

CHEMICAL REACTION ENGINEERING

**From First Principles to
AI-Assisted Practice**

Bengt Andersson
with support from Claude.ai

Preface

This book has been authored by Bengt Andersson, with valuable assistance from Claude.ai and ChatGPT. The goal of this project is to make the book freely accessible to everyone around the globe. Both the text and illustrations are available without any copyright restrictions. Unless otherwise noted, the figures have been created by the author, generated with ChatGPT, or sourced from Wikimedia Commons.

Students can download the book in PDF format at no cost. Teachers who wish to have an open, editable version for customizing their courses can request a Word file by emailing bengt.andersson@chalmers.se. Educators are encouraged to modify or enhance the book as needed for their own courses. If you make improvements or adjustments, please add your name to the list of authors below and send the updated version to me, maintaining the book's no copyright policy.

The course textbook has been made available for you to upload directly to Claude (claude.ai), ChatGPT or any AI. Once uploaded, the AI has full access to the book in any language and can assist you in a range of powerful ways throughout your studies. Appendix A explains what you can do and how to get the most out of this capability.

Gothenburg, January 2026

Bengt Andersson

Department of Chemistry and Chemical Engineering
Chalmers University of Technology
Gothenburg
Sweden

CHEMICAL REACTION ENGINEERING From First Principles to AI-Assisted Practice

© 2026 by Bengt Andersson is licensed under CC BY-NC-SA 4.0.

To view a copy of this license, visit <https://creativecommons.org/licenses/by-nc-sa/4.0/>

List of authors

Author	Date	Affiliation	Alterations
Bengt Andersson	2026	Chalmers University	Prompting Claude.ai, adjust to Word format and correct errors.
Jonas Åvall	2026	IPS (www.ips.se)	Corrected Chapter 11 in Safety and Risk Management

Acknowledgments

I would like to extend my sincere gratitude to the following individuals who made significant contributions to this book:

- Professor Nils-Herman Schön – whose outstanding textbook on Chemical Reaction Engineering from the 1980s provided the structural and pedagogical foundation for my own writing. His work has been an invaluable starting point for this book.
- Professor Ronnie Andersson – who introduced me to the world of artificial intelligence by inviting me to collaborate on his courses about Neural Networks for industry. Our regular discussions have been instrumental in expanding my knowledge in this field.
- Professor Louise Olsson – who placed her trust in this project and generously provided the financial support necessary to bring this book to completion.

To all of you, thank you for your inspiration, support, and belief in this endeavor.

Contents

Chapter 1: Introduction to Chemical Reaction Engineering and AI	13
1.0 Preface	13
1.1 What is Chemical Reaction Engineering?	13
1.2 Chemical Reaction Engineering in Industry and Society	14
1.3 Overview of This Book.....	17
1.4 Using AI Tools for Learning and Professional Practice in Chemical Reaction Engineering.....	21
Chapter 1 Summary: What You Should Have Learned.....	30
Chapter 2: Reactor Classification and Real Reactor Systems.....	31
2.1 Classification by Phase Behavior	32
2.2 Classification by Mixing Pattern	35
2.3 Classification by Operating Mode: Batch vs. Continuous.....	39
2.4 Classification by Thermal Operation Mode	42
2.5 Fixed Bed Reactors	45
2.6 Bubble Column Reactors	48
2.7 Trickle Bed Reactors	50
2.8 Fluidized Bed Reactors	53
2.9 AI-Assisted Problem: Reactor Selection for Multiple Objectives.....	55
Chapter 2 Summary: What You Should Have Learned.....	57
Chapter 3: Reaction Stoichiometry and Kinetics	59
3.1 Stoichiometry and Balanced Chemical Equations	60
3.2 Extent of Reaction and the IUPAC Definition of Reaction Rate.....	62
3.3 Conversion, Completion, and Limiting Reactants	63
3.4 Temperature Dependence of Reaction Rates.....	65
3.5 Concentration Dependence: Rate Laws	67
3.6 Reversible Reactions and Equilibrium.....	69
3.7 Selectivity in Multiple Reaction Systems	71
3.8 Deducing Kinetics for Complex Reactions: An Example.....	73

3.9 AI-Assisted Problem: Temperature Optimization for a Reversible Reaction	74
3.10 Practice Problems (Hand calculations)	76
Chapter 3 Summary: What You Should Have Learned.....	78
Chapter 4: Ideal Reactor Models.....	79
4.1 Introduction to Ideal Reactor Models	80
4.2 Ideal Batch Reactor	80
4.3 Ideal Continuous Stirred Tank Reactor (CSTR)	85
4.4 Ideal Plug Flow Reactor (PFR)	89
4.5 Practice Problems	93
Chapter 4 Summary: What you should have learned	95
Chapter 5: Ideal Reactor Heat Balances	97
5.1 Introduction to Reactor Energy Balances	98
5.2 Energy Balance Fundamentals	99
5.3 Batch Reactor Energy Balance	101
5.4 Continuous Stirred Tank Reactor Energy Balance.....	104
5.5 Plug Flow Reactor Energy Balance	108
5.6 Practice Problems	112
Chapter 5 Summary: What You Should Have Learned.....	116
Chapter 6: Reactor Capacity and Variable Density Systems	117
6.1 Introduction to Variable Density Systems.....	118
6.2 The Extent of Reaction Approach.....	119
6.3 CSTR Design with Extent of Reaction	122
6.4 PFR Design with Extent of Reaction	124
6.5 Multiple Reactions with Variable Density	126
6.6 Practice Problems.....	133
Chapter 6 Summary: What You Should Have Learned.....	134
Chapter 7: Unsteady-State Reactors	135
7.1 Introduction to Unsteady-State Operation.....	136
7.2 Isothermal CSTR Transient Behavior	136

7.3 Non-Isothermal CSTR Transient Behavior	139
7.4 Plug Flow Reactor Transient Behavior.....	143
7.4.2 Transient Energy Balance for PFR	143
7.5 Startup and Shutdown Procedures	145
7.6 Advanced Practice Problems	146
Additional Practice Problems (Hand Calculations).....	147
Chapter 7 Summary: What You Should Have Learned.....	147
Chapter 8: Multiple Reactions and Selectivity	149
8.1 Introduction: The Challenge of Multiple Reactions	150
8.2 Classification of Multiple Reaction Systems	151
8.3 Selectivity and Yield Definitions.....	153
8.4 Reactor Selection for Parallel Reactions	153
8.5 Reactor Selection for Consecutive Reactions	154
8.6 Temperature Effects on Selectivity	154
8.7 Combined Reactor Systems.....	155
8.8 Worked Examples.....	155
8.9 Prompted Examples	159
8.10 Practice Problems	161
Chapter 8 Summary: What You Should Have Learned.....	163
Chapter 9: Equilibrium-Limited Processes.....	165
9.1 Introduction to Reversible Reactions	166
9.2 Equilibrium Relationships for Reversible Reactions	167
9.3 The Equilibrium Conversion Curve	168
9.4 Isothermal Reactor Design with Equilibrium Limitations.....	170
9.5 Adiabatic Reactor Design with Equilibrium Limitations.....	171
9.6 Simplified Heat Balance Models	172
9.7 The x-T Diagram and Rate Contours	172
9.8 Optimizing Reversible Reactions - Multiple Reactor Configurations.....	174
9.9 Worked Examples.....	176

9.10 Guided Learning Examples.....	180
9.11 Practice Problems	182
Chapter 9 Summary: What You Should Have Learned.....	183
Chapter 10: Residence Time Distribution and Non-Ideal Reactors	185
10.1 Introduction to Non-Ideal Reactors.....	186
10.2 The Residence Time Distribution (RTD).....	186
10.3 RTD for Ideal Reactors	189
10.4 The Zero Parameter Model.....	190
10.5 The Tanks-in-Series Model	192
10.6 The Axial Dispersion Model	193
10.7 Worked Examples.....	195
10.8 Guided Learning Examples.....	198
10.9 Practice Problems	199
Chapter 10 Summary: What You Should Have Learned.....	201
Chapter 11: Reactor Stability, Safety, and Risk Management	203
11.1 Introduction: From Stability Analysis to Comprehensive Risk Management.....	205
11.2 Fundamental Concepts in Reactor Stability.....	206
11.3 Risk Assessment Framework for Reactor Systems	213
11.4 Chemical Hazards in Reactor Systems.....	223
11.5 Mathematical Analysis of Reactor Stability	231
11.6 Lyapunov Stability Theory and Eigenvalue Analysis	236
11.6.2 Eigenvalue Calculation and Stability Criteria.....	237
11.7 Parametric Sensitivity and Safe Operating Regions.....	239
11.8 Process-Related Risks in Reactor Operation	244
11.9 Safety Instrumented Systems and Layer of Protection Analysis.....	250
11.10 Summary	253
Chapter 11 Summary: What You Should Have Learned.....	255
Chapter 12: Transport Resistance in Heterogeneous Catalysis	257
12.1 Introduction to Heterogeneous Catalysis	258

12.2 Mass Transfer Steps in Heterogeneous Catalysis	259
12.3 External Mass Transfer - Film Theory	260
12.4 Internal Diffusion and the Effectiveness Factor	261
12.5 The Thiele Modulus.....	263
12.6 The Weisz-Prater Criterion.....	264
12.7 Effect of Mass Transfer on Apparent Kinetics	266
12.8 Design Considerations for Catalyst Pellets	270
12.9 Worked Examples.....	272
12.10 Guided Learning Examples.....	276
Chapter 12 Summary: What You Should Have Learned.....	279
Index.....	281
APPENDIX A: Using the Textbook with AI	285
1. Ask Questions About the Content in any language	285
2. Get Summaries of Chapters or Sections	285
3. Work Through Exercises.....	285
4. Learn Through Guided Questions (Recommended)	285
5. Use It in Any Language.....	286
APPENDIX B Safe Use of AI - Project	287
Common AI mistakes in Chemical Engineering	290
APPENDIX C Examination problems	293

Chapter 1: Introduction to Chemical Reaction Engineering and AI

1.0 Preface

Chemical Reaction Engineering (CRE) lies at the heart of chemical engineering—it unites chemistry, thermodynamics, and transport phenomena into the design and operation of reactors that turn raw materials into useful products. This book introduces the principles of CRE while gradually developing the analytical and practical tools engineers use to design reactors that are efficient, safe, and sustainable.

In later sections, the text introduces modern methods for using Artificial Intelligence (AI) as an applied extension—a companion for both learning (*see APPENDIX A Using the Textbook with AI*) and professional engineering work (*see Safe Use of AI – Project*). By the end of this chapter, you should understand what CRE is, how it differs from related fields, why it matters to industry and society, and how the rest of this book builds toward design expertise.

Learning Objectives

After completing this chapter, you should be able to:

- Define the scope and purpose of chemical reaction engineering and explain how it differs from related disciplines such as chemical kinetics, catalysis, and process design.
- Identify and describe real-world applications where chemical reactor design addresses critical industrial and societal challenges across multiple scales (from microreactors to industrial plants) and sectors (energy, environment, pharmaceuticals, and sustainable chemistry).
- Navigate the structure and content of this textbook by understanding how fundamental principles (mass and energy balances, thermodynamics, kinetics, and transport phenomena) integrate to form reactor design methodologies and apply AI-assisted tools effectively to enhance your learning and professional practice.

1.1 What is Chemical Reaction Engineering?

Chemical Reaction Engineering (CRE) is the branch of chemical engineering that deals with the design, analysis, and optimization of chemical reactors. At its core, CRE asks a deceptively simple question: *How do we build and operate a vessel in which chemical reactions occur efficiently, safely, and economically?*

While chemical kinetics tells us *how fast* reactions proceed and thermodynamics tells us *how far* they can go, chemical reaction engineering tells us *how to make them happen* at the scale and conditions we need. This distinction is crucial. A reaction that works beautifully in a test tube may fail catastrophically in a 10,000-liter reactor. A catalyst that shows excellent selectivity in a

laboratory may become poisoned within hours in an industrial environment. Chemical reaction engineering bridges the gap between molecular-scale chemistry and industrial-scale production.

The scope of CRE encompasses both **design** and **analysis**:

- **Design** involves selecting reactor type, determining size, specifying operating conditions (temperature, pressure, flow rates), and configuring auxiliary systems (heating, cooling, mixing) to achieve desired production rates, conversions, and selectivities.
- **Analysis** involves understanding existing reactor performance, diagnosing problems, predicting behavior under different conditions, and evaluating safety margins and operational limits.

Chemical reaction engineering is distinct from—yet intimately connected to—several related disciplines:

- **Chemical kinetics** focuses on reaction mechanisms and rate laws at the molecular level. CRE *uses* kinetics as input but focuses on reactor-scale phenomena.
- **Catalysis** studies catalyst materials, active sites, and reaction pathways. CRE treats catalysts as components within reactor systems, addressing how to utilize them effectively at scale.
- **Process design** encompasses entire chemical plants, including separation units, heat exchangers, and control systems. CRE focuses specifically on the reactor—often the heart of the process—where chemical transformation occurs.

The chemical reactor is where raw materials become products, where energy is released or consumed, and where the economic viability of a process is often determined. Mastering chemical reaction engineering means mastering the art and science of making chemistry work in the real world.

1.2 Chemical Reaction Engineering in Industry and Society

Chemical reactors are everywhere—from the palm of your hand to facilities spanning square kilometers. They produce the fuels that power our transportation, the materials that build our infrastructure, the medicines that save lives, and increasingly, the solutions to our most pressing environmental challenges. Understanding how to design and operate these reactors is fundamental to addressing both industrial needs and societal problems.

1.2.1 Scale Diversity: From Micro to Mega

One of the remarkable aspects of chemical reaction engineering is its applicability across an enormous range of scales:

Microreactors with channel dimensions of 10-1000 micrometers enable rapid screening of reaction conditions, precise temperature control, and safe handling of hazardous chemistry.

Pharmaceutical companies use microfluidic reactors to explore thousands of synthetic routes in days rather than months, accelerating drug discovery while minimizing waste.

Laboratory and pilot-scale reactors ranging from milliliters to hundreds of liters serve as the crucial bridge between discovery and production. Here, reaction engineers validate kinetic models, test scale-up hypotheses, and identify potential operational challenges before committing to full-scale investment.

Industrial-scale reactors can hold tens of thousands of cubic meters and process millions of tons of material annually. The ammonia synthesis reactor—essential for fertilizer production that feeds billions—operates at extreme conditions (400-500°C, 150-250 bar) and exemplifies the engineering challenges of maintaining efficiency, safety, and catalyst life at massive scale.

The principles you'll learn in this book apply across all these scales, though the dominant phenomena and design challenges shift dramatically as size changes.

1.2.2 Energy Applications

The global energy transition presents some of the most demanding reactor design challenges of our time:

Hydrogen production for fuel cells and industrial processes requires reactors that can efficiently reform methane or electrochemically split water. Steam methane reforming reactors operate at high temperatures (800-900°C) with complex heat integration, while electrochemical reactors must balance reaction kinetics with mass transport of gases and ions across multiple phases.

Battery materials synthesis involves carefully controlled precipitation, calcination, and coating reactions to produce cathode and anode materials with precise particle sizes, morphologies, and compositions. Even small variations in reactor conditions can significantly impact battery performance and cycle life.

Biofuel production from biomass requires reactors that handle solid feedstocks, multiple phases, and reaction networks with dozens of competing pathways. Converting lignocellulosic material to ethanol or converting algal oils to biodiesel involves enzymatic reactors, catalytic upgrading, and careful management of inhibitory byproducts.

1.2.3 Environmental Applications

Reactors increasingly serve as solutions rather than sources of environmental problems:

CO₂ capture and conversion technologies aim to transform greenhouse gas emissions into valuable chemicals and fuels. Amine absorption reactors remove CO₂ from flue gas, while catalytic reactors can convert captured CO₂ into methanol, formic acid, or synthetic fuels—though making these processes economically viable remains a grand challenge.

Wastewater treatment relies on biological reactors where microorganisms break down organic pollutants and remove nutrients. Activated sludge reactors, membrane bioreactors, and anaerobic digesters must be designed to maintain stable microbial populations, handle variable feed compositions, and meet increasingly stringent discharge standards.

Air pollution control uses catalytic reactors to remove NO_x from vehicle exhausts and industrial emissions. The three-way catalytic converter in automobiles simultaneously oxidizes CO and hydrocarbons while reducing NO_x—all within milliseconds and across wide temperature ranges as driving conditions change.

1.2.4 Pharmaceutical Applications

The pharmaceutical industry increasingly embraces continuous manufacturing, fundamentally changing reactor design philosophy:

Active pharmaceutical ingredient (API) synthesis traditionally occurred in batch reactors with campaign-based production. Modern continuous flow reactors enable better control of exothermic reactions, improved product quality consistency, and significantly reduced production times. A synthesis that once required days in batch mode may occur in minutes in a continuous flow reactor.

Biopharmaceutical production uses bioreactors where living cells (bacteria, yeast, mammalian cells) produce complex protein therapeutics like monoclonal antibodies and vaccines. These reactors must maintain sterile conditions, control dissolved oxygen and pH precisely, and provide optimal nutrient feeding strategies—all while monitoring cell health and productivity in real-time.

1.2.5 Sustainable Chemistry

Designing reactors for sustainability requires rethinking traditional approaches:

Biomass conversion reactors transform renewable feedstocks (wood, agricultural residues, algae) into platform chemicals currently derived from petroleum. Hydrothermal liquefaction reactors process wet biomass at high pressures, eliminating energy-intensive drying steps. Gasification reactors convert solid biomass into synthesis gas for subsequent chemical synthesis.

Green chemistry processes minimize or eliminate hazardous substances. Supercritical CO₂ reactors replace organic solvents for polymerization and extraction. Photocatalytic reactors use sunlight to drive chemical transformations. Enzymatic reactors operate at ambient conditions, avoiding the high temperatures and pressures of conventional catalytic processes.

Polymer recycling via chemical depolymerization offers hope for closing the plastics loop. Pyrolysis reactors break down mixed plastic waste into oils and gases that can be re-refined into new plastics or chemicals, while solvolysis reactors selectively depolymerize specific polymers like PET back to monomers.

1.2.6 Traditional Chemical Industry

The foundation of modern chemical industry continues to rely on well-established reactor technologies:

Petrochemical production includes ethylene crackers (processing hundreds of tons per hour), catalytic reformers (converting naphtha to high-octane gasoline), and polymerization reactors (producing the plastics that pervade modern life). These reactors represent decades of optimization but still benefit from advances in modeling, control, and catalyst development.

Bulk chemicals like sulfuric acid, ammonia, and methanol are produced in some of the world's largest reactors. The contact process for sulfuric acid, the Haber-Bosch process for ammonia, and methanol synthesis reactors exemplify how thermodynamic constraints, kinetic limitations, and transport phenomena interact to determine optimal design and operation.

Each of these applications presents unique challenges, but all share common principles. Whether designing a microreactor for drug discovery or an industrial ammonia plant, you'll apply the same fundamental approach: combining mass and energy balances with reaction kinetics, thermodynamics, and transport phenomena to predict and optimize reactor performance.

1.3 Overview of This Book

This textbook guides you systematically from fundamental principles to advanced reactor design and optimization. The approach is integrative: we build complexity gradually, showing how basic conservation laws combine with physical property knowledge, thermodynamic constraints, and kinetic descriptions to create predictive reactor models.

1.3.1 Conceptual Framework: How the Pieces Fit Together

Chemical reaction engineering synthesizes knowledge from multiple disciplines. Understanding how these elements interconnect is crucial for effective reactor design. The concept map below illustrates these relationships:

Core Foundation: Mass and Energy Balances

- Located at the center of reactor design methodology
- Represents conservation principles applied to reactor systems
- All reactor analysis begins and ends here

Supporting Fundamental Principles:

1. **Laws of Continuity** → Mass and Energy Balances
 - Conservation of mass (overall and by species)
 - Conservation of energy (first law of thermodynamics)

- These laws provide the mathematical framework for all reactor models
2. **Transport Properties** → Mass and Energy Balances
 - Diffusion coefficients (mass transport)
 - Thermal conductivity (heat transport)
 - Viscosity (momentum transport)
 - Transport properties determine *how* mass and energy move within reactors
 3. **Chemical Thermodynamics** → Mass and Energy Balances
 - Equilibrium constraints (reaction limits)
 - Heats of reaction (energy source/sink terms)
 - Phase equilibria (for multiphase reactors)
 - Thermodynamics tells us *what is possible*
 4. **Reaction Kinetics** → Mass and Energy Balances
 - Rate laws (concentration and temperature dependence)
 - Activation energies
 - Catalyst activity and selectivity
 - Kinetics tells us *how fast* reactions proceed
 5. **Reaction Models** → Mass and Energy Balances
 - Stoichiometry (multiple reactions, selectivity)
 - Reaction networks (series, parallel, complex)
 - Catalyst deactivation models
 - Reaction models describe *what chemical transformations occur*

Integration into Reactor Models:

Mass and Energy Balances + (Continuity + Transport + Thermodynamics + Kinetics + Reaction Models) → **Reactor Models**

- **Reactor Models** describe spatial and temporal concentration and temperature profiles
- Different reactor types (batch, CSTR, PFR, and nonideal reactors) require different balance formulations
- Transport phenomena become increasingly important for multiphase reactors

Macrokinetic Models:

Reactor Models + Transport Limitations → **Macrokinetic Models**

- Effectiveness factors (diffusion within catalyst particles)
- External mass and heat transfer resistances
- Multiphase contacting (gas-liquid, gas-solid, gas-liquid-solid)
- Macrokinetics bridges molecular-scale kinetics with reactor-scale phenomena

Design and Optimization:

Reactor Models + Macrokinetic Models → **Reactor Design and Process Optimization**

- Sizing reactors for specified conversion/selectivity
- Selecting operating conditions (T, P, flow rates)
- Evaluating reactor stability and control strategies
- Optimizing performance subject to constraints (economic, safety, environmental)

This conceptual framework shows that reactor design is inherently multidisciplinary. You cannot design a reactor considering only kinetics or only thermodynamics or only transport—all elements must be integrated. The mathematics of this integration is the mass and energy balance.

1.3.2 Chapter Roadmap

The book progresses logically from fundamentals to advanced topics. The following roadmap shows how chapters build upon one another:

Chapter 1: Introduction to Chemical Reaction Engineering and AI (Current Chapter)

Introduces the scope and purpose of chemical reaction engineering, explores real-world applications across industries and society, and explains the structure of this textbook including how to effectively use AI tools for learning and professional practice.

Chapter 2: Reactor Classification and Real Reactor Systems

Introduces the different types of reactors used in chemical processes, including batch, continuous stirred-tank, and plug-flow reactors, along with real-world reactor systems and their applications in industry.

Chapter 3: Reaction Stoichiometry and Kinetics

Covers the fundamentals of reaction stoichiometry, including limiting reactants, conversion, and yield, along with chemical kinetics, rate laws, and temperature effects on reaction rates.

Chapter 4: Ideal Reactor mole balances

Develops mole balance equations for ideal reactors (batch, CSTR, PFR) and teaches how to design reactors for specified conversion assuming isothermal operation and constant density.

Chapter 5: Ideal reactor heat balances

Introduces energy balances for non-isothermal reactor operation, covering adiabatic and non-adiabatic cases, temperature effects on reaction rates, and optimal temperature profiles.

Chapter 6: Reactor capacity and density variation (gas phase reactions)

Addresses gas phase reactions where density changes significantly due to pressure, temperature, or molar changes, requiring modified reactor design equations.

Chapter 7: Unsteady-State reactors

Analyzes transient reactor behavior including start-up, shutdown, and response to disturbances using dynamic mole and energy balances for batch and continuous reactors.

Chapter 8: Multiple reactions and selectivity

Treats reaction systems with multiple reactions (parallel, series, complex networks), focusing on maximizing selectivity and yield of desired products through proper reactor selection and operation.

Chapter 9: Equilibrium limited processes

Addresses reversible reactions where equilibrium constraints limit conversion, covering equilibrium reactor design, temperature effects, and strategies to improve conversion such as product removal.

Chapter 10: Residence time distributions and nonideal reactors

Examines real reactor behavior that deviates from ideal flow patterns using residence time distribution theory, dispersion models, and compartment models to diagnose and predict performance.

Chapter 11 Reactor Stability, Safety, and Risk Management

Identify and assess process-related risks in chemical reactor systems, including thermal runaway, overpressure scenarios, equipment failures, human errors, and external hazards, applying systematic risk assessment methodologies.

Chapter 12: Introduction to transport resistance for heterogeneous catalysts

Introduces mass and heat transfer limitations in heterogeneous catalytic reactors, covering external mass transfer, internal pore diffusion, and effectiveness factors for catalyst particles.

1.3.3 How to Use This Book

Each chapter (starting from Chapter 2) follows a consistent structure:

1. **Learning objectives** clearly state what you should master
2. **Chapter-specific nomenclature** lists symbols introduced in that chapter
3. **Fundamental principles** are derived from first principles using SI units
4. **Worked examples** illustrate application of concepts with detailed solution steps
5. **Exercises** provide practice problems designed for AI-assisted solving (see Section 1.4)
6. **Chapter summary** reinforces key concepts

A comprehensive nomenclature table appears at the end of the book, consolidating all symbols used throughout the text. Refer to it whenever you encounter unfamiliar notation from previous chapters.

Mathematics is the language of chemical reaction engineering. While we derive equations from first principles to build understanding, the emphasis is on physical interpretation and engineering judgment. You should always ask: *What does this equation tell me about reactor behavior? How does changing this parameter affect performance? Does this result make physical sense?*

1.4 Using AI Tools for Learning and Professional Practice in Chemical Reaction Engineering

This textbook is designed with a modern reality in mind: powerful AI assistants like ChatGPT, Claude, and others are readily available and represent a transformative tool for both learning chemical reaction engineering and practicing it professionally. These tools serve two distinct but complementary purposes:

As a learning tool: AI helps you develop deeper understanding of CRE concepts, master problem-solving methodologies, and build intuition for reactor behavior through guided exploration. Define one project in your preferred AI bot for all your CRE tasks. In this project you specify that your objective is to learn CRE and the AI should guide you to a better understanding.

As a professional tool: AI accelerates routine calculations, enables rapid exploration of design alternatives, facilitates literature review and data analysis, and allows engineers to focus on higher-level decision-making and innovation.

Understanding how to leverage AI effectively in both contexts is essential for modern chemical engineers. However, AI is most valuable when used strategically—not as an answer generator, but as an intelligent assistant that enhances your capabilities while you maintain ultimate responsibility for engineering decisions.

1.4.1 The Role of AI in Your Learning

During your education, AI tools can assist with chemical reaction engineering in several ways:

For understanding concepts:

- Explaining difficult concepts from multiple perspectives
- Providing analogies and examples that clarify abstract ideas
- Breaking down complex derivations into digestible steps
- Answering "what if" questions to test understanding

For problem-solving:

- Guiding you through systematic problem-solving approaches
- Asking Socratic questions that help you discover solutions yourself

- Checking your work and identifying conceptual errors
- Suggesting alternative solution methods

For numerical computation:

- Solving differential equations (ODEs and PDEs) that arise in reactor modeling
- Performing iterative calculations such as finding reactor volumes, temperatures, or conversions
- Parameter estimation from experimental data
- Generating visualizations through plots and graphs

Critical principle: AI should *guide* you to understanding, not replace your thinking. The goal is not to get answers quickly, but to learn how to approach and solve reactor design problems independently. Use AI as a tutor that helps you work through problems step-by-step, not as a shortcut that bypasses the learning process.

