*http://www.umich.edu/~elements/7e/icg/index.html*). Read the description of the Kinetic Challenge module (*http://www.umich.edu/~elements/7e/icm/kinchal1.html*) and then go to the installation instructions (*http://www.umich.edu/~elements/7e/icm/install.html*) to install the module on your computer.

Play this game and then record your performance number, which indicates your mastery of the material.

Jeopardy Game
Held at Annual
AIChE Student
Chapter Meeting

ICM Quiz Show ICG

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

ICG Kinetics Challenge 1 Performance # ________________________

Problems

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

$$A + B \longrightarrow 2C$$

takes place in an unsteady CSTR. The feed is only A and B in equimolar proportions. Which of the following sets of equations gives the correct set of mole balances on A, B, and C? Species A and B are disappearing and species C is being formed. Circle the correct answer where <u>all</u> the mole balances are correct.

(a)
$$F_{B0} - F_A - \int^V r_A dV = \frac{dN_A}{dt}$$
$$F_{B0} - F_B - \int^V r_A dV = \frac{dN_B}{dt}$$
$$-F_C + 2\int^V r_A dV = \frac{dN_C}{dt}$$

(b)
$$F_{A0} - F_A + \int^V r_A dV = \frac{dN_A}{dt}$$
$$F_{A0} - F_B + \int^V r_A dV = \frac{dN_B}{dt}$$
$$-F_C - 2\int^V r_A dV = \frac{dN_C}{dt}$$

(c)
$$F_{A0} - F_A + \int_0^V r_A dV = \frac{dN_A}{dt}$$
$$F_{A0} - F_B + \int^V r_A dV = \frac{dN_B}{dt}$$
$$F_C + \int^V r_C dV = \frac{dN_C}{dt}$$

(d)
$$F_{B0} - F_A - \int^V r_A dV = \frac{dN_A}{dt}$$
$$F_{B0} - F_{A0} - \int^V r_A dV = \frac{dN_B}{dt}$$
$$-F_C + \int^V r_C dV = \frac{dN_C}{dt}$$

(e) None of the above.

This problem was written in honor of Ann Arbor, Michigan's own Grammy winning artist, Bob Seger (*https://www.youtube.com/channel/UComKJVf5rNLl_RfC_rbt7qg/videos*).

P1-6$_B$ The reaction

$$A \longrightarrow B$$

is to be carried out isothermally in a continuous-flow reactor. The entering volumetric flow rate υ_0 is 10 dm^3/h. *Note:* $F_A = C_A\upsilon$. For a constant volumetric flow rate $\upsilon = \upsilon_0$, then $F_A = C_A\upsilon_0$. Also, $C_{A0} = F_{A0}/\upsilon_0 = ([5 \text{ mol/h}]/[10 \text{ dm}^3\text{/h}]) = 0.5 \text{mol/dm}^3$.

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

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

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

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

P1-7$_A$ **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 then to make reasonable assumptions. He used a process to set bounds on the answer by saying it is probably larger than one number and smaller than another, and arrived at an answer that was within a factor of 10.

See *http://mathforum.org/workshops/sum96/interdisc/sheila2.html.*

Enrico Fermi Problem

(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. And so on, __________

   An answer is given on the CRE Web site 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 2016?

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

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

$$2A \xrightarrow{k} B \quad k = 0.03\,\text{dm}^3/\text{mol}\cdot\text{s}$$

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, υ_0, is constant at 3 dm^3/s. What is the corresponding reactor volume?

Solution

1. Mole Balance

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

2. Rate Law (second order)

$$-r_A = kC_A^2$$

3. Combine

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

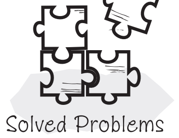
4. $F_{A0} = \nu_0 C_{A0} = \dfrac{3\ \text{dm}^3}{\text{s}} \cdot \dfrac{2\ \text{molA}}{\text{dm}^3} = \dfrac{6\ \text{molA}}{\text{s}}$

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

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

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

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



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

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

SUPPLEMENTARY READING

1. For further elaboration of the development of the general balance equation, see not only the Web site *www.umich.edu/~elements/7e/index.html* but also

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

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

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

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

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

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

4. Short instructional videos (6–9 minutes) that correspond to the topics in this book can be found at *http://www.learncheme.com/*.

5. See the Web site, "Process Safety Across the Chemical Engineering Curriculum," (*http://umich.edu/~safeche/index.html*).

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