1.4.2 The Role of AI in Professional Practice

As a practicing chemical engineer, AI becomes a powerful tool in your professional toolkit:

Design and optimization:

- Rapidly exploring multiple reactor configurations and operating conditions
- Performing sensitivity analyses to identify critical design parameters
- Optimizing complex systems with multiple objectives and constraints
- Generating design alternatives for comparison

Analysis and troubleshooting:

- Diagnosing operational problems by analyzing plant data
- Predicting impacts of process modifications before implementation
- Identifying root causes of performance deviations
- Evaluating safety margins and operating envelopes

Knowledge management:

- Quickly accessing and synthesizing technical literature
- Extracting key information from patents, papers, and reports
- Staying current with emerging technologies and methods
- Documenting decisions and creating technical reports

Collaboration and communication:

- Translating complex technical concepts for non-technical stakeholders
- Preparing presentations and visualizations
- Generating preliminary designs for team discussion
- Facilitating multidisciplinary problem-solving

Important distinction: In professional practice, you use AI to enhance productivity and extend your capabilities, but **you remain responsible for verifying results, ensuring safety, meeting regulatory requirements, and making final engineering judgments.** AI is a tool, not a substitute for professional expertise and accountability.

1.4.3 General Prompting Strategies

Key Principles for Effective AI Prompts:

1. Be Specific and Detailed: Vague prompts yield vague responses. Specify exactly what you need.
2. Provide Context: Include relevant background, assumptions, and constraints.
3. Request Step-by-Step Reasoning: Ask AI to show its work, not just provide answers.
4. Specify Format: Indicate desired output format (code, equations, tables, etc.).
5. Ask for Verification: Request that AI check its own work and identify potential issues.
6. Iterate: Refine prompts based on initial responses to improve results.
7. Request References: Ask for sources or basis for suggestions (but verify independently).
8. Set Boundaries: Clearly state what is known vs. what needs determination.

Effective use of AI requires clear, structured communication. Follow these principles:

Be specific about context: Always state that you're working on a chemical reaction engineering problem. Specify the reactor type, assumptions, and what you're trying to find.

✗ Poor: "Solve this equation"

✓ Good: "I'm analyzing an isothermal batch reactor with a second-order reaction $A \rightarrow B$. I need to solve the differential equation $dC_A/dt = -k \cdot C_A^2$ with initial condition $C_{A,0} = 2 \text{ mol/L}$ and $k = 0.5 \text{ L/(mol}\cdot\text{min)}$. Can you help me solve for C_A as a function of time?"

Request explanations and strategic guidance, not just answers: The most valuable help AI provides is helping you understand *why* you're taking certain steps and *what* strategic decisions need to be made, not just performing algebraic manipulations.

✗ Poor: "What's the answer?"

✓ Good: "Can you help me think through what type of reactor would be best for this highly exothermic consecutive reaction where I want to maximize the intermediate product? What factors should I consider?"

Break complex problems into strategic steps: Don't ask AI to solve entire reactor design problems in one prompt. Work through systematically, focusing on understanding and decision-making at each stage.

✗ Poor: "Design a reactor for this process"

✓ Good: "I'm designing a reactor for this exothermic reaction. Help me think through the key

design decisions: Should I use batch or continuous? What are the trade-offs? How should I handle the heat of reaction? What are the safety considerations?"

Focus on concepts, not arithmetic: AI should help you understand chemical engineering principles and make strategic decisions, not just manipulate equations.

✓ Good: "Why would increasing temperature help with kinetics but hurt with equilibrium for this exothermic reversible reaction? How do I find the optimal temperature?"

✓ Good: "What physical phenomena determine whether I need to account for mass transfer limitations in this catalytic reactor?"

✓ Good: "How do I decide between using a CSTR versus a PFR for this parallel reaction system?"

Verify and validate: Always check if AI results make physical sense. Ask follow-up questions if something seems wrong.

✓ Good follow-up: "The conversion you calculated is 120%. That's impossible—can you check the calculation? What might have gone wrong?"

Request different approaches: AI can show multiple solution methods, helping you understand which approach is most efficient or revealing.

✓ Good: "Can you show me both an analytical solution and a numerical solution to this ODE, and explain when each approach is preferable?"

1.4.4 Specific Prompting Examples for CRE Tasks

Here are example prompts for common chemical reaction engineering tasks, emphasizing conceptual guidance over algebraic manipulation:

Example 1: Understanding Reactor Selection (Conceptual/Strategic)

Task type: Developing engineering judgment for reactor choice

Effective prompt:

"I need to choose a reactor for producing a pharmaceutical intermediate through the consecutive reactions $A \rightarrow B \rightarrow C$, where B is my desired product. The reactions are both first-order with $k_1 = 0.3 \text{ h}^{-1}$ and $k_2 = 0.1 \text{ h}^{-1}$.

Do not solve any equations or do calculations. Instead, help me think through this decision:

1. What are the key characteristics of CSTR, PFR, and batch reactors that matter for consecutive reactions?
2. Why is maximizing intermediate (B) fundamentally different from maximizing conversion?
3. What reactor configuration would you expect to perform best for this case and why?
4. What operational considerations might override the purely technical performance comparison?"

Why this works: Focuses on developing engineering judgment and understanding trade-offs, not on numerical calculations.

Example 2: Interpreting Physical Phenomena (Conceptual)

Task type: Understanding thermal effects in reactors

Effective prompt:

"I'm analyzing an exothermic reaction in a CSTR. When I solve the coupled mass and energy balances, I find three possible steady states: one at low conversion and low temperature, one at medium conversion and medium temperature (which turns out to be unstable), and one at high conversion and high temperature.

Don't solve any equations. Help me understand:

1. What physical phenomena cause multiple steady states to exist?
2. Why is the middle steady state unstable?
3. How does the reactor "choose" between the low and high steady states in practice?
4. What are the safety and operational implications?
5. How might I design the reactor and control system to handle this behavior?"

Why this works: Emphasizes understanding the physics and engineering implications rather than mathematical manipulation.

Example 3: Solving Differential Equations (Computational)

Task type: Numerical solution of reactor design equations

Effective prompt:

"Now that I understand the conceptual framework for my adiabatic PFR with consecutive reactions $A \rightarrow B \rightarrow C$, I need to solve the coupled ODEs:

$$\frac{dC_A}{dV} = -\frac{k_1 C_A}{q}$$
$$\frac{dC_B}{dV} = \frac{(k_1 C_A - k_2 C_B)}{q}$$
$$\frac{dC_C}{dV} = \frac{k_2 C_B}{q}$$

With $T = T_0 + \Delta T_{ad} \cdot X$ and $k_i = A_i \cdot \exp(-E_i/RT)$

Given: $C_{A,0} = 2$ mol/L, $q = 5$ L/s, $T_0 = 400$ K, $\Delta T_{ad} = 50$ K, and kinetic parameters...

Please:

1. Set up the numerical solution
2. Solve from $V = 0$ to $V = 50$ L
3. Plot C_A , C_B , C_C vs. V

4. Identify the volume where C_B is maximum

Explain your numerical approach and show results."

Why this works: Appropriate use of AI for numerical computation after conceptual understanding is established.

Example 4: Design Decision Analysis (Strategic)

Task type: Comparing alternatives and making design decisions

Effective prompt:

"I'm evaluating three options for my reactor system:

- Option A: Single large CSTR
- Option B: Three smaller CSTRs in series with interstage cooling
- Option C: PFR with recycle

Before we calculate anything, help me think systematically about:

1. What are the fundamental performance differences I should expect?
2. What are the capital cost implications (relative equipment costs)?
3. What are the operational complexity trade-offs?
4. How does each option handle temperature control for my exothermic reaction?
5. Which option offers the most operational flexibility?
6. What criteria should I use to make the final decision?

Once we've established this framework, we can do calculations to quantify the differences."

Why this works: Establishes strategic thinking before diving into calculations; focuses on decision-making framework.

Example 5: Troubleshooting and Error Analysis (Diagnostic)

Task type: Understanding and fixing conceptual errors

Effective prompt:

"I'm getting a strange result in my CSTR energy balance. When I increase the cooling water flow rate, my steady-state reactor temperature goes UP instead of down. This seems wrong.

Don't recalculate for me. Instead:

1. What physical explanations could account for this counterintuitive behavior?
2. Is this result actually possible for certain types of reactions/conditions?
3. How would I determine if this is a real physical phenomenon vs. a calculation error?
4. What should I check in my equations and assumptions?
5. If this is real (multiple steady states), what does it mean for reactor operation?"

Why this works: Develops diagnostic thinking and physical intuition; emphasizes understanding over calculation.

Example 6: Professional Engineering Analysis (Application)

Task type: Real-world engineering problem-solving

Effective prompt:

"I'm a process engineer and our plant's ammonia synthesis reactor is showing declining conversion over the past 6 months. Operating data shows:

- Inlet temperature: 450°C (constant)
- Pressure: 200 bar (constant)
- Feed composition: stoichiometric N₂/H₂ (constant)
- Conversion: decreased from 25% to 18%
- Outlet temperature: increased from 520°C to 535°C

Help me diagnose this systematically:

xWhy this works: Real professional application; focuses on diagnostic reasoning and systematic troubleshooting, not just calculation.

Example 7: Find errors in my hand calculations

Task type: Help me correct my errors

- Upload the Problem
- Take a photo of your hand calculations

Effective prompt:

"I'm getting a strange result in my calculations. Are my approach to the problem and calculations correct"

Why this works: Focuses on developing engineering judgment, not on numerical calculations.

1.4.5 Warnings and Limitations

While AI tools are powerful, you must be aware of their limitations in chemical reaction engineering contexts:

⚠ AI can make calculation errors: Always verify numerical results, especially for:

- Limited Numerical Accuracy: LLMs are not designed for precise numerical calculations.
- Units conversions
- Sign conventions (positive/negative for heat effects, reaction rates)
- Boundary conditions in differential equations
- Thermodynamic consistency (e.g., negative absolute temperatures, conversions >100%)

⚠ **AI may not recognize physically impossible results:** You must apply engineering judgment:

- Negative concentrations or reaction rates
- Violations of mass/energy conservation
- Temperatures or pressures outside feasible ranges
- Selectivities that violate stoichiometric constraints

⚠ **AI may misinterpret specialized notation:** Chemical engineering has conventions that differ from other fields:

- Subscripts and superscripts (A^0 vs. A_0 have different meanings)
- Dimensionless numbers and their definitions
- Specific terminology (e.g., "conversion" has a precise definition)

⚠ **AI may not know the latest correlations or data:** For physical properties, safety data, or recent research:

- Verify critical properties against reliable databases (NIST, DIPPR)
- Check safety information against MSDS/SDS
- Confirm that correlations are appropriate for your system

⚠ **AI cannot replace professional judgment and accountability:**

- You are responsible for safety, regulatory compliance, and final decisions
- AI provides analysis and recommendations; you make engineering judgments
- Verify critical results through multiple methods
- Document assumptions and decision rationale
- Never implement AI recommendations without thorough review

⚠ **AI lacks context about your specific learning goals or professional constraints:**

- Your instructor may want you to use specific solution methods
- Your company may have design standards or preferred approaches
- Safety regulations may impose constraints AI doesn't know about
- Economic and practical considerations may override theoretical optimums

Always clarify assignment requirements with your instructor and consult company standards and regulations in professional practice.

Critical AI Limitations:

- No Physical Understanding: AI has no true understanding of physics or engineering principles—it pattern-matches based on training data.
- Hallucination: AI can confidently state false information or generate plausible-sounding but incorrect equations or correlations.
- Context-Dependent Accuracy: Performance varies greatly depending on how common the problem is in training data.

- **No Judgment:** AI cannot assess engineering reasonableness, safety implications, or practical feasibility.
- **Opaque Reasoning:** The basis for AI suggestions is often unclear, making error detection difficult.
- **Limited Numerical Accuracy:** LLMs are not designed for precise numerical calculations.
- **Outdated Information:** Training data has cutoff dates; recent developments may not be included.
- **Licensing and Proprietary Concerns:** AI-generated content may have unclear intellectual property status.

1.4.6 Best Practices for AI-Assisted Learning and Professional Work

For Learning:

1. **Attempt first, then consult:** Try problems independently before asking AI for help. This builds problem-solving skills and helps you ask better questions.
2. **Focus on understanding over answers:** Use AI to help you understand *why* and *how*, not just to get solutions.
3. **Use AI as a dialogue:** Engage in back-and-forth conversation. Ask "why?" and "what if?" questions. Request alternative explanations if something is unclear.
4. **Test your understanding:** After AI helps you solve a problem, try a similar problem independently. If you can't, you relied too heavily on AI.
5. **Document your learning:** Keep notes on concepts AI helped you understand. Write summaries in your own words. This consolidates knowledge.

For Professional Practice:

1. **Use AI to explore alternatives:** Rapidly generate and evaluate multiple design options before detailed analysis.
2. **Verify critical results independently:** For safety-critical or high-stakes decisions, verify AI calculations through alternative methods.
3. **Maintain documentation:** Record what AI tools were used, what assumptions were made, and what verification was performed.
4. **Know when NOT to use AI:** Some situations require traditional methods, established procedures, or regulatory-approved approaches.
5. **Understand liability and responsibility:** You, not the AI, are professionally responsible for engineering decisions.

Ethical Considerations:

For Learning:

- Follow your institution's policies on AI use
- Generally appropriate: Using AI to understand concepts, check work, debug approaches
- Generally not appropriate: Having AI solve assignments you submit as your own work
- When in doubt, ask your instructor

For Professional Practice:

- Comply with company policies and industry standards
- Protect proprietary information (be cautious about what data you share with AI tools)
- Ensure quality and safety are never compromised
- Maintain professional liability insurance awareness

Remember: The goal in learning is to become a competent chemical reaction engineer who can solve problems independently. In professional practice, the goal is to use all available tools—including AI—to deliver safe, efficient, and economical designs. AI is a powerful tool for both purposes, but human expertise, judgment, and accountability remain central.

Nomenclature

The following symbols are introduced in Chapter 1. A comprehensive nomenclature covering all chapters appears in Appendix B at the end of the book.

C	molar concentrations (mol/m^3)
k	Reaction rate constant (varies)
T	Temperature (K)
V	Volume (m^3)
x	Conversion (-)

Chapter 1 Summary: What You Should Have Learned

After completing this chapter, you should be able to:

1. Define chemical reaction engineering and explain its role in transforming laboratory chemistry into industrial-scale production
2. Distinguish between chemical reaction engineering and related disciplines including chemical kinetics, catalysis, and process engineering
3. Recognize applications of chemical reaction engineering across diverse industries
4. Understand the conceptual framework connecting stoichiometry, kinetics, thermodynamics, and reactor models
5. Use AI tools effectively as learning aids while maintaining critical thinking
6. Navigate this textbook effectively using its structure and features

Chapter 2: Reactor Classification and Real Reactor Systems

Learning Objectives

After completing this chapter, you should be able to:

- Classify chemical reactions based on the number and type of phases present (homogeneous vs. heterogeneous), and identify the role of solid phases as either reactants or catalysts in multiphase systems.
- Distinguish between ideal mixing patterns—perfect mixing (CSTR) and plug flow (PFR)—and explain how concentration and temperature profiles differ fundamentally between these two extremes.
- Describe how real reactors can be modeled as combinations of ideal reactors (tanks in series, PFR-CSTR combinations) and predict qualitatively how performance varies with configuration.
- Compare and contrast batch and continuous reactor operation, including advantages, disadvantages, and typical industrial applications for each mode.
- Analyze the implications of isothermal versus adiabatic reactor operation and identify which thermal mode is appropriate for different reaction types (exothermic, endothermic, equilibrium-limited).
- Describe the design, operation, and applications of fixed bed reactors, including how to handle heat management through tube bundles, multiple beds with interstage cooling, and recycle strategies.
- Explain the operating principles of trickle bed reactors for gas-liquid-solid systems, including hydrodynamic regimes, wetting efficiency, and typical applications in petroleum refining and chemical synthesis.
- Analyze fluidized bed reactor characteristics, including fluidization regimes, advantages for temperature control and catalyst regeneration, and challenges related to solid entrainment and gas bypassing.
- Select appropriate reactor types and configurations for given reaction systems based on phase behavior, heat effects, kinetics, and process constraints.

Nomenclature

The following symbols are introduced in this chapter and supplement the comprehensive nomenclature in Appendix B:

Roman Letters

d_p	Particle diameter (m)
L	Reactor length (m)
N	Number of tanks in series (dimensionless)

q	Volumetric flow rate (L/s or m ³ /s)
T_{in}	Inlet temperature (K)
T_{out}	Outlet temperature (K)
u	Superficial velocity (m/s)
u_{mf}	Minimum fluidization velocity (m/s)
V	Reactor volume (L or m ³)
W	Catalyst mass (kg)

Greek Letters

ε	Void fraction or porosity (dimensionless)
ρ_b	Bulk density (kg/m ³)
τ	Space time or mean residence time (s or min)

Abbreviations

CSTR	Continuously Stirred Tank Reactor
PFR	Plug Flow Reactor
FBR	Fixed Bed Reactor
TBR	Trickle Bed Reactor

2.1 Classification by Phase Behavior

Before we can design a reactor, we must understand the physical state of the reacting system. The number and type of phases present profoundly affect reactor design, dictating everything from mixing strategies to heat transfer mechanisms to catalyst contacting patterns. A phase is a physically distinct, homogeneous portion of a system—gas, liquid, or solid—separated from other phases by definite boundaries.

2.1.1 Homogeneous (Single-Phase) Reactions

In homogeneous reactions, all reactants and products exist in a single phase—either gas or liquid. These systems offer the simplest design case because concentration and temperature can be assumed uniform at any point in the reactor (though they may vary with position in plug flow or with time in batch operation).

Gas-phase reactions

Gas-phase reactions occur when all species exist as gases at reaction conditions. Examples include:

- **Ammonia synthesis:** $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ at 400-500°C and 150-250 bar
- **Ethylene oxide production:** $\text{C}_2\text{H}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_2\text{H}_4\text{O}$ at 250-300°C over silver catalyst
- **Thermal cracking:** $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$ at 750-900°C

Gas-phase systems benefit from low viscosity enabling good mixing but often require high temperatures. Volume changes during reaction significantly affect design calculations, particularly when the number of moles changes (we'll address this systematically in Chapter 6).

Liquid-phase reactions

Liquid-phase homogeneous reactions involve all species dissolved in a liquid medium. Examples include:

- **Esterification:** $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$ with acid catalyst
- **Polymerization:** Solution polymerization of styrene in organic solvents
- **Saponification:** Hydrolysis of esters in aqueous base

Liquid-phase reactions typically proceed at moderate temperatures due to molecular proximity enhancing collision frequency. Volume changes are usually negligible (constant density assumption holds), simplifying reactor design. Heat removal is often easier than in gas systems due to higher heat transfer coefficients.

2.1.2 Heterogeneous (Multiphase) Reactions

Heterogeneous reactions involve multiple phases. The presence of phase boundaries introduces mass transfer resistances and complicates reactor analysis. The solid phase may participate as either a reactant (consumed) or a catalyst (unchanged).

Gas-Solid Reactions

Gas-solid systems are perhaps the most industrially important category, encompassing both catalytic and non-catalytic reactions.

Solid as catalyst (non-consumable):

- **Catalytic cracking:** Heavy hydrocarbons \rightarrow lighter products over zeolite catalyst at 500-550°C
- **Fischer-Tropsch synthesis:** $\text{CO} + \text{H}_2 \rightarrow$ hydrocarbons over Co or Fe catalyst
- **Automotive exhaust treatment:** Simultaneous oxidation and reduction over Pt/Pd/Rh catalyst

Catalytic gas-solid systems dominate industrial practice. The catalyst provides active sites where reactions occur at rates orders of magnitude faster than in the gas phase. Catalyst

design involves balancing activity, selectivity, stability, and cost. We'll explore the complexities of catalyst effectiveness and mass transfer limitations in Chapter 12.

Solid as reactant (consumable):

- **Coal combustion:** $C(s) + O_2(g) \rightarrow CO_2(g)$
- **Iron ore reduction:** $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$
- **Roasting of sulfide ores:** $2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$

When the solid is consumed, reactor design must account for changing particle size, surface area, and potentially changing bulk density as reaction proceeds. The shrinking core model provides a framework for analyzing these systems.

Gas-Liquid Reactions

Gas-liquid systems require dissolving gaseous reactants into liquid before reaction can occur. The gas-liquid interface and subsequent liquid-phase diffusion often limit overall rates. Examples include:

- **Chlorination:** Dissolving Cl_2 in organic liquids for chlorination reactions
- **Oxidation:** Air oxidation of cumene to cumene hydroperoxide in liquid phase
- **Absorption with reaction:** CO_2 absorption into amine solutions

Reactor design must promote good gas-liquid contact through agitation, sparging, or specialized contacting devices like bubble columns or packed towers. The interplay between mass transfer and chemical kinetics determines whether the system is kinetically controlled or mass transfer limited.

Liquid-Solid Reactions

Liquid-solid systems are common in fine chemical synthesis and pharmaceutical manufacturing:

- **Adsorption from liquids:** Removing impurities from water
- **Ion exchange:** Water softening using solid resin beds
- **Leaching:** Extraction of copper from ore using sulfuric acid

Slurry reactors suspending fine catalyst particles in liquid are common for these systems, providing good heat transfer and the ability to add or remove catalyst. Alternatively, the liquid can flow through packed beds of catalyst.

Liquid-Liquid Reactions

When reactants reside in immiscible liquid phases, one phase must be dispersed into the other, creating interfacial area for reaction:

- **Nitration:** Organic compound in organic phase reacting with nitric acid in aqueous phase

- **Phase transfer catalysis:** Using catalysts to transfer reactants between phases
- **Polymerization:** Emulsion polymerization with monomer droplets in aqueous medium

Intensive mixing is essential to maximize interfacial area. Coalescence and redispersion dynamics make these systems particularly challenging to model and scale up.

Gas-Liquid-Solid (Three-Phase) Reactions

Three-phase systems combine the challenges of both gas-liquid and liquid-solid mass transfer with chemical reaction. The solid is typically a catalyst:

- **Hydrodesulfurization:** Removing sulfur from petroleum fractions by reaction with H_2 over CoMo or NiMo catalyst
- **Hydrogenation:** Adding H_2 to liquid organic compounds over Pd or Pt catalyst
- **Fischer-Tropsch in slurry phase:** Synthesis gas reacting over suspended catalyst particles

These systems require specialized reactor designs—trickle bed reactors or slurry reactors—which we'll examine in detail in Section 2.7.

2.2 Classification by Mixing Pattern

How fluid elements mix within a reactor fundamentally determines concentration and temperature profiles, and consequently, reactor performance. Real reactors exhibit complex flow patterns, but we can understand their behavior by first mastering two idealized extremes: perfect mixing and plug flow.

2.2.1 Perfect Mixing: The Continuously Stirred Tank Reactor (CSTR)

In a perfectly mixed reactor, every fluid element entering the reactor is instantaneously and uniformly distributed throughout the entire volume. This idealization implies:

- **Uniform composition:** Concentration is the same at every point in the reactor and equals the outlet concentration
- **Uniform temperature:** No spatial temperature gradients exist within the reactor
- **Well-stirred condition:** Mixing is so vigorous that composition and temperature instantly equilibrate throughout

The continuously stirred tank reactor (CSTR)—also called a continuous flow stirred tank reactor (CFSTR), mixed flow reactor, or backmix reactor—is the archetype of perfect mixing. A mechanical agitator or jet mixer ensures that feed entering the reactor immediately encounters the outlet composition and temperature.

This has profound implications: reactants entering the CSTR are immediately diluted to outlet concentrations, which are much lower than inlet concentrations. For a single

irreversible reaction, this means the CSTR operates at the lowest driving force throughout its entire volume. This apparent disadvantage must be weighed against advantages:

- **Easy temperature control:** Uniform temperature simplifies heat exchange design
- **Constant outlet composition:** Steady-state operation provides consistent product quality
- **Forgiving to disturbances:** Large thermal inertia buffers against upsets
- **Favorable for complex kinetics:** Low reactant concentrations may enhance selectivity for certain reaction networks



Figure 2-1 Continuous stirred tank reactor (CSTR)

2.2.2 Plug Flow: The Plug Flow Reactor (PFR)

At the opposite extreme, plug flow assumes that fluid moves through the reactor as a series of infinitesimally thin "plugs" with no axial mixing. Fluid elements enter, travel through the reactor maintaining their identity, and exit in the same order they entered. This idealization implies:

- **Axial concentration gradients:** Concentration varies continuously along the reactor length as reaction proceeds
- **Axial temperature gradients:** Temperature may vary along the length (if non-isothermal)
- **No back-mixing:** Fluid elements at position z have never been in contact with fluid downstream
- **Radial uniformity:** Properties are uniform across any cross-section (no radial gradients)

The plug flow reactor (PFR)—also called a piston flow reactor or tubular reactor—is typically a long tube or pipe through which reactants flow. Fixed bed catalytic reactors closely approximate plug flow when properly designed. Each position along the reactor corresponds

to a different extent of reaction, with reactants progressively consumed as they flow toward the outlet.

For irreversible reactions, the PFR operates at high driving force (high reactant concentration) near the inlet and progressively lower driving force toward the outlet. This generally makes PFRs more volume-efficient than CSTRs for the same conversion. However, PFRs present challenges:

- **Temperature control complexity:** Axial temperature gradients require distributed heat exchange
- **Potential hot spots:** Exothermic reactions can create dangerous temperature excursions
- **Difficult heat exchange:** High surface-area-to-volume ratio needed for effective cooling
- **Sensitivity to upsets:** Less thermal inertia means faster response to disturbances

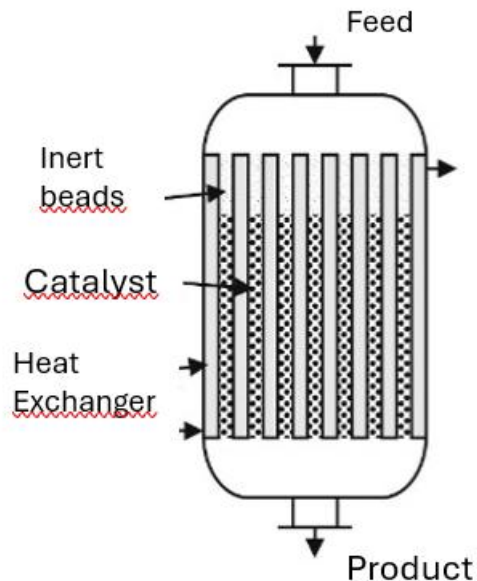


Figure 2-2 Packed bed with heat exchange

2.2.3 Comparison: CSTR vs. PFR Performance

For simple irreversible reactions with positive reaction order, plug flow reactors require less volume than CSTRs to achieve the same conversion. This stems from the concentration profile: in a PFR, high concentrations near the inlet drive fast reaction where it matters most, while the CSTR operates at uniformly low concentration everywhere.

However, this is not universally true. For some reaction networks—particularly those with undesired higher-order side reactions—the CSTR's low concentrations may actually be

advantageous. The choice between reactor types requires careful analysis of the specific kinetics and selectivity objectives.

2.2.4 Real Reactors: Tanks in Series and Combined Configurations

Real reactors rarely achieve perfect mixing or ideal plug flow. Instead, they exhibit intermediate behavior that can be modeled as combinations of ideal reactors.

Tanks in Series

A series of N equal-volume CSTRs approaches plug flow behavior as N increases. With $N = 1$, we have a single CSTR. As $N \rightarrow \infty$, the system approaches a PFR. This model is powerful because:

- It captures real reactor behavior using a single parameter (N)
- Intermediate N values model partial back-mixing
- Multiple physical stirred tanks in series are actually used industrially

Industrial examples include polymerization trains where 3-6 CSTRs in series provide plug-flow-like conversion profiles while maintaining good temperature control in each vessel.

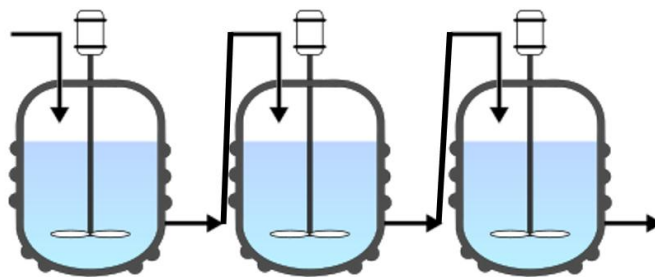


Figure 2-3 Continuous stirred tank reactors in series

PFR with Recycle

Recycling a portion of outlet stream to the inlet creates partial back-mixing, shifting PFR behavior toward CSTR behavior. The recycle ratio (recycle flow/fresh feed flow) quantifies the extent of back-mixing. Applications include:

- Temperature control for highly exothermic reactions (recycle cools inlet)
- Maintaining minimum reactant concentration to avoid extinction
- Improving selectivity by diluting feed

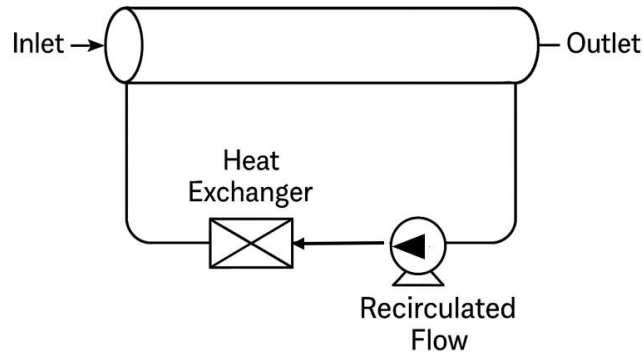


Figure 2-4 Tubular reactor with recirculated flow

CSTR followed by PFR

This configuration combines advantages of both reactor types: the CSTR provides good mixing and temperature control for the initial high-rate region, while the PFR efficiently completes conversion. This arrangement is common in polymerization and other reactions where the optimal mixing pattern changes as conversion increases.

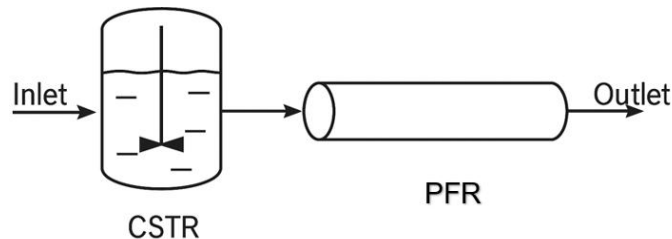


Figure 2-5 CSTR followed by PFR

2.3 Classification by Operating Mode: Batch vs. Continuous

Beyond phase behavior and mixing pattern, reactors are classified by their time-dependence: batch operation (unsteady state) or continuous operation (steady state at the system level).

2.3.1 Batch Reactors

In batch operation, reactants are charged to the reactor, the reaction proceeds for a specified time, then products are discharged. No flow enters or leaves during the reaction period. The batch reactor is inherently unsteady-state: composition and temperature change with time.

Characteristics:

- **Unsteady-state operation:** All properties vary with time

- **Well-mixed contents:** Typically stirred to ensure uniformity
- **Flexible operation:** Easy to change products, recipes, conditions
- **Batch-to-batch variability:** Achieving consistent quality requires careful control
- **Downtime required:** Filling, emptying, cleaning reduce effective production rate

Advantages:

- **Low capital cost:** Simple vessel, minimal auxiliary equipment
- **Flexibility:** Same equipment produces different products
- **High conversion per pass:** Can operate until desired conversion achieved
- **Quality control:** Each batch can be tested before release
- **Contamination isolation:** Problems confined to single batch

Disadvantages:

- **Labor intensive:** Requires manual operations for filling, discharging, cleaning
- **Batch-to-batch variability:** Product quality can vary
- **Downtime:** Filling, emptying, cleaning time is non-productive
- **Scale-dependent heat transfer:** Surface-to-volume ratio decreases with scale, complicating scaleup
- **Safety concerns:** Large inventory of reactive material in single vessel

Typical applications:

- **Pharmaceuticals:** Small production volumes, many products, stringent quality requirements
- **Specialty chemicals:** Diverse product slate, frequent changeovers
- **Polymerization:** Control of molecular weight distribution through batch recipes
- **Biotechnology:** Fermentation processes with sterility requirements

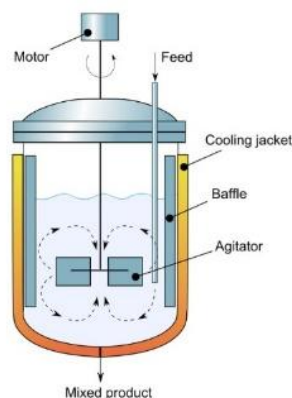


Figure 2-6 Batch reactor with no inflow/outflow

2.3.2 Continuous Reactors

In continuous operation, reactants continuously flow into the reactor and products continuously flow out. After an initial start-up period, the system reaches steady state where all properties at any given location remain constant with time (though they vary with position in plug flow reactors).

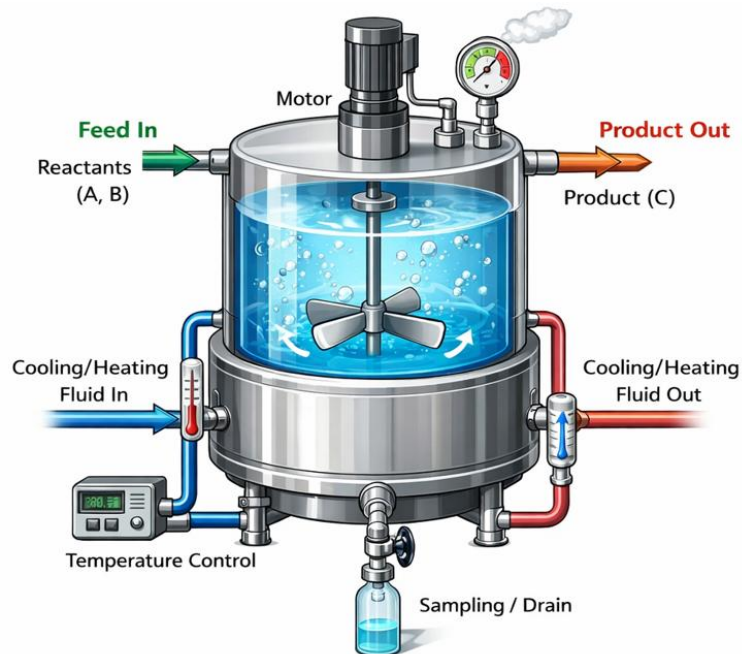


Figure 2-7 CSTR schematic with inlet, outlet, stirrer, and uniform concentration throughout.

Characteristics:

- **Steady-state operation:** Time-invariant at any given location
- **Continuous feed and discharge:** Material flows constantly
- **Consistent product quality:** Steady conditions yield uniform output
- **High throughput:** No downtime for filling/emptying
- **Dedicated operation:** Optimized for specific product

Advantages:

- **High production rates:** No batch cycle downtime
- **Consistent quality:** Steady-state operation eliminates batch-to-batch variation
- **Automation-friendly:** Continuous monitoring and control
- **Better heat integration:** Steady heat flows enable efficient heat exchange networks
- **Smaller reactor volume:** No need to accommodate entire batch; only working volume needed

Disadvantages:

- **High capital cost:** Complex equipment, instrumentation, control systems

- **Inflexibility:** Difficult to change products or conditions
- **Long start-up:** Reaching steady state can take hours to days
- **Contamination propagation:** Problems affect all downstream material until corrected
- **Economic viability:** Only justified for large-volume products

Typical applications:

- **Commodity chemicals:** Ammonia, ethylene, sulfuric acid—high volume, consistent demand
- **Petroleum refining:** Catalytic cracking, reforming, hydrotreating
- **Polymerization:** Polyethylene, polypropylene—high volume polymers
- **Catalytic processes:** Fixed bed catalytic reactors for large-scale synthesis

2.3.3 Semi-Batch Operation

Semi-batch operation combines elements of both batch and continuous modes. Typically, one reactant is charged initially while another is fed continuously, or products are continuously removed while reactants remain. This hybrid approach offers unique advantages:

- **Concentration control:** Continuous feed of one reactant maintains optimal concentration ratios
- **Temperature management:** Controlled addition rate limits heat generation
- **Safety:** Maintaining low concentration of hazardous reactant
- **Selectivity enhancement:** Controlling reactant ratio favors desired pathways

Applications include chlorination reactions (gradual Cl_2 addition), nitration (slow addition of nitrating agent), and polymerization (monomer feed rate controls molecular weight).

2.4 Classification by Thermal Operation Mode

How we manage heat in a reactor profoundly affects performance, safety, and operability. Two limiting cases—*isothermal* and *adiabatic* operation—provide useful reference points for understanding real reactors, which typically fall somewhere between these extremes.

2.4.1 Isothermal Reactors

In *isothermal* operation, temperature remains constant throughout the reactor and over time. For continuous reactors, $T = T_{\text{out}} = T_{\text{in}}$ at every point. For batch reactors, T remains constant throughout the reaction period. Achieving true *isothermal* operation requires:

- **Perfect heat exchange:** Heat generated or consumed by reaction is instantly removed or supplied
- **Perfect temperature control:** Coolant/heating medium maintains constant temperature

Of course, true isothermal operation is impossible—it represents an idealization approached when heat transfer is very efficient relative to heat generation or consumption.

Approaches to isothermal operation:

- **Jacketed stirred tanks:** Thermal fluid in jacket exchanges heat with well-mixed contents
- **Internal coils:** Heat exchange coils immersed in reactor contents
- **Multi-tubular reactors:** Many small-diameter tubes with shell-side coolant/heating medium
- **Dilution:** Inert diluent increases heat capacity, moderating temperature changes

Advantages of isothermal operation:

- **Simplified analysis:** Decouples mass and energy balances
- **Rate constant known:** Single temperature means single k value
- **Selectivity control:** Temperature-sensitive selectivity can be optimized
- **Safety:** Runaway reactions prevented

Challenges:

- **Complex equipment:** Extensive heat exchange surfaces required
- **High capital cost:** Multi-tubular reactors with thousands of tubes are expensive
- **Fouling:** Heat transfer surfaces can foul, reducing effectiveness
- **Scale-up issues:** Surface-to-volume ratio decreases with scale, making isothermal operation harder

2.4.2 Adiabatic Reactors

In adiabatic operation, no heat is exchanged with surroundings. All heat generated or consumed by reaction changes the sensible heat (temperature) of the reacting mixture. This represents the opposite extreme from isothermal: rather than perfect heat exchange, we have zero heat exchange.

Adiabatic operation is approached when:

- **Excellent insulation:** Minimizes heat loss to surroundings
- **High flow rates:** Short residence times limit heat transfer
- **Large diameter:** Low surface-to-volume ratio reduces heat transfer area

The temperature change in an adiabatic reactor depends on heat of reaction and heat capacity:

$$\Delta T_{ad} = -\frac{\Delta H_{rxn} x_A C_{A,0}}{(\sum n_i C_{p,i})}$$

This adiabatic temperature rise (or fall for endothermic reactions) is a critical parameter in reactor design. For highly exothermic reactions, ΔT_{ad} can be hundreds of degrees, creating safety and materials challenges.

Advantages of adiabatic operation:

- **Simple construction:** No heat exchange surfaces needed
- **Low capital cost:** Simpler, less expensive than heat-exchanged reactors
- **No fouling:** No heat transfer surfaces to foul
- **High rates near inlet:** For exothermic reactions, rising temperature accelerates rate

Challenges and limitations:

- **Large temperature changes:** Can be hundreds of degrees for exothermic reactions
- **Materials limitations:** High temperatures require expensive materials
- **Equilibrium limitations:** High temperatures unfavorable for exothermic equilibrium reactions
- **Selectivity issues:** Temperature variation can reduce selectivity
- **Catalyst deactivation:** High temperatures accelerate catalyst sintering and coking

2.4.3 Practical Reactor Thermal Management

Real industrial reactors employ strategies between the isothermal and adiabatic extremes:

Multiple adiabatic beds with interstage cooling/heating:

Each bed operates adiabatically, but temperature is adjusted between beds. This is common for equilibrium-limited exothermic reactions (e.g., ammonia synthesis, SO_2 oxidation, methanol synthesis) where decreasing temperature favors equilibrium but slows kinetics. We operate hot in early stages for high rate, then cool between stages to push equilibrium toward products.

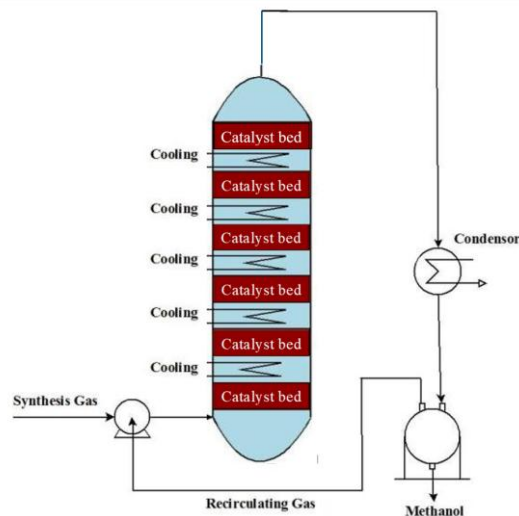


Figure 2-8 Beds with interstage cooling for methanol production

Cold-shot cooling:

Injecting cold feed between catalyst beds provides cooling without external heat exchangers. The additional reactant also shifts equilibrium favorably for some systems.

Recycle cooling:

Recycling cooled product stream to the inlet moderates inlet temperature. Common in highly exothermic reactions.

Distributed cooling:

Coolant flow parallel to reaction (e.g., in tube walls) provides partial temperature control without achieving true isothermal behavior.

2.5 Fixed Bed Reactors

Fixed bed reactors—packed with solid catalyst particles through which fluid flows—are the workhorse of the chemical and petroleum industries. Their simplicity, reliability, and scalability make them the default choice for gas-solid catalytic processes. Understanding their design and operation is essential for any chemical reaction engineer.

2.5.1 Basic Design and Operation

A fixed bed reactor consists of a vessel packed with catalyst particles (typically 2-10 mm diameter). Reactant gas or liquid flows through the bed, contacting catalyst where reaction occurs. The catalyst remains stationary—"fixed"—hence the name.



Figure 2-9 Fixed bed reactor

Key design parameters:

- **Bed length and diameter:** Determine catalyst volume and pressure drop
- **Catalyst particle size:** Smaller particles reduce internal diffusion limitations but increase pressure drop
- **Void fraction (ϵ):** Typically 0.4-0.5 for randomly packed spheres or cylinders
- **Superficial velocity:** Velocity based on empty tube cross-section; actual velocity higher due to void fraction

- **Space velocity:** GHSV (gas hourly space velocity) or LHSV (liquid hourly space velocity) indicate throughput relative to catalyst volume

Flow characteristics:

Fixed beds typically approximate plug flow when properly designed. The packed particles create tortuous flow paths with good radial mixing and minimal axial dispersion (back-mixing). This gives steep concentration gradients along the bed—desirable for high conversion.

However, several non-idealities can occur:

- **Wall effects:** Void fraction higher near walls creates faster flow channels
- **Maldistribution:** Poor inlet design or bed settling creates non-uniform flow
- **Channeling:** Preferential flow paths reduce effective catalyst utilization
- **Hot spots:** Radial temperature gradients from exothermic reaction and poor heat transfer

2.5.2 Heat Management in Fixed Beds

Heat management is the most challenging aspect of fixed bed reactor design, particularly for highly exothermic reactions. Poor heat removal leads to hot spots that can cause catalyst deactivation, selectivity loss, or even thermal runaway.

Adiabatic fixed beds with interstage cooling:

The simplest and most common approach for large-scale operation. Multiple catalyst beds operate adiabatically, with cooling between stages. Consider ammonia synthesis:

- First bed: Operates at high temperature (450-500°C) for high rate but modest conversion (~25%)
- Interstage cooling: Removes heat of reaction, lowering temperature to 400-450°C
- Second bed: Lower temperature favors equilibrium, increases conversion to ~40% total
- Additional beds: Further cooling and reaction increases conversion to 55-65%

This strategy balances kinetics (favors high T) and thermodynamics (favors low T for exothermic reactions) while keeping equipment simple.

Multi-tubular reactors:

For highly exothermic reactions requiring continuous cooling, the reactor is constructed as a bundle of thousands of small-diameter tubes (20-50 mm) packed with catalyst. Coolant flows through the shell side, removing heat through tube walls.

Advantages:

- Continuous heat removal limits temperature rise

- High surface-to-volume ratio (small tube diameter)
- Can approach isothermal operation

Disadvantages:

- Very expensive (thousands of tubes)
- Difficult to load catalyst uniformly
- High pressure drop
- Tube-to-tube maldistribution

Used for ethylene oxide production, phthalic anhydride synthesis, and other highly exothermic processes.



Figure 2-10 Parallel tubular reactors with cooling

Radial flow reactors:

Flow moves radially through an annular catalyst bed, providing larger cross-sectional area and lower pressure drop than axial flow. Heat exchange can occur on the inner and outer walls. Used in some reforming and ammonia synthesis reactors.

2.5.3 Industrial Applications

Fixed bed reactors dominate industrial catalytic processes:

- **Ammonia synthesis:** Multiple adiabatic beds with interstage cooling, Fe catalyst, 150-250 bar, 400-500°C
- **Sulfuric acid production:** Oxidation of SO₂ over V₂O₅ catalyst in multiple beds with cooling
- **Methanol synthesis:** CO + H₂ over Cu/ZnO catalyst, multiple beds, 50-100 bar, 200-300°C
- **Catalytic reforming:** Converting naphtha to high-octane gasoline, multiple reactors with reheating
- **Hydrotreating:** Removing sulfur, nitrogen from petroleum fractions

2.6 Bubble Column Reactors

Bubble column reactors represent one of the simplest yet most versatile contactors for gas-liquid and gas-liquid-solid reactions. In their most basic form, they consist of a vertical cylindrical vessel through which gas bubbles rise through a continuous liquid phase. Despite their apparent simplicity, bubble columns exhibit complex hydrodynamics that profoundly influence mass transfer and reaction performance.

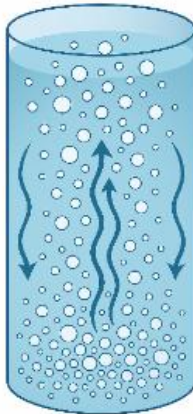


Figure 2-11 Bubble column

2.6.1 Basic Design and Operating Principles

Gas enters at the bottom of the column through a distributor—typically a perforated plate, porous sparger, or nozzle system. As bubbles rise through the liquid, they create circulation patterns that promote mixing. The liquid phase may be batch (bubble rising through stationary liquid) or continuous (liquid flowing counter-current or co-current with gas). The solid catalyst, if present, is suspended in the liquid by the turbulence created by rising bubbles.

Key advantages of bubble columns include:

- **Simple construction:** No moving parts, minimal maintenance requirements
- **Excellent heat transfer:** Liquid circulation provides good temperature uniformity
- **Good mass transfer:** High gas-liquid interfacial area, particularly at high gas velocities
- **Ease of operation:** Straightforward startup, shutdown, and control

However, they also present challenges:

- **Back-mixing:** Liquid circulation creates deviation from plug flow, reducing conversion efficiency
- **Scale-up difficulties:** Hydrodynamics change significantly with column diameter and height

- **Gas holdup prediction:** Difficult to predict accurately, affecting interfacial area calculations

2.6.2 Flow Regimes and Hydrodynamics

Bubble columns exhibit distinct flow regimes depending primarily on superficial gas velocity:

Homogeneous (bubbly flow) regime: At low gas velocities (typically <5 cm/s), bubbles are relatively uniform in size and rise uniformly through the liquid. Bubble-bubble interactions are minimal. This regime provides the most predictable behavior but limited gas throughput.

Heterogeneous (churn-turbulent) regime: At higher gas velocities (>5 cm/s), small and large bubbles coexist. Large bubbles rise faster and create strong liquid circulation. This regime is characterized by chaotic bubble motion, coalescence, and breakup. Most industrial bubble columns operate in this regime due to higher mass transfer rates despite more complex hydrodynamics.

Slug flow regime: In small-diameter columns at high gas velocities, large bubbles can span nearly the entire column diameter, creating gas slugs separated by liquid slugs. This regime is generally avoided in industrial practice due to poor mass transfer and mechanical vibrations.

Gas holdup—the volume fraction occupied by gas—is the most important hydrodynamic parameter. It directly affects residence time, interfacial area, and mass transfer coefficients. Typical gas holdups range from 5-30% depending on operating conditions and liquid properties.

2.6.3 Design Considerations

Column diameter: Affects wall effects and circulation patterns. Industrial columns typically range from 0.5 to 6 meters in diameter. For diameters below about 15 cm, wall effects become significant and hydrodynamics differ from larger columns.

Height-to-diameter ratio: Typically ranges from 2:1 to 6:1. Taller columns provide more contact time but may develop more complex circulation patterns. The aspect ratio affects the transition between flow regimes.

Gas distributor design: Critical for uniform bubble distribution and preventing channeling. Perforated plates with 1-5 mm holes are common, with hole pitch typically 2-5 hole diameters. Porous spargers provide finer bubbles but are prone to plugging. The distributor should create sufficient pressure drop (typically 30-50% of column static head) to ensure uniform distribution.

Internal baffles: Can be used to suppress large-scale circulation and approach plug flow behavior. However, they increase complexity and may create dead zones. Sieve trays or structured packings are sometimes inserted to compartmentalize the column.

2.6.4 Industrial Applications

Bubble columns find extensive use across the chemical and biochemical industries:

- **Fischer-Tropsch synthesis (slurry bubble column):** Converting synthesis gas to liquid fuels using suspended catalyst particles
- **Oxidation reactions:** Producing acetic acid from acetaldehyde, oxidizing paraffins to fatty acids
- **Hydrogenation:** Producing margarine from vegetable oils, hydrogenating aldehydes to alcohols
- **Fermentation:** Aerobic fermentations where oxygen must be supplied to microorganisms
- **Wastewater treatment:** Aerobic biological treatment, ozonation for advanced oxidation
- **Chlorination:** Producing chlorinated hydrocarbons, disinfection processes

The simplicity, reliability, and excellent heat transfer characteristics of bubble columns make them particularly attractive for highly exothermic reactions where temperature control is critical. Their tolerance for solids makes them ideal for slurry-phase processes where catalyst can be continuously added or removed.

2.7 Trickle Bed Reactors

When we need to bring together gas, liquid, and solid catalyst in a single reactor—three-phase catalytic systems—the trickle bed reactor (TBR) offers an elegant solution. Liquid trickles downward through a packed catalyst bed while gas flows concurrently, both phases contacting catalyst where reaction occurs. This seemingly simple configuration enables some of the most important processes in petroleum refining and chemical synthesis.

2.7.1 Operating Principles and Hydrodynamics

In a trickle bed, liquid is distributed at the top of the packed bed and flows downward over catalyst particles, forming thin films on particle surfaces. Gas flows through the remaining void space. The term "trickle" refers to the low liquid flow rate—liquid does not fill the voids but instead wets catalyst surfaces and forms rivulets between contact points.



Figure 2-12 Trickle beds in trickle regime (left) and bubbling regime (right)

Key features:

- **Gas-continuous:** Gas fills most void space; pressure drop primarily determined by gas flow
- **Partial catalyst wetting:** Not all catalyst surface contacts liquid—wetting efficiency typically 60-95%
- **Concurrent downflow:** Both phases flow downward (gravity assists liquid flow)
- **Low liquid holdup:** Liquid occupies only 5-30% of void volume

Flow regimes:

Trickle beds operate in different hydrodynamic regimes depending on gas and liquid flow rates:

- **Trickle flow regime:** Low liquid and gas rates; liquid trickles as rivulets; gas continuous phase
- **Pulse flow regime:** Intermediate rates; liquid and gas form alternating pulses
- **Spray flow regime:** High gas rates atomize liquid into droplets
- **Bubble flow regime:** Very high liquid rates; liquid becomes continuous phase with gas bubbles. Usually both gas and liquid are fed from below.

Many industrial trickle beds operate in the trickle flow regime for stability and predictability, though pulse or bubble flow can offer enhanced mass transfer at the cost of pressure drop fluctuations.

2.7.2 Mass Transfer and Reaction Steps

Reaction in trickle beds involves a complex sequence of mass transfer steps. Consider hydrodesulfurization where H_2 (gas) reacts with organic sulfur compounds (liquid) on catalyst surface:

- (1) H₂ transfers from gas bulk to gas-liquid interface
- (2) H₂ dissolves and diffuses through liquid film to catalyst surface
- (3) Both H₂ and sulfur compound diffuse into catalyst pores
- (4) Reaction occurs on catalyst active sites
- (5) Products diffuse out of catalyst pores to bulk liquid

Any of these steps can be rate-limiting, but often hydrogen mass transfer from gas to liquid phase controls overall rate. This makes catalyst wetting efficiency critical—unwetted catalyst cannot participate in reaction since liquid-phase reactants cannot access it.

2.7.3 Design Considerations

Liquid distribution:

Achieving uniform liquid distribution across the bed cross-section is perhaps the most critical design challenge. Poor distribution creates dry zones (no reaction) and wet zones (excessive pressure drop). Distributors—perforated plates, spray nozzles, or structured packings—must be carefully designed. For tall beds (>5 m), redistribution trays are inserted periodically to counteract liquid spreading toward walls.

Catalyst wetting:

Wetting efficiency depends on:

- Liquid flow rate (higher rates improve wetting)
- Particle size (smaller particles wet more easily)
- Particle shape (trilobes and other special shapes enhance wetting)
- Surface properties (hydrophilic surfaces wet better)

Industrial hydroprocessing catalysts are designed with specific shapes (trilobes, quadralobes) to maximize wetting at typical operating conditions.

Pressure drop:

While generally lower than in bubble columns or slurry reactors, pressure drop must be carefully managed—it determines compression costs and can limit throughput. Pressure drop increases with gas and liquid rates, and with decreasing particle size.

2.7.4 Industrial Applications

Trickle bed reactors are ubiquitous in petroleum refining:

- **Hydrodesulfurization (HDS):** Removing sulfur from diesel, gasoline, jet fuel to meet environmental regulations. CoMo or NiMo catalyst, 300-400°C, 30-150 bar H₂ pressure. This is the largest-volume application of trickle beds.
- **Hydrodenitrogenation (HDN):** Removing nitrogen compounds that poison catalysts in downstream processes

- **Hydrotreating:** General term for removing impurities (S, N, O) and saturating aromatics and olefins
- **Hydrogenation:** Adding H₂ to unsaturated organic compounds in fine chemical and pharmaceutical synthesis
- **Oxidation:** Liquid-phase oxidation with air or O₂ over solid catalysts

2.8 Fluidized Bed Reactors

In a fluidized bed, upward-flowing gas or liquid suspends solid particles, causing them to behave like a fluid—bubbling, flowing, and mixing vigorously. This seemingly chaotic arrangement offers unique advantages that make fluidized beds indispensable for certain processes, despite their operational complexity.

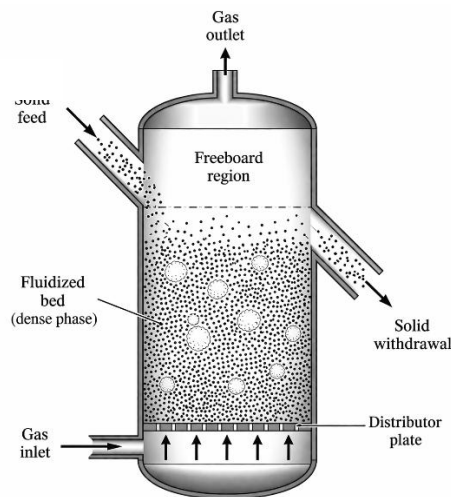


Figure 2-13 Fluidized bed at bubbling flow

2.8.1 Fluidization Principles

When gas flows upward through a packed bed at low velocity, particles remain stationary. As velocity increases, particles begin to separate. At the minimum fluidization velocity (u_{mf}), the drag force equals the particle weight and the bed begins to expand and behave like a fluid. Further velocity increases create different fluidization regimes:

- **Particulate fluidization:** Smooth expansion with particles uniformly suspended (rare in gases, common in liquids)
- **Bubbling fluidization:** Gas bubbles form and rise through denser emulsion phase (typical industrial regime)
- **Slugging:** Bubbles grow to bed diameter, pushing slugs of particles upward (undesirable)
- **Turbulent fluidization:** High velocities destroy bubble structure, creating chaotic motion

- **Fast fluidization:** Even higher velocities transport particles upward (requires solids recycle)
- **Pneumatic transport:** All particles carried upward in dilute phase

Most catalytic reactors operate in bubbling or turbulent regimes, balancing good mixing against gas bypassing in bubbles.

2.8.2 Advantages of Fluidized Beds

Fluidized beds offer several compelling advantages that explain their widespread use despite operational complexity:

- **Excellent temperature control:** Vigorous solid mixing creates uniform temperature throughout bed, eliminating hot spots that plague fixed beds. This is perhaps the single most important advantage—exothermic reactions that would runaway in fixed beds operate safely in fluidized beds.
- **Continuous catalyst regeneration:** Catalyst can be continuously withdrawn, regenerated, and returned to the reactor. Essential for processes where catalyst deactivates rapidly (e.g., catalytic cracking, which would be impossible in fixed bed).
- **High heat transfer coefficients:** Particle motion creates excellent heat transfer to immersed tubes or walls, simplifying temperature control
- **Ability to handle wide particle size distributions:** Elutriation (carrying fines out of bed) naturally segregates particles by size
- **Easy catalyst addition/removal:** Fluid-like behavior allows pumping catalyst in and out
- **Compact design:** High gas throughput in compact volume

2.8.3 Challenges and Limitations

These advantages come with significant challenges:

- **Gas bypassing:** Bubbles rise rapidly with little contact with solids, reducing conversion. Large bubbles are particularly problematic.
- **Solid entrainment:** Particles are carried out of bed in gas stream, requiring cyclones or other separation devices. Catalyst losses can be substantial.
- **Catalyst attrition:** Particle collisions create fines, increasing catalyst consumption
- **Erosion:** Particles wear away internal surfaces, pipes, instrumentation
- **Back-mixing:** Both gas and solids exhibit significant back-mixing, so behavior is closer to CSTR than PFR (usually undesirable for conversion)
- **Scale-up difficulties:** Hydrodynamics changes unpredictably with scale; pilot plants don't always predict commercial performance
- **Operational complexity:** Start-up, shutdown, and control more complex than fixed beds

2.8.4 Industrial Applications

Despite challenges, fluidized beds are essential for several major industrial processes:

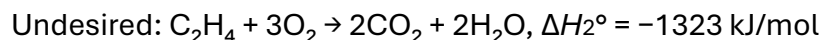
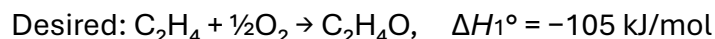
- **Fluid catalytic cracking (FCC):** The single largest application of fluidized beds. Heavy petroleum fractions crack over zeolite catalyst at 500-550°C. Catalyst circulates between reactor (where cracking occurs and carbon deposits) and regenerator (where deposited carbon burns off). This continuous regeneration—impossible in fixed beds—is what makes FCC viable.
 - **Acrylonitrile production:** Ammoxidation of propylene over bismuth molybdate catalyst in fluidized bed. Excellent temperature control essential for selectivity and safety (highly exothermic).
 - **Maleic anhydride synthesis:** Oxidation of butane over VPO catalyst. Fluidized bed controls temperature of this highly exothermic reaction.
 - **Polyolefin production:** Gas-phase polymerization of ethylene and propylene over supported metallocene or Ziegler-Natta catalysts
 - **Combustion and gasification:** Fluidized bed combustors burn coal or biomass with excellent temperature control. Gasifiers convert solid fuels to synthesis gas.
 - **Fischer-Tropsch synthesis:** Some designs use fluidized beds for this highly exothermic reaction converting syngas to hydrocarbons
-

2.9 AI-Assisted Problem: Reactor Selection for Multiple Objectives

This problem asks you to think strategically about reactor selection when facing competing design objectives. The problem is very complex, and you must know the whole book before you can solve it by yourself. Use AI to guide your thinking through trade-offs rather than to simply calculate answers.

Problem Statement

You must design a reactor system for the gas-phase synthesis of ethylene oxide from ethylene and oxygen over a silver catalyst:



Process requirements and constraints:

- Target production: 250,000 metric tons/year ethylene oxide
- Desired selectivity to ethylene oxide: >80%
- Target conversion per pass: 8-12% (limited by selectivity concerns and explosion hazard)
- Operating conditions: 250-300°C, 10-30 bar
- Feed composition: 7% C_2H_4 , 8% O_2 in inert (N_2/CH_4) to avoid flammability limits
- Catalyst: Silver on α -alumina support, $d_p = 5\text{-}10 \text{ mm}$
- Both reactions are highly exothermic, with complete oxidation producing 12× more heat per mole of ethylene

Suggested AI Prompting Strategy

Step 1: Understanding Constraints and Objectives

Prompt:

"I need to select a reactor configuration for ethylene oxide production. Before considering specific reactor types, help me understand the design challenges:

- What makes this reaction system particularly challenging from a safety and selectivity standpoint?
- Why is conversion limited to 8-12% rather than pushed to completion?
- Given that $\Delta H_2/\Delta H_1 \approx 12.6$, what does this tell us about heat removal requirements?
- What happens to selectivity if we allow the temperature to rise too high?"

Step 2: Evaluating Reactor Options

Prompt:

"Let's systematically evaluate possible reactor configurations. For each option, discuss advantages, disadvantages, and suitability for this specific application:

- Single large fixed bed reactor (adiabatic)
- Multiple fixed bed reactors with interstage cooling
- Multi-tubular reactor (thousands of cooled tubes)
- Fluidized bed reactor
- CSTR (although uncommon for gas-phase catalytic reactions)

For each configuration, consider: temperature control capability, selectivity implications, safety, capital cost, and operational complexity."

Step 3: Detailed Analysis of Most Promising Option

Prompt:

"The industrial standard for ethylene oxide production is the multi-tubular reactor. Help me understand why:

- Why is continuous heat removal critical for maintaining selectivity?
- If we have 6000 tubes, each 10 m long and 25 mm diameter, estimate the total catalyst volume
- For a feed rate of $100,000 \text{ Nm}^3/\text{hr}$, what would be the superficial gas velocity in each tube?
- What would be the approximate space velocity?
- What coolant would you use and why?"

Step 4: Alternative Approaches and Trade-offs

Prompt:

"Despite being the industrial standard, multi-tubular reactors are very expensive (tens of millions of dollars). What alternative approaches might reduce capital cost while managing the heat removal challenge:

- Could we use multiple adiabatic beds with cold-shot cooling or interstage heat exchange?
- What about running at lower inlet temperature and accepting the adiabatic temperature rise?
- Could diluting the feed with more inert help manage the heat?
- What would be the trade-offs of each alternative?"

Step 5: Safety Analysis

Prompt:

"Ethylene oxide production involves explosive mixtures and highly exothermic reactions. What safety features and considerations are essential:

- Why is the feed composition maintained at 7% C₂H₄ and 8% O₂?
- What safety instrumentation would be critical?
- How would you design for runaway reaction scenarios?
- What are the risks of hot spots in the catalyst bed?"

Learning Objectives

Through this AI-guided exploration, you should develop:

- Systematic approach to reactor selection considering multiple competing objectives
- Understanding of how heat management drives reactor configuration choices
- Appreciation for the trade-offs between selectivity, conversion, safety, and economics
- Insight into why certain reactor types dominate specific industrial applications

Chapter 2 Summary: What You Should Have Learned

After completing this chapter, you should be able to:

1. Classify reactors by phase behavior and understand heterogeneous systems
2. Distinguish between ideal mixing patterns: perfect mixing, plug flow, and other patterns
3. Compare batch, continuous, and semi-batch operating modes
4. Understand thermal operation modes: isothermal, adiabatic, and non-isothermal
5. Describe fixed bed, bubble column, trickle bed, and fluidized bed reactors
6. Select appropriate reactor types based on reaction characteristics and requirements

Chapter 3: Reaction Stoichiometry and Kinetics

Learning Objectives

After completing this chapter, you should be able to:

- Define stoichiometric coefficients and write balanced chemical equations for single and multiple reaction systems, recognizing the sign convention and its implications for reaction direction.
- Apply the IUPAC definition of reaction rate based on the extent of reaction ($d\xi/dt$) and explain how reaction rates are affected by volume changes during reaction, particularly for gas-phase systems.
- Calculate fractional conversion, degree of completion, and identify limiting reactants in reaction systems, and relate extent of reaction to fractional conversion for systems with parallel, consecutive, and reversible reactions.
- Describe the general dependencies of reaction rates on temperature and concentration and apply the Arrhenius equation to predict rate constant variation with temperature while understanding the physical meaning and limitations of the activation energy and pre-exponential factor.
- Write rate expressions for elementary reactions using collision theory principles, for empirical power-law correlations, and for surface-catalyzed reactions using Langmuir-Hinshelwood kinetics.
- Develop rate equations for reversible reactions incorporating equilibrium constraints and relate the equilibrium constant to thermodynamic properties (ΔG° , ΔH° , ΔS°) to predict how equilibrium position changes with temperature.
- Define selectivity and yield for multiple reaction systems and apply these concepts to optimize reactor operation for maximum production of desired products.
- Deduce simplified kinetic expressions for complex reaction mechanisms involving reactive intermediates, illustrated through the example of ethane-ethylene coupling to produce methane and propylene.

Nomenclature

The following symbols are introduced in this chapter and supplement the comprehensive nomenclature in Appendix B:

Roman Letters

A	Pre-exponential factor or frequency factor in Arrhenius equation (units depend on reaction order)
C_i	Concentration of species i (mol/L or mol/m ³)

E_a	Activation energy (J/mol or kJ/mol)
f_A	Fractional conversion of species A (dimensionless)
K	Equilibrium constant (units depend on reaction stoichiometry)
k	Reaction rate constant (units depend on reaction order)
K_i	Adsorption equilibrium constant for species i in Langmuir-Hinshelwood kinetics (L/mol or m ³ /mol)
n_i	Number of moles of species i (mol)
r	Reaction rate per unit volume (mol/(L·s) or mol/(m ³ ·s))
r_i	Rate of formation of species i per unit volume (mol/(L·s) or mol/(m ³ ·s))
R	Universal gas constant, 8.314 J/(mol·K)
S	Selectivity (dimensionless or as ratio)
T	Temperature (K)
V	Volume (L or m ³)
x_A	Conversion of species A (use lowercase x) (dimensionless)
Y	Yield (dimensionless)
θ_i	Surface coverage of species i (dimensionless)

Greek Letters

ν_i	Stoichiometric coefficient of species i (dimensionless, negative for reactants, positive for products)
ξ	Extent of reaction (mol)
$\dot{\xi}$	Rate of change of extent of reaction (mol/s or mol/min)

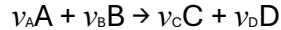
Subscripts

0	Initial condition or reference state
i	Species index
j	Reaction index

3.1 Stoichiometry and Balanced Chemical Equations

Before we can analyze reaction rates and design reactors, we must understand the stoichiometric relationships that govern chemical transformations. Stoichiometry describes the quantitative relationships between reactants and products in chemical reactions—the "bookkeeping" that ensures mass conservation at the molecular level.

A chemical reaction can be written in general form as:



where the stoichiometric coefficients ν represent the number of molecules or moles of each species participating in the reaction. However, in chemical reaction engineering, we adopt a more systematic notation that proves essential for complex systems with multiple reactions.

$$0 = \nu_A A + \nu_B B + \nu_C C + \nu_D D \quad (3.1)$$

3.1.1 Stoichiometric Coefficient Sign Convention

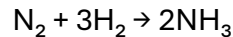
We write the general reaction equation in the form:

$$\sum \nu_i A_i \quad (3.2)$$

where, by convention:

- $\nu_i < 0$ for reactants (consumed)
- $\nu_i > 0$ for products (formed)
- $\nu_i = 0$ for inert species (not participating)

For example, the ammonia synthesis reaction:



is written as:

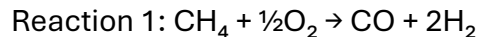
$$0 = -N_2 - 3H_2 + 2NH_3 \quad (3.3)$$

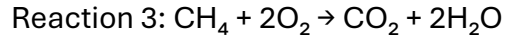
giving $\nu_{N_2} = -1$, $\nu_{H_2} = -3$, and $\nu_{NH_3} = +2$. This sign convention, while initially seeming cumbersome, proves invaluable when dealing with multiple simultaneous reactions and automated computational analysis.

The negative sign for reactants and positive sign for products creates a mathematically consistent framework. When we calculate changes in mole numbers, the signs automatically ensure that reactants decrease while products increase as the reaction proceeds. For instance, if extent of reaction (ξ) increases by 2 moles in the ammonia synthesis, nitrogen decreases by 2 moles (since $\nu_{N_2} = -1$), hydrogen decreases by 6 moles (since $\nu_{H_2} = -3$), and ammonia increases by 4 moles (since $\nu_{NH_3} = +2$), all consistent with the balanced equation.

3.1.2 Multiple Reaction Systems

Most industrial processes involve multiple reactions occurring simultaneously. Consider the partial oxidation of methane, where several reactions compete:





Each reaction has its own set of stoichiometric coefficients, and we must track the extent of each reaction independently. The total change in moles of any species is the sum of contributions from all reactions in which it participates.

3.2 Extent of Reaction and the IUPAC Definition of Reaction Rate

The International Union of Pure and Applied Chemistry (IUPAC) provides a rigorous definition of reaction rate based on a fundamental concept: the extent of reaction. This approach offers mathematical elegance and physical clarity that becomes increasingly valuable as reactions grow more complex.

3.2.1 Extent of Reaction

The extent of reaction ξ (Greek letter xi) is defined such that the change in the number of moles of any species i is:

$$n_i = n_{i,0} + \nu_i \xi \quad (3.4)$$

where n_i is the current number of moles of species i , $n_{i,0}$ is the initial number of moles, ν_i is the stoichiometric coefficient, and ξ is the extent of reaction in moles.

The beauty of this definition is that ξ is the same for all species in the reaction. When ξ increases by 1 mole, exactly ν_i moles of species i are produced (if $\nu_i > 0$) or consumed (if $\nu_i < 0$), in accordance with stoichiometry. The extent of reaction provides a single variable that tracks the progress of the entire reaction.

To illustrate this concept, consider a reaction starting with 5 moles of N_2 and 15 moles of H_2 . When $\xi = 2$ moles, we can immediately calculate: $n_{\text{N}_2} = 5 + (-1)(2) = 3$ moles, $n_{\text{H}_2} = 15 + (-3)(2) = 9$ moles, and $n_{\text{NH}_3} = 0 + (+2)(2) = 4$ moles. This single variable ξ elegantly captures the state of the entire reacting system.

3.2.2 IUPAC Definition of Reaction Rate

The IUPAC defines the reaction rate as the time derivative of the extent of reaction per unit volume:

$$r = \frac{1}{V} \frac{d\xi}{dt} \quad (3.5)$$

For species i , the rate of formation r_i is:

$$r_i = \nu_i r = \frac{\nu_i}{V} \frac{d\xi}{dt} \quad (3.6)$$

Alternatively, since $dn_i = v_i d\xi$, we can also write:

$$r_i = \frac{1}{V} \frac{dn_i}{dt} \quad (3.7)$$

For systems with constant volume (typical for liquid-phase reactions and some gas-phase reactions), the concentration $C_i = n_i/V$, and thus:

$$r_i = \frac{dC_i}{dt} \quad (\text{constant volume}) \quad (3.8)$$

This familiar form—rate equals the time derivative of concentration—is valid only when volume is constant. Recognizing when this simplification applies and when it doesn't is crucial for correct reactor analysis.

3.2.3 Effect of Volume Changes on Reaction Rate

When volume changes during reaction (common in gas-phase reactions where the total number of moles changes), we must account for this in our rate expressions. Starting from the definition:

$$r_i = \frac{1}{V} \frac{dn_i}{dt} \quad (3.9)$$

and noting that $n_i = C_i V$, we apply the product rule:

$$r_i = \frac{1}{V} \left[V \frac{dC_i}{dt} + C_i \frac{dV}{dt} \right] \quad (3.10)$$

which simplifies to:

$$r_i = \frac{dC_i}{dt} + \frac{C_i}{V} \frac{dV}{dt} \quad (\text{variable volume}) \quad (3.11)$$

The second term represents the effect of volume change. For gas-phase reactions where the number of moles changes (e.g., $2A \rightarrow B$), volume must expand or contract at constant pressure and temperature, affecting measured concentrations even without reaction. This correction becomes particularly important in batch reactors processing gas-phase reactions.

3.3 Conversion, Completion, and Limiting Reactants

In reactor design, we rarely think in terms of extent of reaction. Instead, engineers use more intuitive measures like conversion and completion that directly relate to feed and product compositions.

3.3.1 Fractional Conversion

The fractional conversion x_A of a reactant A is defined as:

$$x_A = \frac{n_{A,0} - n_A}{n_{A,0}} \quad (3.12)$$

where $n_{A,0}$ is the initial moles of A and n_A is the current moles. Conversion ranges from 0 (no reaction) to 1 (complete consumption of A). We can relate conversion to extent of reaction:

$$x_A = - \frac{v_A \xi}{n_{A,0}} \quad (3.13)$$

The negative sign accounts for the fact that $v_A < 0$ for reactants, ensuring x_A remains positive as the reaction proceeds. This relationship allows us to express the moles of any species in terms of conversion:

$$n_i = n_{i,0} + \frac{v_i}{v_A} n_{A,0} x_A \quad (3.14)$$

This powerful expression links the composition of the entire reaction mixture to a single variable—the conversion of the chosen reference species.

3.3.2 Limiting Reactant

In reactions with multiple reactants, the limiting reactant is the species that would be completely consumed first if the reaction proceeded to completion. Consider the reaction:

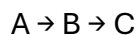


with $n_{A,0} = 10$ mol and $n_{B,0} = 15$ mol. Species B requires 2 moles per mole of A, so complete conversion of A would consume 20 mol of B—but only 15 mol are available. Therefore, B is the limiting reactant, and maximum possible conversion is $x_B = 1.0$, corresponding to $x_A = 0.75$.

Choosing the limiting reactant as the basis for conversion ensures that conversion can range from 0 to 1 without encountering nonsensical negative mole numbers. This choice is particularly important for reactor design calculations.

3.3.3 Conversion in Multiple Reaction Systems

When multiple reactions occur simultaneously, the concept of conversion becomes more nuanced. Consider consecutive reactions:



Species A is consumed by the first reaction, but its conversion x_A represents total consumption regardless of whether it forms B or eventually C. However, we cannot uniquely determine the composition from x_A alone—we need additional information about the relative rates of the two reactions.

For multiple reactions, we define separate extents of reaction ξ_j for each reaction j . The total change in moles of species i is:

$$n_i = n_{i,0} + \sum_j \nu_{i,j} \xi_j \quad (3.15)$$

where the sum extends over all reactions in which species i participates. This formulation is essential for analyzing selectivity in competing reaction pathways.

3.4 Temperature Dependence of Reaction Rates

Reaction rates are not constants—they depend strongly on both temperature and the concentrations of reacting species. Understanding these dependencies is fundamental to predicting reactor performance and optimizing operating conditions.

3.4.1 General Observations

Empirically, we observe the following general trends:

Temperature dependence: Reaction rates typically increase exponentially with temperature. A rough rule of thumb suggests that rates double for every 10°C temperature increase, though the actual sensitivity varies widely depending on the activation energy of the reaction. This strong temperature dependence stems from the exponential nature of the Boltzmann distribution—only molecules with sufficient energy can overcome the activation barrier to react.

Concentration dependence: Reaction rates generally increase with increasing reactant concentrations, following power-law relationships. The specific functional form depends on the reaction mechanism—whether molecules must collide in specific ways, whether reaction occurs on catalyst surfaces, or whether the rate-limiting step involves multiple species.

These dependencies are not independent. Temperature affects not only the rate constant but also, indirectly, the concentrations through equilibrium constraints in reversible reactions. Separating these effects mathematically proves essential for reactor design.

3.4.2 The Arrhenius Equation

The temperature dependence of the rate constant k is described by the Arrhenius equation, one of the most important relationships in chemical kinetics:

$$k = A e^{\frac{-E_a}{RT}} \quad (3.16)$$

where k is the rate constant, A is the pre-exponential factor (or frequency factor), E_a is the activation energy, R is the universal gas constant (8.314 J/(mol·K)), and T is absolute temperature in Kelvin.

Physical Meaning of Parameters

Activation Energy (E_a): Represents the minimum energy molecules must possess to react. Reactions with high activation energies are very sensitive to temperature—a small temperature increase produces a large rate increase. Typical values range from 40-200 kJ/mol. The exponential term $\exp(-E_a/RT)$ represents the fraction of molecular collisions with sufficient energy to overcome the activation barrier, derived from the Boltzmann distribution of molecular energies.

Pre-exponential Factor (A): Represents the frequency of collisions between reactant molecules with proper orientation for reaction. Its units depend on reaction order—for a second-order reaction, typical values are 10^8 - 10^{11} L/(mol·s). The pre-exponential factor captures geometric and steric effects: even molecules with sufficient energy won't react if they approach with wrong orientation.

Assumptions and Limitations

The Arrhenius equation rests on several assumptions that are important to recognize:

- **Single activation barrier:** The equation assumes a single rate-limiting step with one activation energy. Complex mechanisms with multiple elementary steps may not follow simple Arrhenius behavior over wide temperature ranges.
- **Temperature-independent E_a and A :** Both parameters are assumed constant. In reality, they can vary slightly with temperature, particularly over very wide temperature ranges (hundreds of degrees).
- **No equilibrium limitations:** The equation applies to the forward rate constant. For reversible reactions approaching equilibrium, the net rate decreases not because k changes but because the reverse reaction becomes significant.
- **Ideal gas behavior:** The theoretical derivation assumes ideal molecular collisions. At very high pressures or for reactions involving ions in solution, corrections may be needed.

Despite these limitations, the Arrhenius equation remarkably accurately describes most reaction systems over practical temperature ranges (typically $\pm 50^\circ\text{C}$ around the measurement temperature). Its semi-logarithmic form provides a powerful tool for data correlation:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (3.17)$$

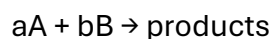
A plot of $\ln k$ versus $1/T$ yields a straight line with slope $-E_a/R$ and intercept $\ln A$. This "Arrhenius plot" is the standard method for determining activation energies from experimental data.

3.5 Concentration Dependence: Rate Laws

While the Arrhenius equation describes temperature effects on the rate constant, we must also specify how the rate depends on species concentrations. This concentration dependence takes different forms depending on whether we're dealing with elementary reactions, empirical correlations, or surface-catalyzed processes.

3.5.1 Elementary Reactions

An elementary reaction is one that occurs exactly as written at the molecular level—a single step with no intermediates. For elementary reactions, the rate law follows directly from the stoichiometry and collision theory. Consider the elementary reaction:



The rate is proportional to the probability that a molecules of A and b molecules of B collide simultaneously:

$$r = kC_A^a C_B^b \quad (3.18)$$

The sum of exponents ($a + b$) defines the molecularity—the number of molecules involved in the elementary step. Molecularity is always an integer and typically 1 (unimolecular) or 2 (bimolecular). Termolecular reactions (three molecules colliding simultaneously) are rare because such collisions are statistically improbable.

Important: This direct relationship between stoichiometry and rate law applies only to elementary reactions. For overall reactions composed of multiple steps, the rate law must be determined experimentally or derived from the detailed mechanism.

3.5.2 Empirical Power-Law Rate Expressions

Most reactions involve complex mechanisms with multiple elementary steps, intermediates, and competing pathways. Rather than deriving rate laws from first principles (which requires knowing the complete mechanism), we often use empirical power-law expressions:

$$r = k C_A^\alpha C_B^\beta C_C^\gamma \quad (3.19)$$

where α , β , and γ are empirically determined exponents that need not be integers and may differ from stoichiometric coefficients. The sum ($\alpha + \beta + \gamma$) defines the overall reaction order.

These exponents are determined by measuring how the reaction rate changes when concentrations are varied systematically.

Common reaction orders include:

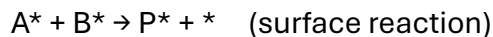
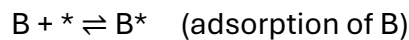
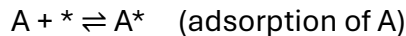
- **Zero-order:** $r = k$ (rate independent of concentration, typical when catalyst surface is saturated)
- **First-order:** $r = kC_A$ (radioactive decay, many unimolecular decompositions)
- **Second-order:** $r = kC_A C_B$ (many bimolecular reactions)
- **Fractional-order:** $r = kC_A^{1/2}$ (indicative of complex mechanisms, often involving radicals or surface reactions)

While empirical rate laws lack the theoretical foundation of elementary reactions, they provide practical working equations for reactor design when mechanisms are unknown or too complex to analyze in detail.

3.5.3 Langmuir-Hinshelwood Kinetics for Surface-Catalyzed Reactions

Catalytic reactions occurring on solid surfaces require a different kinetic treatment because reaction rates depend not on bulk concentrations but on surface coverage—the fraction of catalyst sites occupied by adsorbed species. The Langmuir-Hinshelwood mechanism provides a widely used framework for describing these reactions.

Consider a simple catalytic reaction $A + B \rightarrow P$ occurring on a solid catalyst. The Langmuir-Hinshelwood mechanism involves several steps:



where $*$ denotes an empty catalyst site and A^* , B^* , P^* denote adsorbed species. If the surface reaction is rate-limiting and adsorption equilibria are established, the rate depends on surface coverages θ_A and θ_B :

$$r = k_s \theta_A \theta_B \quad (3.20)$$

Surface coverages are related to gas-phase concentrations through Langmuir adsorption isotherms. For non-dissociative adsorption:

$$\theta_A = \frac{K_A C_A}{1 + K_A C_A + K_B C_B + K_P C_P} \quad (3.21)$$

where K_A , K_B , K_P are adsorption equilibrium constants. The denominator accounts for site competition—all species compete for the same surface sites. Substituting these expressions into the rate equation yields:

$$r = \frac{k_s K_A K_B C_A C_B}{(1 + K_A C_A + K_B C_B + K_P C_P)^2} \quad (3.22)$$

This expression exhibits interesting behavior:

- At low concentrations (dilute limit), the denominator ≈ 1 , giving $r \propto C_A C_B$ (second-order kinetics)
- At high concentrations (surface saturation), one term dominates the denominator, and the rate becomes insensitive to further concentration increases (zero-order kinetics)
- Products can inhibit the reaction by occupying sites (product inhibition)

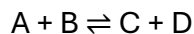
Langmuir-Hinshelwood kinetics thus naturally explains the transition from high-order to low-order kinetics as concentration increases—a phenomenon often observed in catalytic systems. Different rate-limiting steps (adsorption, surface reaction, or desorption) lead to different forms of the rate expression, providing diagnostic information about the catalytic mechanism.

3.6 Reversible Reactions and Equilibrium

All chemical reactions are, in principle, reversible. Whether a reaction appears irreversible in practice depends on the equilibrium constant—if overwhelmingly large, reverse reaction is negligible. However, many industrially important reactions have equilibrium constants that significantly limit conversion, requiring careful consideration of reversibility in reactor design.

3.6.1 Rate Expressions for Reversible Reactions

Consider the reversible reaction:



The net rate of reaction is the difference between forward and reverse rates:

$$r = k_f C_A C_B - k_r C_C C_D \quad (3.23)$$

where k_f and k_r are the forward and reverse rate constants. At equilibrium, $r_f = r_r$ and the net rate is zero. The equilibrium condition gives:

$$k_f C_{A,\text{eq}} C_{B,\text{eq}} = k_r C_{C,\text{eq}} C_{D,\text{eq}} \quad (3.24)$$

Defining the equilibrium constant K as:

$$K = \frac{k_f}{k_r} \quad (3.24)$$

We can express the reverse rate constant in terms of the forward rate constant and equilibrium constant:

$$k_r = \frac{k_f}{K} \quad (3.25)$$

This relationship is powerful: if we know k_f and K (determined from thermodynamics), we can calculate k_r without additional kinetic experiments. The net rate expression becomes:

$$r = k_f \left(C_A C_B - \frac{C_C C_D}{K} \right) \quad (3.26)$$

This form clearly shows that as the system approaches equilibrium ($C_C C_D \rightarrow K C_A C_B$), the net rate approaches zero, as it must.

3.6.2 Thermodynamic Basis of the Equilibrium Constant

The equilibrium constant is not an arbitrary parameter but is rigorously determined by the thermodynamics of the reaction. For the general reaction:

$$\sum_i \nu_i A_i = 0 \quad (3.27)$$

For an ideal solution the equilibrium constant relates to the standard Gibbs free energy change of reaction:

$$\Delta G^\circ = -RT \ln K \quad (3.28)$$

where ΔG° is calculated from standard formation free energies:

$$\Delta G^\circ = \sum_i \nu_i \Delta G_i^\circ \quad (3.29)$$

The temperature dependence of the equilibrium constant follows from the van't Hoff equation:

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (3.30)$$

where ΔH° is the standard enthalpy change of reaction. This equation reveals that:

- **Exothermic reactions ($\Delta H^\circ < 0$):** K decreases with increasing temperature—high temperatures favor reactants
- **Endothermic reactions ($\Delta H^\circ > 0$):** K increases with increasing temperature—high temperatures favor products

Integrating the van't Hoff equation assuming ΔH° is approximately constant over the temperature range:

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (3.31)$$

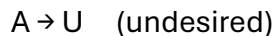
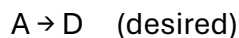
This relationship allows us to predict equilibrium limitations at any temperature if we know K at one temperature and ΔH° . The coupling of kinetics (reaction rates) with thermodynamics (equilibrium position) is central to reactor optimization, particularly for reversible exothermic reactions where we must balance the competing effects of temperature on rate and equilibrium.

3.7 Selectivity in Multiple Reaction Systems

In industrial practice, we rarely deal with single reactions producing a single product. Instead, reactants typically follow multiple pathways, producing desired products alongside unwanted byproducts. Maximizing selectivity toward desired products while minimizing byproduct formation is often more economically important than maximizing conversion.

3.7.1 Definitions

Consider a system where reactant A forms desired product D and undesired product U:



Selectivity is defined as the ratio of the rate of formation of desired product to the rate of consumption of reactant:

$$S_D = \frac{r_D}{-r_A} \quad (3.32)$$

Yield is the amount of desired product formed relative to the amount of reactant fed:

$$Y_D = \frac{n_D}{n_{A,0}} \quad (3.33)$$

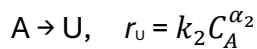
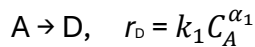
For stoichiometric coefficients $\neq 1$, these definitions are adjusted to account for molecular ratios. Selectivity and yield are related through conversion:

$$Y_D = S_D x_A \quad (3.34)$$

This relationship highlights a fundamental trade-off: high conversion with poor selectivity may give lower yield than moderate conversion with excellent selectivity. Optimizing reactor operation requires balancing these competing objectives.

3.7.2 Parallel Reactions

For parallel reactions where A simultaneously forms D and U, selectivity depends on the relative magnitudes of rate constants and concentration dependencies. Consider:



The instantaneous selectivity is:

$$S_D = \frac{r_D}{r_D + r_U} = \frac{k_1 C_A^{\alpha_1}}{k_1 C_A^{\alpha_1} + k_2 C_A^{\alpha_2}} \quad (3.35)$$

Simplifying:

$$S_D = \frac{1}{1 + \left(\frac{k_2}{k_1}\right) C_A^{\alpha_2 - \alpha_1}} \quad (3.36)$$

This reveals design principles:

- If $\alpha_1 > \alpha_2$ (desired reaction has higher order), **high CA favors D**. Use batch or plug flow reactors.
- If $\alpha_1 < \alpha_2$ (undesired reaction has higher order), **low CA favors D**. Use CSTR or feed dilution.
- If $\alpha_1 = \alpha_2$, selectivity is independent of concentration and determined solely by k_1/k_2 , which varies with temperature according to different activation energies.

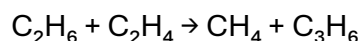
3.7.3 Consecutive Reactions

For consecutive reactions $A \rightarrow D \rightarrow U$, the desired intermediate product D is formed and then consumed. Selectivity becomes a function of conversion. To maximize yield of D, we must stop the reaction at optimal conversion—neither too low (insufficient D formed) nor too high (D consumed to U).

The optimization of selectivity in consecutive reaction systems requires analyzing the interplay between residence time, concentration, and temperature—topics we'll explore in depth in Chapter 8: when we study multiple reaction systems in detail.

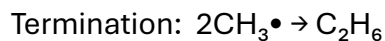
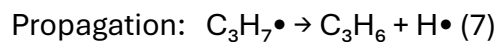
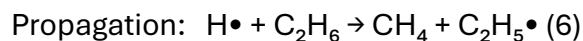
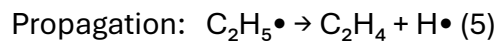
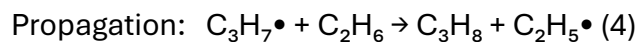
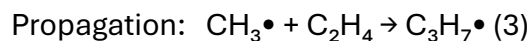
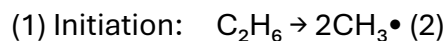
3.8 Deducing Kinetics for Complex Reactions: An Example

Many industrially important reactions proceed through complex mechanisms involving reactive intermediates like free radicals. While the detailed mechanism may involve dozens of elementary steps, we often can deduce simplified kinetic expressions by applying steady-state approximations to short-lived intermediates. This section illustrates the approach using the coupling of ethane and ethylene to produce methane and propylene:



3.8.1 Proposed Mechanism

This reaction proceeds through a free-radical chain mechanism. A plausible sequence of elementary steps includes:



The overall stoichiometry emerges from appropriate linear combinations of these steps. Species with bullets (\cdot) are free radicals—highly reactive intermediates with unpaired electrons that exist at very low concentrations.

3.8.2 Application of Steady-State Approximation

Free radicals are so reactive that their concentrations quickly reach small steady-state values where their rates of formation equal their rates of consumption. This steady-state approximation allows us to eliminate radical concentrations from the rate expressions.

For each radical species, we write:

$$\frac{d[\text{CH}_3\cdot]}{dt} = 0 = 2k_1[\text{C}_2\text{H}_6] - k_2[\text{CH}_3\cdot][\text{C}_2\text{H}_4] - 2k_7[\text{CH}_3\cdot]^2 \quad (3.37)$$

$$\frac{d[\text{C}_3\text{H}_7 \cdot]}{dt} = 0 = k_2[\text{CH}_3 \cdot][\text{C}_2\text{H}_4] - k_3[\text{C}_3\text{H}_7 \cdot][\text{C}_2\text{H}_6] - k_6[\text{C}_3\text{H}_7 \cdot] \quad (3.38)$$

Similar expressions apply for $[\text{C}_2\text{H}_5 \cdot]$ and $[\text{H} \cdot]$. Solving this system of algebraic equations (considerably simpler than the original differential equations) yields radical concentrations as functions of stable species concentrations and rate constants.

3.8.3 Simplified Rate Expression

After applying the steady-state approximation and making reasonable assumptions (e.g., that certain fast steps equilibrate or certain slow steps are rate-limiting), we can derive a simplified overall rate expression. For this system, analysis shows:

$$r \approx k_{\text{eff}}[\text{C}_2\text{H}_6]^{1/2} [\text{C}_2\text{H}_4]$$

where the effective rate constant k_{eff} is a combination of elementary rate constants. The fractional order dependence on ethane concentration (1/2) arises from the balance between radical generation (initiation step, order 1 in C_2H_6) and radical termination (order 2 in radical concentration, which itself depends on $[\text{C}_2\text{H}_6]^{1/2}$).

This example demonstrates how complex mechanisms reduce to relatively simple empirical rate laws. The fractional reaction order—puzzling if encountered empirically without mechanistic insight—becomes understandable as a natural consequence of radical chemistry. Such analysis bridges the gap between molecular-level mechanisms and practical reactor design equations.

3.9 AI-Assisted Problem: Temperature Optimization for a Reversible Reaction

Step 2: Equilibrium Analysis (Strategic calculation)

Prompt:

"Now let's check equilibrium limits. The equilibrium constant is $K(400 \text{ K}) = 10 \text{ L/mol}$ and $\Delta H^\circ = -50 \text{ kJ/mol}$. I need to:

- Calculate K at different temperatures (350 K, 400 K, 450 K, 500 K) using the van't Hoff equation
- For each temperature, calculate the equilibrium conversion starting with $C_{A,0} = 2 \text{ mol/L}$
- Create a plot showing how equilibrium conversion varies with temperature

- Identify the temperature range where 70% conversion is thermodynamically feasible"

Step 3: Kinetic Analysis

Prompt:

"Now analyze how fast we can achieve 70% conversion at different temperatures within the feasible range. For temperatures where equilibrium allows 70% conversion:

- Calculate k_f at each temperature
- Calculate $k_r = k_f/K$ at each temperature
- For a batch reactor, estimate the time required to reach 70% conversion
- Plot reaction time versus temperature and discuss the trade-off"

Step 4: Synthesis and Recommendation

Prompt:

"Based on the equilibrium and kinetic analyses, help me synthesize:

- What is the minimum temperature that allows 70% equilibrium conversion?
- Within the feasible temperature range, what temperature gives the fastest approach to 70% conversion?
- Are there practical considerations (catalyst stability, side reactions, energy costs) that might modify this recommendation?
- Could we do better than isothermal operation? What would be the ideal temperature profile?"

Learning Objectives

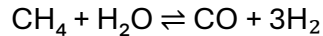
Through this AI-assisted exploration, you should develop:

- Deep understanding of the equilibrium-kinetics trade-off for reversible exothermic reactions
- Ability to use the van't Hoff equation to predict equilibrium conversion at different temperatures
- Skill in combining thermodynamic constraints with kinetic analysis for reactor optimization
- Practice in structured problem-solving using AI as a conceptual guide rather than an answer generator. It is designed for solving using AI assistance. Follow the prompting strategies from Chapter 1, focusing on conceptual understanding and strategic decision-making rather than just computation,

3.10 Practice Problems (Hand calculations)

Problem 3.1: Stoichiometry and Extent of Reaction

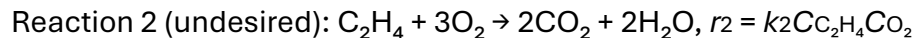
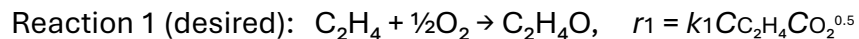
Consider the steam reforming of methane:



A reactor is fed with 10 mol/s CH_4 and 20 mol/s H_2O at 800°C and 1 bar. **(a)** Write the reaction in the standard form $0 = \sum v_i A_i$ and identify all stoichiometric coefficients. **(b)** Express the molar flow rate of each species as a function of the extent of reaction ξ . **(c)** If the extent of reaction reaches $\xi = 7$ mol/s, calculate the molar flow rate and mole fraction of each species in the outlet stream. **(d)** What is the fractional conversion of CH_4 when $\xi = 7$ mol/s? What is the fractional conversion of H_2O ? Why are they different? **(e)** Identify the limiting reactant and calculate the maximum possible extent of reaction.

Problem 3.2: Multiple Reactions and Selectivity

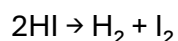
Ethylene oxide is produced by partial oxidation of ethylene over a silver catalyst. Two competing reactions occur:



At 250°C, $k_1 = 0.15 \text{ mol}^{0.5}/(\text{L}^{0.5}\cdot\text{s})$ and $k_2 = 0.08 \text{ L}/(\text{mol}\cdot\text{s})$. **(a)** Write expressions for the rates of formation of $\text{C}_2\text{H}_4\text{O}$, CO_2 , and consumption of C_2H_4 in terms of the two reaction rates. **(b)** Derive an expression for the instantaneous selectivity to ethylene oxide as a function of CO_2 concentration. **(c)** At what oxygen concentration does the selectivity equal 0.75? **(d)** Reaction 1 has $E_{a,1} = 60 \text{ kJ/mol}$ and Reaction 2 has $E_{a,2} = 80 \text{ kJ/mol}$. How does selectivity change with temperature? Should you operate at high or low temperature to maximize ethylene oxide yield? **(e)** The feed contains 7% C_2H_4 and 8% O_2 in nitrogen. Considering safety, kinetics, and selectivity, discuss whether you would operate fuel-rich or fuel-lean, and what oxygen concentration would be optimal.

Problem 3.3: Temperature Dependence and Arrhenius Analysis

The decomposition of hydrogen iodide follows the reaction:



Kinetic experiments at different temperatures give the following rate constants:

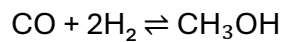
T (K) **k (L/(mol·s))**

556	0.0389
575	0.1146
590	0.2500
629	1.1016
647	2.0929

(a) Verify graphically that the Arrhenius equation describes this data. Create an Arrhenius plot ($\ln k$ vs. $1/T$) and assess linearity. **(b)** Determine the activation energy E_a and pre-exponential factor A from the plot. **(c)** Predict the rate constant at 700 K. **(d)** Calculate the temperature at which the rate constant doubles relative to 590 K. **(e)** Discuss potential limitations of using your Arrhenius correlation to predict k at 400 K or at 1000 K.

Problem 3.4: Langmuir-Hinshelwood Kinetics for Catalytic Reaction

The synthesis of methanol from CO and H_2 over a Cu/ZnO/Al₂O₃ catalyst follows Langmuir-Hinshelwood kinetics:



The rate expression derived from a proposed mechanism is:

$$r = \frac{kK_{CO}C_{CO}C_{H_2}}{(1 + K_{CO}C_{CO} + K_{H_2}C_{H_2})^2} \quad (3.39)$$

At 250°C and 50 bar: $k = 2.5 \times 10^{-3}$ mol/(kg_{cat}·s) $K_{CO} = 5.0$ bar⁻¹ $K_{H_2} = 0.5$ bar⁻¹ **(a)** What physical steps does this rate expression imply? Draw a reaction coordinate diagram showing the adsorption, surface reaction, and desorption steps. **(b)** Calculate the reaction rate when $C_{CO} = 2$ mol/L and $C_{H_2} = 10$ mol/L (equivalent to partial pressures of approximately 4 bar CO and 20 bar H_2 at these conditions). **(c)** Investigate how the rate changes with C_{H_2} while keeping $C_{CO} = 2$ mol/L. Plot r versus C_{H_2} for C_{H_2} ranging from 1 to 50 mol/L. Identify dilute and saturated regimes. **(d)** What is the apparent reaction order with respect to H_2 in: (i) the dilute limit (low C_{H_2}), (ii) the saturated limit (high C_{H_2})? **(e)** If product methanol also adsorbs on the catalyst surface with $K_{CH_3OH} = 10$ bar⁻¹, modify the rate expression to include product inhibition. How would accumulation of methanol affect the reaction rate?

Chapter Summary

This chapter has established the fundamental framework for analyzing chemical reactions from both stoichiometric and kinetic perspectives. These concepts form the foundation for reactor design and process optimization in chemical engineering.

Chapter 3 Summary: What You Should Have Learned

After completing this chapter, you should be able to:

1. Write balanced chemical equations and apply stoichiometric relationships
2. Define and use extent of reaction as a fundamental measure of reaction progress
3. Apply the IUPAC definition of reaction rate and understand its relationship to stoichiometry
4. Define and calculate fractional conversion, identify limiting reactants, and handle multiple reaction systems
5. Understand temperature dependence of reaction rates through the Arrhenius equation and activation energy
6. Write and interpret rate laws for elementary and non-elementary reactions
7. Analyze reversible reactions and understand the relationship between kinetics and equilibrium
8. Define selectivity and yield for multiple reaction systems
9. Deduce reaction kinetics from experimental data for complex reactions

Chapter 4: Ideal Reactor Models

Learning Objectives

After completing this chapter, you should be able to:

- Describe the three ideal reactor models—batch reactor (BR), continuous stirred tank reactor (CSTR), and plug flow reactor (PFR)—and identify the key assumptions underlying each model, including perfect mixing, isothermal operation, and ideal flow patterns.
- Derive and apply the design equations for batch reactors, expressing reaction time as a function of conversion for reactions of various orders, and analyze how reactor size and residence time requirements depend on kinetic parameters and desired conversion.
- Derive and apply the design equation for CSTRs, calculating required reactor volume to achieve specified conversion for single reactions, and understand how CSTR performance compares to batch and plug flow reactors for reactions of different orders.
- Derive and apply the design equation for PFRs, relating reactor volume to conversion through integration of the rate expression, and recognize the mathematical equivalence between batch reactor time and PFR space time for identical kinetics and feed conditions.
- Compare the relative performance of CSTR and PFR configurations for reactions of different orders, explaining why plug flow reactors generally require smaller volumes than CSTRs to achieve the same conversion for positive-order reactions.
- Apply reactor design equations to practical problems involving selection and sizing of reactors, considering trade-offs between capital cost (reactor volume), operating cost (residence time), and conversion requirements.

Nomenclature

The following symbols are introduced in this chapter and supplement the comprehensive nomenclature in Appendix B:

Roman Letters

C	Concentration (mol/L or mol/m ³)
$C_{A,0}$	Initial or feed concentration of species A (mol/L or mol/m ³)
F	Molar flow rate (mol/s or mol/min)
$F_{A,0}$	Feed molar flow rate of species A (mol/s or mol/min)
k	Reaction rate constant (units depend on reaction order)
n	Reaction order (dimensionless)
r	Reaction rate per unit volume (mol/(L·s) or mol/(m ³ ·s))

t	Time (s or min)
V	Reactor volume (L or m ³)
q_0	Volumetric feed flow rate (L/s or m ³ /s)
X_A	Conversion of species A (dimensionless, $0 \leq X_A \leq 1$)

Greek Letters

τ	Space time or nominal residence time (s or min)
--------	---

4.1 Introduction to Ideal Reactor Models

Chemical reactors are vessels in which chemical transformations occur under controlled conditions of temperature, pressure, and composition. The design and analysis of chemical reactors constitute one of the most important tasks in chemical reaction engineering. To predict reactor performance—relating feed conditions, reactor size, and operating conditions to product composition and conversion—we need mathematical models that describe how species concentrations change with time and position within the reactor.

Real reactors exhibit complex behavior: temperature and concentration gradients, non-ideal mixing, residence time distributions, and mass transfer limitations. However, we can often approximate real reactor behavior using three idealized models that capture essential features while remaining mathematically tractable. These *ideal reactor models* are the batch reactor (BR), the continuous stirred tank reactor (CSTR), and the plug flow reactor (PFR).

The utility of these ideal models lies not just in their simplicity but in their ability to bound the performance of real reactors. Real reactors typically behave somewhere between the extremes of perfect mixing (CSTR) and perfect plug flow (PFR), making these models invaluable for preliminary design, optimization, and troubleshooting. Understanding the assumptions underlying each model and recognizing when they apply is essential for effective reactor engineering.

4.2 Ideal Batch Reactor

4.2.1 Description and Assumptions

The batch reactor is the simplest reactor configuration. Reactants are charged into a closed vessel, allowed to react for a specified time under controlled conditions (often with mixing and temperature control), and then the product mixture is discharged. No material enters or leaves the reactor during the reaction period.

Key Assumptions of the Ideal Batch Reactor:

- 1. Perfectly mixed:** The reactor contents are uniform in composition and temperature at any instant. Mixing is instantaneous and complete, eliminating concentration and temperature gradients.
- 2. Closed system:** No material enters or leaves during the reaction. The total number of moles may change due to reaction stoichiometry, but the system boundary is impermeable.
- 3. Isothermal operation:** Temperature is maintained constant throughout the reaction, either through external heating/cooling or because the heat of reaction is negligible. Non-isothermal batch reactors require additional energy balances.
- 4. Constant volume:** For liquid-phase reactions, volume changes due to density variations are typically negligible. For gas-phase reactions, if operating at constant pressure, volume may change with the number of moles, requiring modification of the design equation.
- 5. Negligible startup/shutdown:** The time required for charging, heating to reaction temperature, and discharging is negligible compared to reaction time. This assumption breaks down for very fast reactions or large reactors with significant thermal inertia.

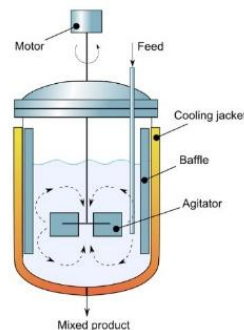


Figure 4-1 Ideal stirred batch reactor

These assumptions allow us to describe reactor performance using ordinary differential equations in time, significantly simplifying the mathematical analysis compared to spatially distributed models.

4.2.2 Design Equation Derivation

We derive the batch reactor design equation from a species balance on the reactor. For species A participating in a reaction, the rate of accumulation equals the rate of generation by reaction:

$$\text{Rate of accumulation} = \text{Rate of generation by reaction}$$

For a constant-volume batch reactor:

$$\frac{dC_A}{dt} = r_A \quad (4.1)$$

where C_A is the concentration of species A and r_A is its rate of formation (negative for reactants being consumed). For a reaction where A is consumed, $r_A = \nu_A r$, where ν_A is the stoichiometric coefficient (negative for reactants) and r is the reaction rate.

It is often more convenient to express the design equation in terms of conversion x_A . The conversion is defined as:

$$x_A = \frac{C_{A,0} - C_A}{C_{A,0}} \quad (4.2)$$

Rearranging: $C_A = C_{A,0}(1 - x_A)$. Differentiating with respect to time:

$$\frac{dC_A}{dt} = -\frac{C_{A,0} dx_A}{dt} \quad (4.3)$$

Substituting into Equation 4.1 (with $r_A = -r$ for a reactant A being consumed):

$$\frac{C_{A,0} dx_A}{dt} = r \quad (4.4)$$

Separating variables and integrating from initial conditions ($t = 0, x_A = 0$) to final conditions (t, x_A):

$$t = C_{A,0} \int_0^{x_A} \frac{1}{r} dx_A \quad (4.5)$$

This is the fundamental batch reactor design equation. It relates the time required to achieve a given conversion to the initial concentration and the rate expression. The integral must be evaluated either analytically (for simple rate laws) or numerically (for complex kinetics). Note that this equation applies regardless of whether volume changes during reaction—the derivation assumed constant volume, but a similar form results for variable volume if we work consistently with moles rather than concentrations.

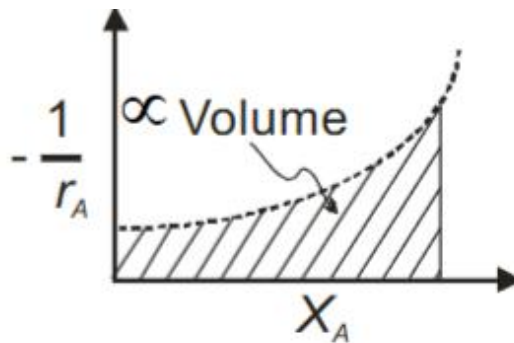


Figure 4-2 The reactor volume is proportional to the integrated surface below the function $1/r$

4.2.3 Design Equations for Common Reaction Orders

For power-law kinetics of the form $r = kC_A^n$, we can derive explicit expressions for reaction time as a function of conversion. Expressing concentration in terms of conversion ($C_A = C_{A,0}(1 - x_A)$):

Zero-order reaction (n = 0):

$r = k$ (constant, independent of concentration)

$$t = \frac{C_{A,0}x_A}{k} \quad (4.6)$$

First-order reaction (n = 1):

$r = kC_A$

$$t = -\frac{\ln(1 - x_A)}{k} \quad (4.7)$$

Second-order reaction (n = 2):

$r = kC_A^2$

$$t = \frac{x_A}{[kC_{A,0}(1 - x_A)]} \quad (4.8)$$

These expressions reveal how reaction order profoundly affects reactor performance. For first-order reactions, the time to reach a given conversion is independent of initial concentration. For second-order reactions, higher initial concentrations reduce the required reaction time—a fact exploited in industrial practice by feeding reactants at high concentrations.

The batch reactor is particularly suitable for small-scale production, reactions requiring long residence times, or when flexibility in operating conditions (such as temperature profiles) is needed. However, the cyclic nature of batch operation (charging, reaction, discharging, cleaning) introduces dead time that reduces productivity. For large-scale continuous production, continuous reactors (CSTR or PFR) are generally preferred.

Worked Example 4.1: Batch Reactor Design for Second-Order Reaction

The liquid-phase dimerization reaction $2A \rightarrow P$ follows second-order kinetics with $k = 0.15$ L/(mol·min) at 80°C. A batch reactor is charged with a solution containing $C_{A,0} = 2.5$ mol/L. Calculate: (a) the time required to achieve 90% conversion, and (b) the time required to achieve 95% conversion. (c) Comment on how the additional 5% conversion affects the required reaction time.

Solution:

(a) Time for 90% conversion

For a second-order reaction $2A \rightarrow P$, the rate expression is $r = kC_A^2$. Using Equation (4.7):

$$t = \frac{X_A}{[kC_{(A,0)}(1 - X_A)]}$$

Substituting $X_A = 0.90$, $k = 0.15 \text{ L}/(\text{mol}\cdot\text{min})$, and $C_{A,0} = 2.5 \text{ mol/L}$:

$$t = 0.90/[0.15 \times 2.5 \times (1 - 0.90)] = 0.90/(0.375 \times 0.10) = 24 \text{ minutes}$$

(b) Time for 95% conversion

Using the same equation with $X_A = 0.95$:

$$t = 0.95/[0.15 \times 2.5 \times (1 - 0.95)] = 0.95/(0.375 \times 0.05) = 50.7 \text{ minutes}$$

(c) Analysis

Increasing conversion from 90% to 95% (an additional 5%) more than doubles the required reaction time from 24 minutes to 50.7 minutes. This dramatic increase occurs because as conversion approaches completion, the reactant concentration becomes very small, causing the reaction rate to slow significantly. For second-order reactions, this effect is particularly pronounced—the term $(1 - X_A)$ in the denominator approaches zero, causing t to increase rapidly. This illustrates why achieving very high conversions in batch reactors becomes increasingly expensive in terms of time (and thus productivity). In practice, engineers must balance the desire for high conversion against the economic penalty of long reaction times.

Prompted Example 4.1: Batch Reactor with First-Order Kinetics

Problem:

The thermal decomposition of compound A follows first-order kinetics with a rate constant $k = 0.05 \text{ min}^{-1}$ at 120°C . You need to design a batch reactor to decompose 75% of A starting with an initial concentration of 3.0 mol/L . The available reactor has a volume of 500 L . Your task is to determine the required reaction time and assess whether the reactor size is appropriate for a production target of 1000 kg of product per day (assuming the molecular weight of the product P is 100 g/mol and each mole of A produces one mole of P).

Approach: My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the fundamental

assumptions in the modelling by asking me questions and wait for my answer to each question.

4.3 Ideal Continuous Stirred Tank Reactor (CSTR)

4.3.1 Description and Assumptions

The continuous stirred tank reactor (CSTR), also called a continuous flow stirred tank reactor or backmix reactor, operates at steady state with continuous feed and product streams. The reactor contents are vigorously stirred such that composition and temperature are spatially uniform throughout the vessel. Due to perfect mixing, the composition in the reactor is identical to the composition in the exit stream—a distinctive feature that profoundly affects reactor performance.

Key Assumptions of the Ideal CSTR:

- 1. Perfect mixing:** Mixing is instantaneous and complete. The reactor contents are spatially uniform in composition, temperature, and reaction rate at all locations. The exit stream composition equals the composition inside the reactor.
- 2. Steady state:** Operating conditions (flow rates, concentrations, temperature) do not change with time. All accumulation terms in the material balance are zero: input = output + consumption.
- 3. Isothermal operation:** Temperature is uniform and constant throughout the reactor. This requires effective heat removal (for exothermic reactions) or heat addition (for endothermic reactions) to balance the heat of reaction.
- 4. Constant density:** For liquid-phase reactions, density changes are typically negligible. For gas-phase reactions at constant temperature and pressure, density may vary with molecular weight changes, affecting volumetric flow rates.
- 5. Single inlet and outlet:** The reactor has one inlet stream (though multiple components may be fed) and one outlet stream. Extensions to multiple feeds or recycle streams require modification of the design equations.

The perfect mixing assumption means that reactants entering the CSTR are immediately diluted to the exit concentration. This is both an advantage (exit conditions are easily controlled and measured) and a disadvantage (reactants are exposed to the lowest driving force throughout their residence time).

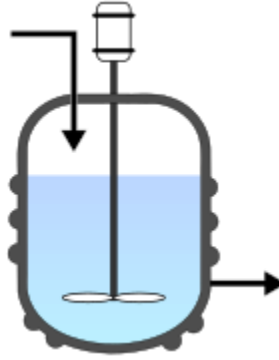


Figure 4-3 Continuous stirred tank reactor

4.3.2 Design Equation Derivation

The CSTR design equation is derived from a steady-state material balance on species A:

$$\text{Rate of A in} - \text{Rate of A out} + \text{Rate of A generation} = 0$$

In terms of molar flow rates:

$$F_{A,0} - F_A + r_A V = 0 \quad (4.9)$$

where $F_{A,0}$ is the inlet molar flow rate of A, F_A is the outlet molar flow rate, r_A is the rate of formation of A per unit volume (negative for a reactant), and V is the reactor volume.

For constant volumetric flow rate q_0 , we can express molar flow rates as $F = q_0 C$:

$$q_0 C_{A,0} - q_0 C_A + r_A V = 0 \quad (4.10)$$

For a reactant A being consumed, $r_A = -r$, where r is the positive reaction rate. Substituting and rearranging:

$$\frac{V}{q_0} = \frac{C_{A,0} - C_A}{r} \quad (4.11)$$

The ratio V/q_0 is called the *space time* or *nominal residence time* τ . It represents the time required to process one reactor volume of feed at the inlet conditions.

In terms of conversion:

$$\tau = \frac{V}{q_0} = \frac{C_{A,0} x_A}{r} \quad (4.12)$$

This is the **fundamental CSTR design equation**. It states that the space time equals the initial concentration times the conversion divided by the reaction rate *evaluated at exit conditions*. This last point is crucial: unlike the batch reactor where rate changes continuously with conversion, in a CSTR the rate is constant at its exit value throughout the entire reactor.

4.3.3 Graphical Interpretation and Comparison with Batch Reactors

The CSTR design equation can be interpreted graphically. Rearranging Equation (4.12):

$$\tau = \frac{C_{A,0}x_A}{r}$$

On a plot of $1/r$ versus x_A , the space time for a CSTR is represented by a rectangle with height $1/r(x_A)$ and width x_A i.e. the area below the horizontal lines. In contrast, the batch reactor time (from Equation (4.5)) is the area under the curve from 0 to x_A .

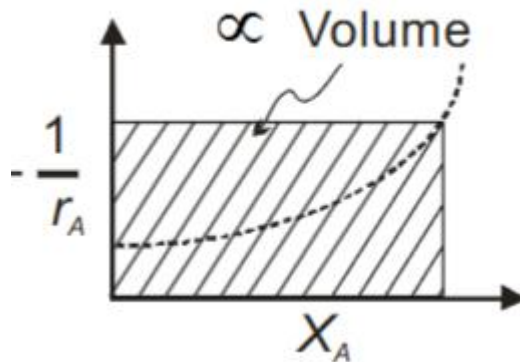


Figure 4-4 $1/r$ vs x for a first and a second order reaction

For positive-order reactions ($n > 0$), the reaction rate decreases as conversion increases. This means $1/r$ increases with x_A . The rectangular area (CSTR) extends to the highest value of $1/r$ (at the exit), making the CSTR space time larger than the batch time for the same conversion. **A CSTR requires more volume (or time) than a batch reactor to achieve the same conversion for positive-order reactions.**

This apparent disadvantage of the CSTR is offset by practical considerations: continuous operation eliminates batch downtime, simplifies heat removal due to uniform temperature, and provides easier control of product quality. For very fast reactions or highly exothermic reactions, the CSTR's ability to maintain low reactant concentrations throughout can actually be advantageous, moderating the rate and heat generation.

Worked Example 4.2: CSTR Design for First-Order Reaction

Problem:

A first-order liquid-phase reaction $A \rightarrow P$ with $k = 0.25 \text{ min}^{-1}$ is to be carried out in a CSTR. The feed concentration is $C_{A,0} = 4.0 \text{ mol/L}$, and the volumetric flow rate is $q_0 = 100 \text{ L/min}$.

Calculate: (a) the reactor volume required to achieve 80% conversion, (b) the reactor volume required to achieve 95% conversion.

Solution:

(a) Reactor volume for 80% conversion

For a first-order reaction, $r = kC_A$. In a CSTR, the exit concentration is:

$$C_A = C_{A,0}(1 - X_A) = 4.0(1 - 0.80) = 0.80 \text{ mol/L}$$

The reaction rate at the exit is:

$$r = kC_A = 0.25 \times 0.80 = 0.20 \text{ mol/(L}\cdot\text{min)}$$

Using the CSTR design equation (Equation (4.12)):

$$\tau = (C_{A,0}X_A)/r = (4.0 \times 0.80)/0.20 = 16 \text{ min}$$

Therefore, the reactor volume is:

$$V = \tau q_0 = 16 \times 100 = 1600 \text{ L}$$

(b) Reactor volume for 95% conversion

At 95% conversion:

$$C_A = 4.0(1 - 0.95) = 0.20 \text{ mol/L}$$

$$r = 0.25 \times 0.20 = 0.05 \text{ mol/(L}\cdot\text{min)}$$

$$\tau = (4.0 \times 0.95)/0.05 = 76 \text{ min}$$

$$V = 76 \times 100 = 7600 \text{ L}$$

Analysis: Despite this volumetric disadvantage, CSTRs are widely used industrially because of superior temperature control, ease of operation, and flexibility for handling catalyst particles or multiple phases.

Prompted Example 4.2: CSTR Network Design

Problem:

A second-order liquid-phase reaction $2A \rightarrow P$ with $k = 0.08 \text{ L}/(\text{mol}\cdot\text{min})$ is to be carried out with a feed flow rate of $50 \text{ L}/\text{min}$ and $C_{A,0} = 3.0 \text{ mol}/\text{L}$. The target conversion is 85%. You have been asked to compare two configurations: (a) a single CSTR, and (b) two equal-volume CSTRs in series. Your task is to determine the total volume required for each configuration and explain which would be more economical. Additionally, consider how

temperature control requirements might differ between the two configurations for this exothermic reaction.

Approach: My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the fundamental assumptions in the modelling by asking me questions and wait for my answer to each question.

4.4 Ideal Plug Flow Reactor (PFR)

4.4.1 Description and Assumptions

The plug flow reactor (PFR), also called a piston flow or tubular reactor, operates with continuous flow through a pipe or tube. The distinguishing feature is that there is no mixing in the axial (flow) direction—each fluid element moves through the reactor as a coherent "plug" with no overtaking or backmixing. Radial mixing (perpendicular to flow) is typically assumed complete, resulting in uniform properties across any cross-section.

Key Assumptions of the Ideal PFR:

- 1. Plug flow (no axial mixing):** Fluid elements move through the reactor in the same order they enter. There is no backmixing, molecular diffusion in the flow direction, or turbulent dispersion. Each element maintains its identity as it traverses the reactor.
- 2. Perfect radial mixing:** Concentration and temperature are uniform across any cross-section perpendicular to flow. Properties vary only along the axial direction. This assumption is valid for turbulent flow in tubes with length-to-diameter ratios exceeding about 50.
- 3. Steady state:** Conditions at any axial position do not change with time, though they vary with position along the reactor length. The time derivative of concentration at any fixed position is zero.
- 4. Isothermal operation:** Temperature is uniform throughout the reactor. For tubular reactors with high surface-to-volume ratio, this is often achievable through jacket cooling or heating.
- 5. Negligible pressure drop:** For liquid-phase reactions, pressure variations are usually negligible. For gas-phase reactions in long tubes, pressure drop may be significant and must be accounted for in the design equations.
- 6. Constant cross-sectional area:** The reactor tube has uniform diameter. Variations in cross-section require modification of the continuity equation.

The plug flow assumption is an idealization—real reactors exhibit some degree of axial mixing. However, for turbulent flow in long tubes ($L/D > 50$), packed bed reactors with small particles, and laminar flow in very narrow channels, the plug flow model provides excellent approximations. The key advantage of the PFR over the CSTR is that reactants experience high concentrations (and thus high rates) early in the reactor, making PFRs more volumetrically efficient for positive-order reactions.

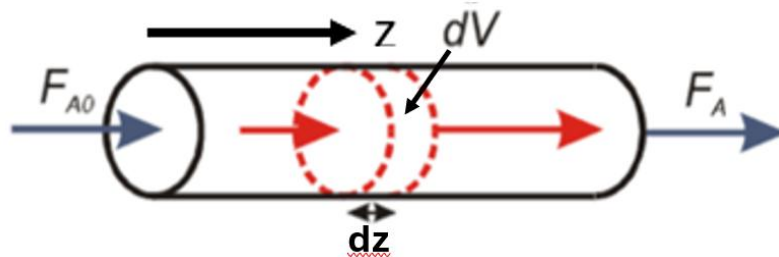


Figure 4-5 Ideal plug flow reactor

4.4.2 Design Equation Derivation

We derive the PFR design equation by performing a material balance on a differential slice of the reactor at position z with thickness dz . The volume of this slice is $dV = A \cdot dz$, where A is the cross-sectional area. Concentration are assumed to be constant within dV .

At steady state, the material balance on species A for this differential element is:

$$(\text{Flow in at } z) - (\text{Flow out at } z + dz) + (\text{Generation in } dV) = 0$$

$$F_A|_{z+dz} - F_A|_z + r_A dV = 0 \quad (4.13)$$

Recognizing that $F_A|_{z+dz} - F_A|_z = dF_A$:

$$\frac{dF_A}{dV} = r_A \quad (4.14)$$

For a reactant being consumed, $r_A = -r$ and $F_A = F_{A,0}(1 - x_A)$, so $dF_A = -F_{A,0} dx_A$:

$$F_{A,0} \frac{dx_A}{dV} = r_A \quad (4.15)$$

Integrating from reactor inlet ($V = 0, x_A = 0$) to outlet (V, x_A):

$$V = F_{A,0} \int_0^{x_A} \frac{1}{r_A} dx_A \quad (4.16)$$

For constant volumetric flow rate, $F_{A,0} = q_0 C_{A,0}$, and the space time $\tau = V/q_0$ is:

$$\tau = C_{A,0} \int_0^{x_A} \frac{1}{r} dx_A \quad (4.17)$$

This is the fundamental PFR design equation. Notice that it is **mathematically identical** to the batch reactor design equation (Equation (4.5)). This equivalence is profound: the time required in a batch reactor equals the space time required in a PFR for the same reaction kinetics and feed conditions. However, the physical interpretation differs—in the batch reactor, time represents actual elapsed time at a fixed location; in the PFR, space time represents the nominal residence time of fluid elements flowing through the reactor.

4.4.3 Comparison of Ideal Reactors

For positive-order reactions ($n > 0$), the PFR consistently requires less volume than a CSTR to achieve the same conversion. This occurs because:

1. In a PFR, reactants enter at high concentration, experiencing high reaction rates early in the reactor. Rates decrease gradually as conversion increases.
2. In a CSTR, reactants are instantly diluted to exit concentration, experiencing only the low reaction rate corresponding to high conversion throughout the entire reactor volume.
3. The batch reactor and PFR give identical performance (same time or space time for a given conversion) when compared on a consistent basis.

The volumetric advantage of the PFR becomes more pronounced as conversion increases and as reaction order increases. For first-order reactions, the ratio V_{CSTR}/V_{PFR} can be analytically shown to be:

$$\frac{V_{CSTR}}{V_{PFR}} = \frac{x_A}{\left[(1 - x_A) \ln \left(\frac{1}{1 - x_A} \right) \right]} \quad (4.18)$$

This ratio equals 1 at $x_A = 0$, increases to 1.33 at $x_A = 0.50$, reaches 2.0 at $x_A = 0.75$, and grows without bound as $x_A \rightarrow 1$. For second-order reactions, the difference is even more dramatic. Despite this volumetric disadvantage, CSTRs remain widely used because they offer superior temperature control (particularly important for highly exothermic reactions), easier maintenance, and flexibility for handling solids or multiple liquid phases.

Worked Example 4.3: PFR Design and Reactor Comparison

Problem:

The liquid-phase decomposition $A \rightarrow 2B$ follows second-order kinetics with $k = 2.0 \text{ L}/(\text{mol}\cdot\text{s})$ at 400°C . The feed contains pure A at $C_{A,0} = 0.5 \text{ mol/L}$ with a flow rate of 200 L/s . Design a PFR to achieve 80% conversion. Then, calculate how much larger a CSTR would need to be for the same conversion and discuss the implications for reactor selection.

Solution:

PFR design

For a second-order reaction $r = kC_{A,0}^2$, with $C_A = C_{A,0}(1 - x_A)$

$$r = kC_{A,0}^2(1 - x_A)^2$$

Substituting into Equation (4.16):

$$\tau = C_{A,0} \int_0^{x_A} 1/[kC_{A,0}^2(1 - x_A)^2] dx_A$$

Evaluating the integral:

$$\int \frac{dx_A}{(1 - x_A)^2} = \frac{x_A}{1 - x_A}$$

Therefore:

$$\tau = \frac{x_A}{[kC_{A,0}(1 - x_A)]}$$

Substituting values ($x_A = 0.80$, $k = 2.0 \text{ L}/(\text{mol}\cdot\text{s})$, $C_{A,0} = 0.5 \text{ mol/L}$):

$$\tau = 0.80/[2.0 \times 0.5 \times (1 - 0.80)] = 0.80/(1.0 \times 0.20) = 4.0 \text{ s}$$

The required PFR volume is:

$$V_{\text{PFR}} = \tau q_0 = 4.0 \times 200 = \mathbf{800 \text{ L}}$$

CSTR comparison

For a CSTR, using Equation (4.11) with the rate evaluated at exit conditions:

$$C_A = 0.5(1 - 0.80) = 0.1 \text{ mol/L}$$

$$r = 2.0 \times (0.1)^2 = 0.02 \text{ mol}/(\text{L}\cdot\text{s})$$

$$\tau_{\text{CSTR}} = \frac{C_{A,0}x_A}{r} = (0.5 \times 0.80)/0.02 = 20 \text{ s}$$

$$V_{\text{CSTR}} = 20 \times 200 = 4000 \text{ L}$$

Analysis

The CSTR requires $4000/800 = 5$ times more volume than the PFR to achieve the same conversion. This dramatic difference arises because the second-order kinetics strongly penalizes the low concentration in the CSTR. The rate at the CSTR exit ($0.02 \text{ mol}/(\text{L}\cdot\text{s})$) is only 1/25th of the initial rate that would occur in a PFR ($2.0 \times 0.5^2 = 0.5 \text{ mol}/(\text{L}\cdot\text{s})$). From a purely volumetric efficiency standpoint, the PFR is strongly favored. However, if this exothermic reaction produces significant heat (which would need to be removed to maintain isothermal conditions), the CSTR's lower average reaction rate could make temperature control easier. A tubular reactor with 800 L volume would have significant

length and potentially challenging heat transfer, while the CSTR's compact geometry might allow easier jacketing. The final choice depends on balancing capital cost (favoring smaller PFR) against operational considerations including heat transfer, pressure drop, and ease of temperature control.

Prompted Example 4.3: PFR Design with Variable Volumetric Flow

Problem:

The gas-phase reaction $2A \rightarrow B + C$ is carried out in a PFR at constant temperature and pressure. The reaction follows second-order kinetics with $k = 0.5 \text{ L}/(\text{mol}\cdot\text{min})$. The feed is pure A at 5 atm and 300°C with a total molar flow rate of $100 \text{ mol}/\text{min}$. Design a PFR to achieve 70% conversion. Note that for this gas-phase reaction, the total number of moles changes from 2 moles of reactant to 2 moles of product, so volumetric flow rate remains constant. However, if the stoichiometry were different (e.g., $2A \rightarrow B$), you would need to account for changing volumetric flow rate with conversion. Your task is to: (a) calculate the required reactor volume, (b) determine the reactor length if the tube diameter is 10 cm, and (c) verify that the L/D ratio justifies the plug flow assumption.

Approach: My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the fundamental assumptions in the modelling by asking me questions and wait for my answer to each question.

4.5 Practice Problems

Problem 4.1: Batch Reactor with Mixed-Order Kinetics

The liquid-phase reaction $A \rightarrow P$ follows 1.5-order kinetics: $r = kC_A^{1.5}$ with $k = 0.08 \text{ (L/mol)}^{0.5}/\text{min}$ at 90°C . A 2000 L batch reactor is charged with $C_{A,0} = 3.5 \text{ mol/L}$. (a) Derive the integrated form of the batch reactor design equation for this 1.5-order reaction. (b) Calculate the time required to reach 75% conversion. (c) If the activation energy is 65 kJ/mol , at what temperature would the time be reduced by half? (d) The reactor has 30 minutes of downtime between batches for charging, heating, and discharging. Calculate the production rate of P in kg/day at 75% conversion ($M_P = 120 \text{ g/mol}$). (e) Would increasing conversion to 90% improve productivity? Calculate the new production rate and discuss the trade-off.

Problem 4.2: CSTR Design with Product Inhibition (Hand calculation)

An enzymatic reaction $A \rightarrow P$ is carried out in a CSTR with Michaelis-Menten kinetics modified for product inhibition: $r = (V_{\max}C_A)/[(K_m + C_A)(1 + C_P/K_i)]$, where $V_{\max} = 2.0$ mol/(L·min), $K_m = 0.5$ mol/L, and $K_i = 1.5$ mol/L. The feed contains $C_{A,0} = 4.0$ mol/L at 80 L/min. (a) Write the steady-state material balance equations for A and P in the CSTR. (b) Calculate the reactor volume required for 60% conversion (you'll need to solve numerically or iteratively). (c) Plot conversion versus space time for τ from 0 to 10 minutes and identify optimal operating conditions. (d) Explain physically why product inhibition affects the CSTR more severely than it would affect a PFR. (e) Propose two strategies to mitigate product inhibition in this system.

Problem 4.3: Series vs. Parallel CSTR Configuration (Hand calculation)

A second-order reaction $A \rightarrow P$ with $k = 0.12$ L/(mol·min) is to be carried out with $q_0 = 200$ L/min and $C_{A,0} = 2.5$ mol/L to achieve 85% conversion. Compare three configurations: (a) single CSTR, (b) two equal-volume CSTRs in series, and (c) three equal-volume CSTRs in series. For each configuration: (i) Calculate the total reactor volume required. (ii) Determine the intermediate conversions. (iii) Plot conversion versus cumulative volume. (d) Derive a general expression for the volume of the n th reactor in a series of equal-volume CSTRs carrying out a second-order reaction. (e) As the number of CSTRs in series approaches infinity, what does the total volume approach? Verify your answer by comparing with a PFR calculation. (f) Discuss practical considerations: why not always use many small CSTRs in series to approach PFR performance?

Problem 4.4: PFR Design for Autocatalytic Reaction

The autocatalytic reaction $A \rightarrow P$ is catalyzed by product P with rate law $r = kC_A C_P$, where $k = 0.20$ L/(mol·s). Feed contains 3.0 mol/L A and 0.10 mol/L P (seed concentration) at 150 L/s. (a) Express C_P in terms of $C_{A,0}$, $C_{P,0}$, and x_A . (b) Substitute into the rate expression and derive the PFR design equation as an integral. (c) Calculate the volume required for 80% conversion (evaluate the integral numerically). (d) Autocatalytic reactions show unusual behavior—the rate first increases then decreases with conversion. Find the conversion where the rate is maximum. (e) What happens if the seed concentration $C_{P,0}$ is too small? Explore by plotting r versus x_A for $C_{P,0} = 0.01, 0.10,$ and 0.50 mol/L. (f) Would a CSTR or PFR be preferable for this autocatalytic system? Justify your answer based on the rate profile.

Problem 4.5: Reversible Reaction in Different Reactor Types

The reversible liquid-phase reaction $A \rightleftharpoons P$ has forward rate constant $k_f = 0.40 \text{ min}^{-1}$ and equilibrium constant $K_c = 8.0$ at 100°C . Pure A is fed at $C_{A,0} = 5.0 \text{ mol/L}$. (a) Calculate the equilibrium conversion. (b) For a batch reactor, derive an expression for time as a function of conversion accounting for reversibility. Calculate the time to reach 95% of equilibrium conversion. (c) For a CSTR, derive the design equation accounting for reversibility. Calculate the space time to reach 95% of equilibrium conversion with $q_0 = 100 \text{ L/min}$. (d) For a PFR, set up the design equation and calculate the space time to reach 95% of equilibrium conversion. (e) Compare the three reactor types: calculate the ratio of volumes (or times) required for the same fractional approach to equilibrium. (f) Discuss how reversibility affects the performance comparison between CSTR and PFR. Does the PFR's advantage diminish as we approach equilibrium? Why?

Problem 4.6: Reactor Selection and Scale-Up

A pharmaceutical company has developed a new synthesis route: $A + B \rightarrow P$ with rate law $r = kC_A C_B$, where $k = 0.15 \text{ L}/(\text{mol}\cdot\text{min})$ at 60°C . The reaction is highly exothermic ($\Delta H_{rxn} = -180 \text{ kJ/mol}$) and requires careful temperature control. Feed conditions: $C_{A,0} = 2.0 \text{ mol/L}$, $C_{B,0} = 2.4 \text{ mol/L}$ (20% excess), $q_0 = 50 \text{ L/min}$. Target: 90% conversion of A. (a) Calculate required volumes for: (i) batch reactor (report time, assuming 1000 L working volume), (ii) single CSTR, (iii) PFR. (b) For the batch reactor, plot temperature rise versus conversion assuming adiabatic operation (heat capacity = $3.5 \text{ J}/(\text{g}\cdot\text{K})$, density = 1.05 g/mL). What cooling rate (kW) is needed to maintain isothermal operation? (c) For the CSTR, calculate the heat generation rate at steady state. Discuss heat exchanger design implications. (d) For the PFR, calculate the temperature profile along the reactor length assuming adiabatic operation. At what conversion does temperature exceed 80°C (assumed safe limit)? (e) Based on your analysis of volumes, temperature control, and safety considerations, recommend a reactor type with justification. (f) Consider hybrid configurations: Would a CSTR followed by a PFR offer advantages? What about a PFR with interstage cooling?

Chapter 4 Summary: What you should have learned

After completing this chapter, you should be able to:

1. Derive and apply design equations for ideal batch reactors
2. Derive and apply design equations for CSTRs
3. Derive and apply design equations for PFRs

4. Compare reactor volumes for batch, CSTR, and PFR configurations
5. Analyze reactors in series configurations
6. Apply space time and space velocity concepts

Chapter 5: Ideal Reactor Heat Balances

Learning Objectives

After completing this chapter, you should be able to:

- Derive and apply energy balance equations for batch reactors, CSTRs, and PFRs, incorporating terms for heat of reaction, sensible heat effects, and heat transfer, and recognize when simplifications such as constant heat capacity or negligible shaft
- endothermic reactions, understanding how heat capacity, initial temperature, and reaction stoichiometry affect the temperature change during adiabatic operation.
- Design isothermal reactor systems by determining heat transfer requirements, selecting appropriate heat exchange configurations (jackets, coils, external exchangers), and calculating required heat transfer areas based on overall heat transfer coefficients and temperature driving forces.
- Analyze non-isothermal, non-adiabatic reactor operation by solving coupled material and energy balances simultaneously, predicting temperature and conversion profiles, and identifying optimal operating conditions that balance reaction rate enhancement with selectivity and safety constraints.
- Identify and analyze multiple steady states in CSTRs for exothermic reactions, constructing heat generation and heat removal curves to determine stability of steady states, and understanding the practical implications for startup, shutdown, and control.
- Design reactor networks with interstage cooling or heating, including CSTRs in series with intercoolers, PFRs with recycle and heat exchange, and combinations of different reactor types, optimizing the configuration to achieve desired conversion while maintaining safe temperatures.
- Apply the concept of optimal temperature trajectories to maximize selectivity in complex reaction systems, recognizing that different reactions have different temperature sensitivities (activation energies) and using this to favor desired products over undesired byproducts.

Nomenclature

The following symbols are introduced in this chapter and supplement the comprehensive nomenclature in Appendix B:

Roman Letters

A_{HT}	Heat transfer area (m^2)
C_p	Heat capacity at constant pressure ($J/(mol \cdot K)$ or $J/(g \cdot K)$)
\bar{C}_p	Mean heat capacity of reaction mixture ($J/(mol \cdot K)$ or $J/(g \cdot K)$)

E_a	Activation energy (J/mol or kJ/mol)
Q	Heat transfer rate (W or J/s)
\dot{Q}	Heat transfer rate (W or J/s)
T	Temperature (K or °C)
T_o	Feed or initial temperature (K or °C)
T_{ad}	Adiabatic temperature rise (K or °C)
T_c	Coolant temperature (K or °C)
U	Overall heat transfer coefficient (W/(m ² ·K))
W_s	Shaft work (W or J/s)

Greek Letters

ΔH_{rxn}	Heat of reaction (J/mol or kJ/mol, negative for exothermic)
ΔH_{rxn}°	Standard heat of reaction at reference temperature (J/mol or kJ/mol)
ΔT_{ad}	Adiabatic temperature rise (K or °C)
ρ	Density (kg/m ³ or g/L)

Subscripts and Superscripts

ad	Adiabatic
c	Coolant
gen	Heat generation
rem	Heat removal
rxn	Reaction

5.1 Introduction to Reactor Energy Balances

In Chapter 4, we developed design equations for ideal reactors operating under isothermal conditions—a significant simplification that allowed us to focus on material balances and reaction kinetics without the added complexity of temperature variations. However, real chemical reactions are rarely isothermal. Nearly all reactions involve heat effects: exothermic reactions release energy that tends to raise temperature, while endothermic reactions absorb energy that tends to lower temperature. These temperature changes profoundly affect reactor performance through the exponential temperature dependence of reaction rate constants described by the Arrhenius equation.

Temperature control in chemical reactors represents one of the most critical challenges in reactor design and operation. Inadequate cooling of exothermic reactions can lead to

thermal runaway—a dangerous condition where temperature rises accelerate reaction rates, which in turn generate more heat, creating a positive feedback loop that may result in explosions or product degradation. Conversely, insufficient heating of endothermic reactions reduces reaction rates to economically unviable levels. Even when safety is not a concern, temperature affects product selectivity: different reactions in a complex network often have different activation energies, making temperature a powerful tool for favoring desired products.

This chapter extends our reactor models to include energy balances. We'll examine three limiting cases that bound real reactor behavior:

Isothermal operation: Temperature is maintained constant through external heating or cooling. This represents perfect temperature control—all heat generated (or consumed) by reaction is exactly balanced by heat transfer.

Adiabatic operation: No heat transfer occurs between the reactor and surroundings. All heat of reaction manifests as temperature change in the reactor contents. This represents the other extreme—no temperature control.

Non-isothermal, non-adiabatic operation: The most general case where partial heat transfer occurs. Temperature varies, but heat exchange with surroundings moderates the temperature change compared to adiabatic operation.

We'll develop coupled material and energy balance equations for batch reactors, CSTRs, and PFRs under these various thermal regimes. Understanding these models is essential not just for reactor design but for safe operation, process optimization, and troubleshooting. The interplay between kinetics, thermodynamics, and heat transfer creates rich and sometimes counterintuitive behavior—including multiple steady states in CSTRs and optimal temperature trajectories for maximizing selectivity—that we'll explore through worked examples and problems.

5.2 Energy Balance Fundamentals

5.2.1 General Energy Balance

The general energy balance for a reactor system states that the rate of energy accumulation equals the net rate of energy input:

$$\text{Accumulation} = \text{Energy in} - \text{Energy out} + \text{Heat generated by reaction} - \text{Heat transferred to surroundings} + \text{Shaft work}$$

For most chemical reactors, we can neglect kinetic and potential energy terms, and shaft work (stirring) is small compared to heat of reaction. The energy balance simplifies to:

$$\frac{dE}{dt} = \sum F_{i,in} H_{i,in} - \sum F_{i,out} H_{i,out} + \dot{Q} \quad (5.1)$$

where E is the total internal energy of the system, F_i are molar flow rates, H_i are specific enthalpies, and \dot{Q} is the net rate of heat addition to the system. For liquids and ideal gases at moderate pressure, enthalpy and internal energy are essentially equal, and both are strong functions of temperature.

5.2.2 Heat of Reaction

The heat of reaction ΔH_{rxn} is the enthalpy change when reactants at a specified temperature and pressure are completely converted to products at the same temperature and pressure. By convention:

Exothermic reactions: $\Delta H_{rxn} < 0$ (energy released, temperature tends to increase)

Endothermic reactions: $\Delta H_{rxn} > 0$ (energy absorbed, temperature tends to decrease)

The standard heat of reaction at reference temperature T_{ref} (usually 25°C or 298 K) is calculated from standard heats of formation:

$$\Delta H_{rxn}^0(T_{ref}) = \sum \nu_i \Delta H_i^0 \quad (5.2)$$

where ν_i are stoichiometric coefficients (negative for reactants, positive for products) and ΔH_i^0 are standard heats of formation.

The heat of reaction varies with temperature according to Kirchhoff's equation:

$$\Delta H_{rxn}(T) = \Delta H_{rxn}^0(T_{ref}) + \int_{T_{ref}}^T \Delta C_p dT \quad (5.3)$$

where $\Delta C_p = \sum \nu_i C_{p,i}$ is the heat capacity change of the reaction mixture. For moderate temperature ranges (< 100 K), the variation of ΔH_{rxn} with temperature is often small enough to neglect, and we treat ΔH_{rxn} as constant.

5.2.3 Adiabatic Temperature Rise

For an adiabatic reactor ($\dot{Q} = 0$), all heat of reaction manifests as temperature change. The maximum possible temperature change, called the *adiabatic temperature rise* ΔT_{ad} , occurs when conversion is complete. For a reactor initially at T_0 with complete conversion:

$$\Delta T_{ad} = - \frac{\Delta H_{rxn} C_{A,0}}{\rho \bar{C}_p} \quad (5.4)$$

where $C_{A,0}$ is initial reactant concentration, ρ is density, and \bar{C}_p is the mean heat capacity of the mixture. At any intermediate conversion X_A , the temperature is:

$$T = T_0 + \Delta T_{ad} X_A \quad (5.5)$$

This linear relationship between temperature and conversion is a key simplification for adiabatic reactor analysis. In reality ΔH_{rxn} , ρ and \bar{C}_p have a small temperature dependence that must be accounted for in detailed analysis. The adiabatic temperature rise provides immediate insight into thermal management requirements:

If $|\Delta T_{ad}| < 10$ K: Reaction heat effects are small; isothermal assumption is reasonable

If $10 \text{ K} < |\Delta T_{ad}| < 50$ K: Moderate heat effects; temperature control required but manageable

If $|\Delta T_{ad}| > 50$ K: Large heat effects; careful thermal design essential; consider staged operation with interstage cooling

5.3 Batch Reactor Energy Balance

5.3.1 General Energy Balance for Batch Reactors

For a well-mixed batch reactor, the energy balance accounts for heat generated by reaction and heat transferred through the reactor walls:

$$V\rho\bar{C}_p\frac{dT}{dt} = (-\Delta H_{rxn})rV + \dot{Q} \quad (5.6)$$

where V is reactor volume, ρ is density, \bar{C}_p is mean heat capacity, r is the reaction rate, and \dot{Q} is the rate of heat addition to the system. For heat transfer through the reactor wall:

$$\dot{Q} = UA_{HT}(T_c - T) \quad (5.7)$$

where U is the overall heat transfer coefficient, A_{HT} is the heat transfer area, T_c is the coolant (or heating medium) temperature, and T is the reactor temperature.

Substituting Equation (5.7) into (5.6) and combining with the material balance yields coupled differential equations:

$$\frac{dx_A}{dt} = \frac{r}{C_{A,0}} \quad (5.8)$$

$$\frac{dT}{dt} = \frac{[(-\Delta H_{rxn})r + UA_{HT}(T_c - T)]}{\rho V \bar{C}_p} \quad (5.9)$$

These equations must be solved simultaneously, typically numerically, to obtain conversion and temperature as functions of time. The rate r depends on both concentration (through conversion) and temperature (through the Arrhenius equation), creating strong coupling between material and energy balances.

5.3.2 Limiting Cases for Batch Reactors

Isothermal Operation ($T = T_0 = \text{constant}$)

For perfect temperature control, all heat of reaction is removed (exothermic) or supplied (endothermic) such that $dT/dt = 0$. The required heat removal rate is:

$$\dot{Q} = -(-\Delta H_{rxn})rV \quad (5.10)$$

The material balance reduces to the isothermal forms developed in Chapter 4. The design task becomes: given the rate at operating temperature, determine reactor size (or time), and separately calculate the required heat transfer area to maintain isothermal conditions.

Adiabatic Operation ($\dot{Q} = 0$)

With no heat transfer, Equation (5.9) simplifies to:

$$\frac{dT}{dt} = \frac{(-\Delta H_{rxn})r}{\rho \bar{C}_p} \quad (5.11)$$

Dividing Equation (5.11) by Equation (5.8):

$$\frac{dT}{dx_A} = \frac{(-\Delta H_{rxn})C_{A,0}}{\rho \bar{C}_p} = \Delta T_{ad} \quad (5.12)$$

Integrating with initial condition $T = T_0$ at $x_A = 0$ gives Equation (5.5). This elegant result—temperature is a linear function of conversion—greatly simplifies adiabatic reactor analysis. We can substitute $T = T_0 + \Delta T_{ad}x_A$ into the rate expression, reducing the problem to a single differential equation in x_A .

Non-Isothermal, Non-Adiabatic Operation

This general case requires numerical solution of the coupled Equations (5.8) and (5.9). The trajectory in T - x_A space depends on the relative magnitudes of heat generation by reaction and heat removal by cooling. If UA_{HT} is large (good heat transfer), behavior approaches isothermal. If UA_{HT} is small (poor heat transfer), behavior approaches adiabatic.

Worked Example 5.1: Adiabatic Batch Reactor Temperature Rise

Problem:

The exothermic liquid-phase reaction $A \rightarrow P$ has $\Delta H_{rxn} = -80$ kJ/mol and follows first-order kinetics with $k = 0.10$ min⁻¹ at 60°C and $E_a = 75$ kJ/mol. A batch reactor is charged with $C_{A,0} = 4000$ mol/m³ at 60°C. The mixture has density $\rho = 1000$ kg/m³ and heat capacity

$\bar{C}_p = 3.5 \text{ kJ}/(\text{kg}\cdot\text{K})$. (a) Calculate the adiabatic temperature rise for complete conversion. (b) If the reactor operates adiabatically, determine the final temperature and time required to reach 95% conversion. (c) What maximum temperature is reached, and at what conversion does it occur?

Solution:

(a) Adiabatic temperature rise

Using Equation 5.4:

$$\Delta T_{ad} = -(-80 \text{ kJ/mol})(4.0 \text{ mol/L})/[(1000 \text{ kg/m}^3)(3.5 \text{ kJ}/(\text{kg}\cdot\text{K}))]$$

$$\Delta T_{ad} = 320 \text{ kJ/L} / 3500 \text{ kJ}/(\text{m}^3\cdot\text{K}) = 320/3.5 = 91.4 \text{ K}$$

This is a very large temperature rise! If allowed to proceed adiabatically to complete conversion, the temperature would increase by over 90°C, reaching about 151°C. Such a large temperature rise requires careful safety considerations.

(b) Temperature and time for 95% conversion

At 95% conversion, using Equation 5.5:

$$T = 60^\circ\text{C} + (91.4 \text{ K})(0.95) = 60^\circ\text{C} + 86.8 \text{ K} = 146.8^\circ\text{C} \text{ or } 420 \text{ K}$$

For the time calculation, we must account for temperature variation. The rate constant at any temperature is:

$$k(T) = k_0 \exp\left[-\frac{Ea}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

With $k_0 = 0.10 \text{ min}^{-1}$ at $T_0 = 333 \text{ K}$. Substituting $T = T_0 + \Delta T_{ad}X_A$ into the design equation for a first-order reaction:

$$t = \int_0^{0.95} \frac{1}{k(T) \cdot (1 - X_A)} dX_A$$

This integral must be evaluated numerically. Using numerical integration (Simpson's rule or similar):

$$t \approx 1.84 \text{ minutes}$$

The reaction is quite fast due to the accelerating effect of temperature. Compare this to isothermal operation at 60°C where $t = -\ln(0.05)/0.10 = 30 \text{ minutes}$ —more than 10 times longer!

(c) Maximum temperature

For this first-order reaction in an adiabatic batch reactor, temperature increases monotonically with conversion following $T = T_0 + \Delta T_{ad}X_A$. Therefore, maximum temperature occurs at maximum conversion. At 95% conversion, $T_{max} = 146.8^\circ\text{C}$. For complete

conversion, temperature would reach 151.4°C. This illustrates why adiabatic operation of highly exothermic reactions requires careful safety analysis—temperatures can easily exceed boiling points or decomposition temperatures.

Prompted Example 5.1: Non-Isothermal Batch Reactor with Cooling

Problem:

A second-order liquid-phase reaction $2A \rightarrow P$ ($\Delta H_{rxn} = -120$ kJ/mol) is carried out in a 1500 L jacketed batch reactor. The reaction has $k = 0.05$ L/(mol·min) at 80°C and $E_a = 85$ kJ/mol. The reactor is charged with $C_{A,0} = 3.5$ mol/L at 80°C. The cooling jacket has area $A_{HT} = 15$ m² and overall heat transfer coefficient $U = 800$ W/(m²·K). Coolant temperature is maintained at 75°C. Mixture properties: $\rho = 950$ kg/m³, $\bar{C}_p = 3.2$ kJ/(kg·K). The target is 85% conversion. Your task is to: (a) calculate the adiabatic temperature rise, (b) determine if the reactor can maintain safe operation ($T < 110^\circ\text{C}$) with the given cooling capacity, (c) if not, what coolant temperature is needed, and (d) plot temperature and conversion versus time to visualize the thermal behavior.

Approach: My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the fundamental assumptions in the modelling by asking me questions and wait for my answer to each question.

5.4 Continuous Stirred Tank Reactor Energy Balance

5.4.1 General Energy Balance for CSTRs

For a CSTR at steady state, the energy balance becomes algebraic rather than differential. Energy in equals energy out:

$$F_{A,0}\bar{C}_p T_0 = F_{A,0}\bar{C}_p T - (-\Delta H_{rxn})rV + \dot{Q} \quad (5.13)$$

Rearranging and using $V = F_{A,0}\tau/C_{A,0}$:

$$T = T_0 + \frac{(-\Delta H_{rxn})\tau r}{\rho\bar{C}_p C_{A,0}} - \frac{\dot{Q}}{F_{A,0}\bar{C}_p} \quad (5.14)$$

This equation, combined with the material balance (from Chapter 4), determines reactor temperature and conversion simultaneously. Unlike batch reactors where we integrate over time, CSTRs require solving coupled algebraic equations—often graphically or iteratively.

5.4.2 Multiple Steady States in Exothermic CSTRs

One of the most fascinating—and practically important—phenomena in reactor engineering is the existence of *multiple steady states* in exothermic CSTRs. Under certain conditions, the same feed conditions and reactor parameters can result in three different operating points with vastly different temperatures and conversions.

Consider Equation 5.14 with heat transfer $\dot{Q} = UA_{HT}(T_c - T)$. Define:

Heat generation curve: $Q_{\text{gen}} = (-\Delta H_{\text{rxn}})r(T)V$

Heat removal curve: $Q_{\text{rem}} = F_{A,0}\bar{C}_p(T - T_0) + UA_{HT}(T - T_c)$

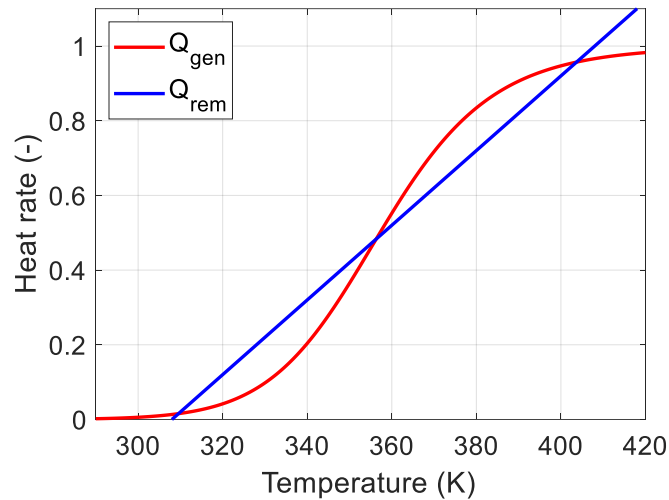


Figure 5-1 Multiple steady-states in a CSTR

At steady state, $Q_{\text{gen}} = Q_{\text{rem}}$. The heat generation curve is S-shaped due to the exponential Arrhenius temperature dependence and decreasing concentration at high conversion. The heat removal curve is typically linear or nearly linear. Where these curves intersect represents steady-state operating points.

At steady state, $Q_{\text{gen}} = Q_{\text{rem}}$. The heat generation curve is S-shaped due to the exponential Arrhenius temperature dependence and decreasing concentration at high conversion. The heat removal curve is typically linear or nearly linear. Where these curves intersect represents steady-state operating points.

For certain parameter combinations, the curves can intersect at **three points**:

Lower steady state: Low temperature, low conversion, stable. The reaction "barely ignites."

Middle steady state: Intermediate temperature and conversion, unstable. Any perturbation drives the system toward either the lower or upper state. Above this point, the heat generation > heat removal and below this point heat removal > heat generation.

Upper steady state: High temperature, high conversion, stable. The reaction "fully ignites."

The existence of multiple steady states has profound practical implications. A reactor may need careful startup procedures to reach the desired high-conversion state. Disturbances (feed temperature changes, coolant temperature fluctuations) can cause the reactor to "blow out" to the lower state or "run away" to dangerously high temperatures. Understanding stability through graphical analysis of heat generation and removal curves is essential for safe operation.

Worked Example 5.2: CSTR with Heat Effects and Multiple Steady States

Key Problem:

An exothermic first-order reaction $A \rightarrow P$ is carried out in a CSTR. Parameters: $k_0 = 1.0 \times 10^{10} \text{ min}^{-1}$, $E_a = 80 \text{ kJ/mol}$, $\Delta H_{rxn} = -500 \text{ kJ/mol}$. Feed: $C_{A,0} = 2.0 \text{ mol/L}$ at $T_0 = 300 \text{ K}$, $q_0 = 100 \text{ L/min}$. Reactor: $V = 500 \text{ L}$, $UA_{HT} = 1,000 \text{ W/K}$, $T_c = 290 \text{ K}$. Mixture: $\rho = 1000 \text{ kg/m}^3$, $\bar{C}_p = 4.0 \text{ kJ/(kg}\cdot\text{K)}$. (a) Calculate the adiabatic temperature rise. (b) Determine steady-state temperature and conversion. (c) Check if multiple steady states exist by analyzing heat generation and removal curves.

Solution:

(a) *Adiabatic temperature rise*

$$\Delta T_{ad} = -(-500 \text{ kJ/mol})(2.0 \text{ mol/L}) / [(1000 \text{ kg/m}^3)(4.0 \text{ kJ/(kg}\cdot\text{K)})]$$

$$\Delta T_{ad} = 1000 \cdot 103 / 4000 = 250 \text{ K}$$

(b) *Steady-state conditions*

$$\text{Space time: } \tau = V/q_0 = 500/100 = 5.0 \text{ min}$$

$$\text{Material balance: } \tau = X_A / (k(1 - X_A))$$

$$\text{Energy balance: } T = T_0 + \Delta T_{ad} X_A - UA_{HT}(T - T_c) / (\rho q \bar{C}_p)$$

These equations must be solved simultaneously. The rate constant at temperature T is:

$$k(T) = 1.0 \times 10^{10} \exp[-80,000 / (8.314 \cdot T)]$$

Using iterative solution (Newton-Raphson or similar):

THREE Steady-State Solutions Found:

State	Temperature	Conversion	Stability	Description
SS1	298.8 K (25.7°C)	0.05%	✓ STABLE	Extinguished/Quenched
SS2	383.7 K (110.5°C)	39.10%	✗ UNSTABLE	Intermediate/Transition
SS3	515.5 K (242.4°C)	99.75%	✓ STABLE	Ignited/High-conversion

Key Findings:

Two stable operating points (SS1 and SS3)

One unstable transition point (SS2)

Dramatic difference in performance: 0.05% vs 99.75% conversion!

(c) Multiple Steady States Analysis: YES, MULTIPLICITY EXISTS!

Why Multiple Steady States Occur:

S-shaped heat generation curve due to:

Exponential temperature dependence (Arrhenius)

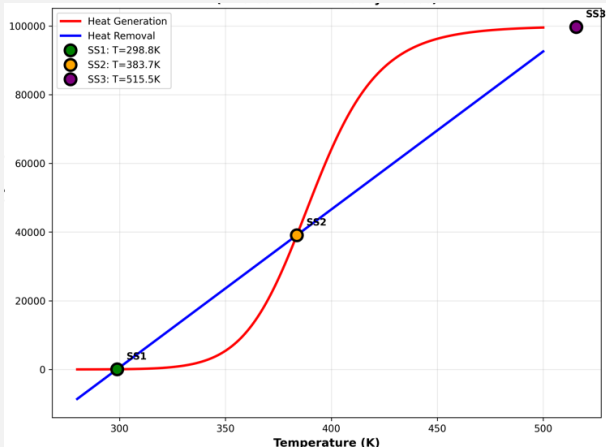
Conversion saturation at high temperature

Moderate slope heat removal line (460 kJ/min/K):

Not too steep (which would eliminate multiplicity)

Not too flat (which would cause runaway)

Three intersections between curves create three steady states



Stability Analysis:

At each steady state, compared heat generation and removal slopes

SS1 (Low-T): $dQ_{rem}/dT (460) \gg dQ_{gen}/dT (5.6) \rightarrow$ STABLE ✓

SS2 (Mid-T): $dQ_{rem}/dT (460) \ll dQ_{gen}/dT (1556) \rightarrow$ UNSTABLE ✗

SS3 (High-T): $dQ_{rem}/dT (460) \gg dQ_{gen}/dT (9.2) \rightarrow$ STABLE ✓

Critical Engineering Implications - Cannot Reach High-Conversion State from Cold Start!

The Problem:

Starting with feed at 300 K leads to SS1 (0.05% conversion)

Cannot spontaneously jump to SS3 (99.75% conversion)

Solution - Startup Strategies:

Feed Preheating: Heat feed to >400 K during startup

Temporary Cooling Reduction: Reduce cooling initially to force transition

Once at SS3: System is stable and can handle normal operations.

Prompted Example 5.2: CSTRs in Series with Interstage Cooling

Problem:

A highly exothermic consecutive reaction system $A \rightarrow B \rightarrow C$ (where B is desired) has $\Delta H_1 = -150$ kJ/mol and $\Delta H_2 = -100$ kJ/mol. Both reactions follow first-order kinetics with $k_{1,0} = 1.0 \times 10^8$ min⁻¹, $E_{a,1} = 70$ kJ/mol, $k_{2,0} = 5.0 \times 10^7$ min⁻¹, $E_{a,2} = 65$ kJ/mol. Feed: $C_{A,0} = 3.0$ mol/L at 350 K, 200 L/min. To maximize yield of B, you're considering two equal-volume CSTRs in series with interstage cooling. Total volume available is 1000 L (500 L each). Coolant can be supplied at 340 K to each reactor with $U = 600$ W/(m²·K) and available heat transfer area 6 m² per reactor. Mixture: $\rho = 980$ kg/m³, $\bar{C}_p = 3.6$ kJ/(kg·K). Your task: (a) analyze temperature profiles through both reactors, (b) determine if the cooling capacity is sufficient to keep both reactors below 450 K, (c) calculate yields of B and C at the exit, (d) compare with a single 1000 L CSTR, and (e) propose an optimal temperature strategy.

Approach: My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the fundamental assumptions in the modelling by asking me questions and wait for my answer to each question.

5.5 Plug Flow Reactor Energy Balance

5.5.1 General Energy Balance for PFRs

For a PFR, the energy balance is performed on a differential element at position z with volume dV :

$$\frac{F_{A,0}\bar{C}_p dT}{dV} = (-\Delta H_{rxn})r + Ua(T_c - T) \quad (5.15)$$

where $a = dA_{HT}/dV$ is the heat transfer area per unit volume (m^2/m^3 or m^{-1}). For a circular tube, $a = 4/d$ where d is tube diameter. This equation must be solved simultaneously with the material balance:

$$\frac{dx_A}{dV} = \frac{r}{F_{A,0}} \quad (5.16)$$

Together, these form a system of coupled ordinary differential equations that describe how temperature and conversion evolve along the reactor length. The coupling is strong: temperature affects rate through the Arrhenius equation, while rate affects temperature through heat generation.

5.5.2 Adiabatic PFR

For an adiabatic PFR ($UA = 0$), dividing Equation 5.15 by 5.16 yields:

$$\frac{dT}{dx_A} = \frac{(-\Delta H_{rxn})C_{A,0}}{\rho\bar{C}_p} = \Delta T_{ad} \quad (5.17)$$

Integrating: $T = T_0 + \Delta T_{ad}x_A$ (identical to batch and CSTR adiabatic relationships). This allows us to express temperature explicitly in terms of conversion, reducing the problem to a single differential equation:

$$\frac{dx_A}{dV} = \frac{r(T_0 + \Delta T_{ad} x_A)}{F_{A,0}} \quad (5.18)$$

For exothermic reactions with large ΔT_{ad} , adiabatic PFRs can develop *hot spots*—regions of very high temperature that may damage catalyst, cause unwanted side reactions, or create safety hazards. The maximum temperature occurs where $d^2T/dx_A^2 = 0$, which can be found by analyzing the rate expression.

5.5.3 PFR with Recycle

A powerful configuration for temperature control is the *PFR with product recycle*. A fraction R of the product stream is cooled (or heated) and mixed with fresh feed. The recycle ratio R is defined as:

$$R = \frac{\text{Recycle flow rate}}{\text{Fresh feed flow rate}} \quad (5.19)$$

The total flow through the reactor is $(1 + R)$ times the fresh feed rate. The inlet concentration and temperature to the reactor are diluted by mixing with product:

$$C_{A,in} = \frac{C_{A,0} + RC_{A,exit}}{1 + R} \quad (5.20)$$

$$T_{in} = \frac{T_0 + RT_{exit}}{1 + R} \quad (5.21)$$

The benefits of recycle include:

Temperature moderation: Mixing hot product with cool feed reduces inlet temperature, preventing excessive temperature rise.

Approach to CSTR behavior: As $R \rightarrow \infty$, the PFR with recycle approaches CSTR behavior—uniform composition throughout.

Startup assistance: Recycle helps achieve ignition by using hot product to preheat incoming feed.

Worked Example 5.3: Adiabatic PFR with Hot Spot Formation

Problem:

An exothermic first-order gas-phase reaction $A \rightarrow B$ is carried out in an adiabatic PFR. Parameters: $k_0 = 2.0 \times 10^9 \text{ s}^{-1}$, $E_a = 90 \text{ kJ/mol}$, $\Delta H_{rxn} = -180 \text{ kJ/mol}$. Feed: pure A at $C_{A,0} = 0.5 \text{ mol/m}^3$, $T_0 = 360 \text{ K}$, 50 L/s . Mixture: $\rho = 2.0 \text{ kg/m}^3$, $\bar{C}_p = 1.5 \text{ kJ/(kg}\cdot\text{K)}$. Target: 90% conversion. (a) Calculate the adiabatic temperature rise and final temperature. (b) Determine the reactor volume required. (c) Find the position and magnitude of the maximum temperature (hot spot). (d) If the safe operating limit is 500 K, assess whether this design is acceptable.

Solution:

(a) Temperature rise

$$\Delta T_{ad} = -(-180 \text{ kJ/mol})(0.5 \text{ mol/L}) / [(2.0 \text{ kg/m}^3)(1.5 \text{ kJ/(kg}\cdot\text{K)})] = 90/3 = 30 \text{ K}$$

$$\text{At 90\% conversion: } T = 360 + 30(0.90) = 387 \text{ K}$$

(b) Required reactor volume

For an adiabatic PFR, $T = T_0 + \Delta T_{ad}X_A$. The design equation becomes:

$$V = q_{A,0} \int_0^{0.9} \frac{1}{k(360 + 30x_A)(1 - x_A)} dx_A$$

With $k(T) = 2.0 \times 10^9 \exp[-90,000/(8.314 \cdot T)]$, numerical integration yields:

$$V \approx 188.3 \text{ m}^3$$

(c) Hot spot location and temperature

The rate of temperature increase is:

$$dT/dV = (dT/dx_A)(dx_A/dV) = \Delta T_{ad} \cdot r / (q_{A,0})$$

The maximum temperature occurs where $d^2T/dV^2 = 0$, which requires $dr/dV = 0$. For a first-order reaction:

$$dr/dV = d[k(1 - x_A)]/dV \quad k > 0 \text{ and } (1 - x_A) > 0 \Rightarrow x_A = 1$$

Target: $x_A = 0.9$

$$x_{A, \text{hot spot}} \approx 0.9, T_{\text{hot spot}} \approx 360 + 30(0.9) = \mathbf{387 \text{ K}}$$

(d) Safety assessment

The maximum temperature (387 K) is well below the safe operating limit of 500 K (227°C). The design is acceptable from a temperature perspective. However, the moderate adiabatic temperature rise of 30 K means that better temperature control could be achieved if desired. For reactions with larger ΔT_{ad} (> 50 K), hot spots become more pronounced and may require staged cooling, recycle, or dilution with inerts to maintain safe operation.

Prompted Example 5.3: PFR with Recycle and Heat Exchange

Problem:

An endothermic catalytic reaction $A \rightarrow 2B$ requires high temperature for acceptable rates but product B degrades above 600 K. The reaction has $k_0 = 5.0 \times 10^{11} \text{ s}^{-1}$, $E_a = 120 \text{ kJ/mol}$, $\Delta H_{\text{rxn}} = +150 \text{ kJ/mol}$, first-order kinetics. Feed: $C_{A,0} = 1.5 \text{ mol/L}$ at 550 K, 30 L/s. Mixture: $\rho = 800 \text{ kg/m}^3$, $\bar{C}_p = 2.8 \text{ kJ/(kg}\cdot\text{K)}$. You propose a PFR with recycle where the recycled stream is heated back to 580 K before remixing with fresh feed. Recycle ratio $R = 2.0$. Target: 75% conversion (based on fresh feed). Your task: (a) determine inlet conditions to the PFR (concentration and temperature after mixing), (b) calculate exit temperature, (c) determine required reactor volume, (d) calculate heating requirement for the recycled stream, (e) compare with a single-pass PFR ($R = 0$) achieving the same conversion, and (f) discuss the trade-offs between recycle ratio, reactor volume, and heating costs.

Approach: My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the fundamental assumptions in the modelling by asking me questions and wait for my answer to each question.

5.6 Practice Problems

Problem 5.1: Batch Reactor Thermal Runaway Analysis (Hand calculation)

A highly exothermic decomposition $A \rightarrow \text{Products}$ has $\Delta H_{\text{rxn}} = -320 \text{ kJ/mol}$, $k_0 = 1.5 \times 10^{14} \text{ min}^{-1}$, $E_a = 95 \text{ kJ/mol}$, first-order kinetics. A 2000 L batch reactor with $A_{HT} = 12 \text{ m}^2$ and $U = 600 \text{ W}/(\text{m}^2 \cdot \text{K})$ is charged with $C_{A,0} = 4.5 \text{ mol/L}$ at 60°C . Coolant is available at 50°C . Mixture: $\rho = 1100 \text{ kg/m}^3$, $\bar{C}_p = 3.0 \text{ kJ}/(\text{kg} \cdot \text{K})$. (a) Calculate the adiabatic temperature rise. (b) Determine if the cooling system can maintain temperature below 100°C throughout the reaction to 80% conversion. (c) Use the criterion for thermal runaway: $Q_{\text{gen,max}} > Q_{\text{rem,max}}$. Plot heat generation and removal rates versus temperature to identify critical conditions. (d) What coolant temperature would you recommend to ensure safe operation with 15°C safety margin? (e) Develop a startup procedure: should the reactor start cold or be preheated? At what rate should reactant be added? (f) Design an emergency cooling system: if the primary cooling fails, what backup capacity (in kW) is needed to prevent temperature exceeding 120°C ?

Problem 5.2: Optimal Temperature Trajectory for Selectivity

Parallel reactions $A \rightarrow B$ (desired) and $A \rightarrow C$ (undesired) have different activation energies: $k_{AB,0} = 2.0 \times 10^7 \text{ min}^{-1}$, $E_{a,AB} = 60 \text{ kJ/mol}$, $\Delta H_{AB} = -100 \text{ kJ/mol}$; $k_{AC,0} = 1.0 \times 10^8 \text{ min}^{-1}$, $E_{a,AC} = 75 \text{ kJ/mol}$, $\Delta H_{AC} = -120 \text{ kJ/mol}$. Both first-order. Feed: $C_{A,0} = 3.0 \text{ mol/L}$, 500 L batch reactor. Mixture: $\rho = 980 \text{ kg/m}^3$, $\bar{C}_p = 3.4 \text{ kJ}/(\text{kg} \cdot \text{K})$. (a) At what temperature does k_B/k_C reach its maximum? Derive a general criterion for optimal constant temperature. (b) Since the undesired reaction has higher activation energy, it becomes relatively faster at high temperature. Derive the optimal temperature trajectory: $T_{\text{opt}}(X_A)$ that maximizes selectivity $S_{B/C}$ at each conversion. (c) Compare three strategies to 85% conversion: (i) isothermal at optimal constant temperature, (ii) adiabatic operation, (iii) controlled cooling following optimal trajectory. Calculate yields of B and C for each. (d) For strategy (iii), design the cooling system: plot required $\dot{Q}(t)$ and determine peak heat removal rate. (e) Economic analysis: if B is worth $\$150/\text{kg}$ and C costs $\$50/\text{kg}$ disposal ($M_B = 100 \text{ g/mol}$, $M_C = 110 \text{ g/mol}$), calculate profit per batch for each strategy. (f) What activation energy difference would make the optimal trajectory approach isothermal operation?

Problem 5.3: CSTR Stability and Startup Dynamics

An exothermic first-order reaction $A \rightarrow P$ is carried out in a 1200 L CSTR: $k_0 = 3.5 \times 10^{10} \text{ min}^{-1}$, $E_a = 85 \text{ kJ/mol}$, $\Delta H_{\text{rxn}} = -180 \text{ kJ/mol}$. Feed: $C_{A,0} = 2.5 \text{ mol/L}$ at 310 K, 150 L/min. Cooling: $U = 750 \text{ W/(m}^2 \cdot \text{K)}$, $A_{HT} = 18 \text{ m}^2$, $T_c = 300 \text{ K}$. Mixture: $\rho = 1050 \text{ kg/m}^3$, $\bar{C}_p = 3.6 \text{ kJ/(kg} \cdot \text{K)}$. (a) Construct heat generation and removal diagrams. Identify all steady states and classify stability. (b) For the high-conversion steady state, perform linear stability analysis: small perturbations δT decay if $d(Q_{\text{rem}} - Q_{\text{gen}})/dT > 0$. Calculate this derivative at each steady state. (c) Startup procedure: reactor starts at 300 K. Plot temperature and conversion versus time during startup with normal cooling. Does it reach the high-conversion state? (d) Design a startup strategy to ensure ignition: options include (i) reduced coolant flow initially, (ii) preheating feed, (iii) adding hot solvent. Compare these approaches. (e) Once at high-conversion steady state, analyze response to disturbances: plot trajectories after $\pm 10 \text{ K}$ feed temperature change and $\pm 20\%$ flow rate change. (f) Safety: if cooling fails completely, how long until temperature exceeds 450 K? Design an automatic shutdown system with appropriate response time.

Problem 5.4: PFR Hot Spot Mitigation Strategies

Catalytic oxidation $2A + O_2 \rightarrow 2P$ on a packed bed proceeds with $k_0 = 1.2 \times 10^8 \text{ (mol/L)}^{-0.5} \cdot \text{s}^{-1}$, $E_a = 100 \text{ kJ/mol}$, $\Delta H_{\text{rxn}} = -400 \text{ kJ/mol}$, rate $r = kC_A C_{O_2}^{0.5}$. Feed: $C_{A,0} = 1.0 \text{ mol/L}$, $C_{O_2,0} = 0.6 \text{ mol/L}$ at 400 K, 20 L/s. Mixture: $\rho = 1.8 \text{ kg/m}^3$, $\bar{C}_p = 1.2 \text{ kJ/(kg} \cdot \text{K)}$. Catalyst deactivates above 550 K. Target: 95% A conversion. (a) For adiabatic operation, calculate temperature profile and identify hot spot location and magnitude. Is catalyst temperature limit exceeded? (b) Explore dilution strategy: mix feed with 50% inert (same heat capacity) to reduce $C_{A,0}$. Recalculate profiles. What dilution ratio keeps $T_{\text{max}} < 550 \text{ K}$? (c) Staged cooling: divide PFR into three sections with intercoolers. Design the system: section lengths, intercooler duties, temperatures. (d) Cold shot cooling: inject cold feed at intermediate points. Calculate injection locations and flow rates. (e) Recycle configuration: recycle cooled product at $R = 1.5$. Analyze inlet conditions and temperature profile. (f) Compare all strategies: plot temperature profiles, calculate total reactor volume, heat exchange area, and compression work (if needed). Recommend the optimal configuration considering capital and operating costs.

Problem 5.5: Series Reactor Network with Optimal Temperature Control

Consecutive reactions $A \rightarrow B \rightarrow C$ where B is valuable product: $k_{1,0} = 8.0 \times 10^6 \text{ min}^{-1}$, $E_{a,1} = 55 \text{ kJ/mol}$, $\Delta H_1 = -90 \text{ kJ/mol}$; $k_{2,0} = 2.0 \times 10^7 \text{ min}^{-1}$, $E_{a,2} = 70 \text{ kJ/mol}$, $\Delta H_2 = -110 \text{ kJ/mol}$. Both first-order. Feed: $C_{A,0} = 2.8 \text{ mol/L}$ at 340 K, 100 L/min. Mixture: $\rho = 950 \text{ kg/m}^3$, $\bar{C}_p = 3.3 \text{ kJ/(kg} \cdot \text{K)}$. You have three 400 L CSTRs with intercoolers ($U = 700$

W/(m²·K), $A_{HT} = 10 \text{ m}^2$ each). (a) Determine optimal temperature for each CSTR to maximize B yield. Hint: higher $E_{a,2}$ means reaction 2 accelerates faster with temperature; balance rapid production of B with its consumption. (b) Calculate the trajectory through C_A - C_B - C_C space for optimal temperature policy. (c) Design cooling systems: determine required T_c for each intercooler to achieve target temperatures. (d) Compare with isothermal operation at single temperature maximizing overall B yield. (e) Sensitivity analysis: how does optimal temperature policy change if $E_{a,2}$ varies $\pm 10 \text{ kJ/mol}$? (f) Economic optimization: B is worth \$200/kg, A costs \$80/kg, C is waste. Calculate profit per day for optimal versus isothermal operation ($M_A = 90 \text{ g/mol}$, $M_B = 95 \text{ g/mol}$). Is sophisticated temperature control economically justified?

Problem 5.6: Complex Reactor Network Design Challenge

You're designing a reactor system for the reversible exothermic reaction $A + B \rightleftharpoons C + D$ with $k_{f,0} = 5.0 \times 10^9 \text{ L}/(\text{mol}\cdot\text{min})$, $E_{a,f} = 80 \text{ kJ/mol}$, $\Delta H_{rxn} = -120 \text{ kJ/mol}$, $K_{eq}(400 \text{ K}) = 10$. Feed: equimolar A and B at $C_{A,0} = C_{B,0} = 2.0 \text{ mol/L}$, 380 K, 80 L/min. Mixture: $\rho = 1000 \text{ kg/m}^3$, $\bar{C}_p = 3.5 \text{ kJ}/(\text{kg}\cdot\text{K})$. Target: maximize C production while maintaining safe temperatures ($< 450 \text{ K}$). Capital cost constraints limit total reactor volume to 1500 L. (a) Calculate equilibrium conversion at various temperatures (350-450 K) and plot equilibrium constraint line. Notice high temperature increases rate but decreases equilibrium conversion. (b) Analyze single-reactor options: CSTR versus PFR, isothermal versus adiabatic. Calculate conversions and identify limitations. (c) Design a two-stage system: CSTR (high temperature for rapid initial reaction) followed by PFR (cooled to favor equilibrium). Optimize volumes and temperatures. (d) Explore three-CSTR cascade with decreasing temperatures. Optimize volume distribution and temperature profile. (e) Consider PFR with distributed cooling: develop a temperature profile $T(z)$ that starts hot (fast kinetics) and ends cool (favorable equilibrium). (f) Conduct comprehensive comparison: tabulate all configurations showing conversion, production rate, temperatures, heat duties, and estimated costs. Recommend the best design with full justification considering kinetics, equilibrium, heat transfer, and economics. (g) Discuss startup, shutdown, and control strategies for your recommended configuration.

5.7 Additional Practice Problems (Hand Calculations)

The following problems are designed to be solved with hand calculations (calculator permitted) to reinforce fundamental concepts in reactor energy balances.

Problem 5.7: Adiabatic Temperature Rise

A liquid-phase reaction $A \rightarrow P$ has $\Delta H_{\text{rxn}} = -65 \text{ kJ/mol}$. A batch reactor is charged with $C_{A,0} = 3.0 \text{ mol/L}$. The mixture has density $\rho = 1050 \text{ kg/m}^3$ and heat capacity $\bar{C}_p = 3.8 \text{ kJ/(kg}\cdot\text{K)}$. If the reactor operates adiabatically: (a) Calculate the adiabatic temperature rise for complete conversion. (b) If the initial temperature is 50°C , what is the final temperature at 90% conversion? (c) Would you classify this as a reaction with small, moderate, or large heat effects?

Problem 5.8: Isothermal Batch Reactor Heat Duty

An exothermic first-order reaction ($\Delta H_{\text{rxn}} = -80 \text{ kJ/mol}$, $k = 0.15 \text{ min}^{-1}$) is carried out isothermally at 70°C in a 1000 L batch reactor with $C_{A,0} = 2.5 \text{ mol/L}$. (a) Calculate the initial reaction rate. (b) Determine the initial heat generation rate in kW. (c) At 60% conversion, what is the instantaneous heat removal rate required? (d) Calculate the total heat that must be removed to reach 85% conversion.

Problem 5.9: CSTR Energy Balance

A first-order exothermic reaction ($k = 0.25 \text{ min}^{-1}$ at 80°C , $\Delta H_{\text{rxn}} = -100 \text{ kJ/mol}$) is carried out in a 500 L CSTR. Feed: $C_{A,0} = 4.0 \text{ mol/L}$ at 80°C , 100 L/min. The reactor achieves 75% conversion at steady state. Mixture: $\rho = 1000 \text{ kg/m}^3$, $\bar{C}_p = 4.2 \text{ kJ/(kg}\cdot\text{K)}$. Assuming adiabatic operation: (a) Calculate the exit temperature. (b) Verify that the material balance is satisfied at this temperature (you may assume rate constant temperature dependence is negligible over this small temperature range). (c) Calculate the heat generation rate at steady state.

Problem 5.10: Heat Transfer Area Calculation

A 2000 L jacketed batch reactor operates isothermally at 90°C for an exothermic reaction generating 150 kW of heat at maximum rate. The cooling jacket uses water at 75°C with an overall heat transfer coefficient $U = 850 \text{ W/(m}^2\cdot\text{K)}$. (a) Calculate the required heat transfer area. (b) For a cylindrical reactor with height-to-diameter ratio of 1.5, what is the reactor diameter? (c) If only the cylindrical wall is jacketed (not the top or bottom), does the available surface area meet the requirement?

Problem 5.11: PFR Temperature at Exit

An adiabatic PFR processes a first-order exothermic reaction with $\Delta H_{\text{rxn}} = -150$ kJ/mol. Feed enters at $T_0 = 350$ K with $C_{A,0} = 1.5$ mol/L. The PFR achieves 80% conversion. Mixture: $\rho = 900$ kg/m³, $\bar{C}_p = 2.5$ kJ/(kg·K). (a) Calculate the adiabatic temperature rise. (b) What is the exit temperature? (c) Express the temperature as a function of conversion along the reactor: $T(x_A)$. (d) At what conversion does the temperature reach 400 K?

Problem 5.12: Isothermal vs. Adiabatic Comparison

A second-order reaction $2A \rightarrow P$ has $k = 0.10$ L/(mol·min) at 60°C, $E_a = 75$ kJ/mol, and $\Delta H_{\text{rxn}} = -90$ kJ/mol. A batch reactor starts with $C_{A,0} = 3.5$ mol/L at 60°C. Mixture: $\rho = 1000$ kg/m³, $\bar{C}_p = 3.5$ kJ/(kg·K). (a) For isothermal operation at 60°C, calculate the time to reach 80% conversion using the integrated rate equation for second-order reactions. (b) For adiabatic operation, calculate the final temperature at 80% conversion. (c) Estimate the rate constant at the final adiabatic temperature using the Arrhenius equation. (d) Compare the average rates for isothermal versus adiabatic operation. Which is faster? (e) What is the trade-off between isothermal and adiabatic operation for this reaction?

Chapter 5 Summary: What You Should Have Learned

After completing this chapter, you should be able to:

1. Apply conservation of energy principles to reactors
2. Derive and use energy balances for batch, CSTR, and PFR
3. Couple material and energy balances for non-isothermal problems
4. Understand adiabatic temperature rise implications
5. Analyze temperature profiles and their effects on conversion

Chapter 6: Reactor Capacity and Variable Density Systems

Learning Objectives

After completing this chapter, you should be able to:

- Define and calculate the extent of reaction (ξ) as a fundamental measure of reaction progress, understanding how it quantifies the number of times a reaction has occurred and how it relates to changes in molar flow rates of all species.
- Derive expressions for molar flow rates and concentrations as functions of extent of reaction for gas-phase systems, recognizing that volume changes occur when the total number of moles changes at constant temperature and pressure.
- Apply the extent of reaction approach to modify CSTR design equations for variable density systems, expressing the design equation in terms of extent and evaluating concentrations that account for volumetric flow rate changes.
- Apply the extent of reaction approach to modify PFR design equations for variable density systems, understanding that both the material balance and concentration relationships must account for changing volumetric flow rate along the reactor length.
- Analyze parallel reaction systems using multiple extents of reaction (ξ_1, ξ_2, \dots), deriving coupled design equations and calculating individual selectivities while accounting for volumetric changes caused by each reaction pathway.
- Analyze consecutive reaction systems using multiple extents of reaction, understanding how intermediate species concentrations depend on both formation and consumption reactions and how total volumetric flow rate reflects the cumulative effect of all reactions.
- Evaluate the effect of operating conditions (pressure, temperature, inert dilution) on reactor volume requirements and selectivity for systems with multiple reactions, recognizing the trade-offs between conversion and desired product formation.

Nomenclature

The following symbols are introduced in this chapter and supplement the comprehensive nomenclature in Appendix B:

Roman Letters

$C_{T,0}$	Total inlet concentration (mol/L or mol/m ³)
F_i	Molar flow rate of species i (mol/s)
$F_{i,0}$	Inlet molar flow rate of species i (mol/s)

F_T	Total molar flow rate (mol/s)
$F_{T,0}$	Total inlet molar flow rate (mol/s)
N_i	Number of moles of species i (mol)
P	Total pressure (Pa, bar, or atm)
q	Volumetric flow rate at position in reactor (L/s or m ³ /s)
q_0	Inlet volumetric flow rate (L/s or m ³ /s)
x_A	Conversion of species A (dimensionless, 0 to 1)
ν_i	Mole fraction of species i (dimensionless)

Greek Letters

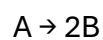
ξ	Extent of reaction (mol)
ξ_j	Extent of reaction j for multiple reactions (mol)
ν_i	Stoichiometric coefficient of species i (negative for reactants, positive for products)
τ	Space time based on exit conditions (s)
τ_0	Space time based on inlet conditions (s)

Subscripts

0	Inlet or initial conditions
i	Species i (A, B, C, etc.)
j	Reaction j (for multiple reactions)
T	Total (sum over all species)

6.1 Introduction to Variable Density Systems

In Chapters 4 and 5, we developed reactor design equations under the simplifying assumption of constant density—an assumption that holds well for liquid-phase reactions where density changes due to reaction are typically negligible. However, for gas-phase reactions where the number of moles changes during reaction, this assumption breaks down. Consider the simple decomposition:



Starting with one mole of A, complete conversion produces two moles of B. At constant temperature and pressure, the ideal gas law dictates that volume must double ($PV = nRT$).

For a flowing system, this means the volumetric flow rate doubles as the reaction proceeds. This phenomenon affects reactor design in several important ways:

- **Reactor volume requirements:** Volumetric expansion (or contraction) affects the residence time distribution and thus the required reactor size.
- **Concentration profiles:** The relationship between conversion and concentration becomes more complex, affecting rate predictions.
- **Design equation modifications:** Both CSTR and PFR design equations must be modified to account for variable volumetric flow rate.
- **Multiple reactions:** When parallel or consecutive reactions occur with different stoichiometries, tracking the overall volume change becomes more complex.

This chapter develops the framework for handling variable density gas-phase systems using the **extent of reaction** approach. The extent of reaction ξ (Greek letter xi) is a fundamental variable that quantifies how many times a reaction has occurred. Unlike conversion, which is specific to a single reactant, extent of reaction provides a universal measure that works for any species in the reaction and is particularly powerful for systems with multiple reactions.

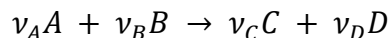
Common industrial examples where variable density effects are significant include:

- Ammonia synthesis: $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ (volume contraction)
- Ethane cracking: $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$ (volume expansion)
- Methanol synthesis: $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$ (volume contraction)
- Steam reforming: $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ (volume expansion)

6.2 The Extent of Reaction Approach

6.2.1 Definition and Fundamental Relationships

For a general chemical reaction:



the extent of reaction ξ is defined such that the change in the number of moles of any species i is:

$$N_i = N_{i,0} + \nu_i \xi \quad (6.1)$$

where ν_i is the stoichiometric coefficient of species i (negative for reactants, positive for products). The extent of reaction has units of moles and represents the number of times the reaction has occurred.

Physical interpretation:

- If $\xi = 0$: No reaction has occurred (initial state)
- If $\xi = 10$ mol: The reaction has occurred 10 times (i.e., 10 moles of A have reacted according to the stoichiometry)
- At complete conversion of limiting reactant A: $\xi_{max} = -\frac{N_{A,0}}{\nu_A}$

For a flow system, we work with molar flow rates f_i instead of moles, and the relationship becomes:

$$F_i = F_{i,0} + \nu_i \xi \tag{6.2}$$

where ξ now has units of mol/s (or mol/time). The total molar flow rate is obtained by summing over all species:

$$F_T = \sum_i F_i = \sum_i (F_{i,0} + \nu_i \xi) = F_{T,0} + (\sum_i \nu_i) \xi \tag{6.3}$$

Since $\sum_i \nu_i$ represents the change in total moles per occurrence of the reaction, we can write:

$$F_T = F_{T,0} + \Delta \nu \cdot \xi \tag{6.4}$$

where $\Delta \nu = \sum_i \nu_i$ is the change in total moles of gas per occurrence of the reaction.

6.2.2 Relationship Between Extent and Conversion

For a key reactant A, conversion x_A is defined as the fraction of A that has reacted:

$$x_A = \frac{F_{A,0} - F_A}{F_{A,0}} \tag{6.5}$$

From Equation 6.2 with $i = A$:

$$F_A = F_{A,0} + \nu_A \xi$$

Substituting into the definition of conversion:

$$x_A = \frac{F_{A,0} - F_{A,0} - \nu_A \xi}{F_{A,0}} = -\frac{\nu_A \xi}{F_{A,0}} \tag{6.6}$$

Since ν_A is negative for a reactant, $-\nu_A$ is positive. Rearranging:

$$\xi = -\left(\frac{F_{A,0}}{\nu_A}\right)x_A \quad (6.7)$$

This relationship allows us to convert between extent and conversion. While conversion is intuitive for single reactions, extent of reaction becomes essential when dealing with multiple reactions.

6.2.3 Volumetric Flow Rate and Concentration

For an ideal gas at constant temperature and pressure, the volumetric flow rate is proportional to the total molar flow rate:

$$q = \left(\frac{RT}{P}\right)F_T \quad (6.8)$$

At the inlet ($\xi = 0$):

$$q_0 = \left(\frac{RT}{P}\right)F_{T,0}$$

Taking the ratio and using Equation 6.4:

$$\frac{q}{q_0} = \frac{F_T}{F_{T,0}} = \frac{F_{T,0} + \Delta\nu \cdot \xi}{F_{T,0}} = 1 + \left(\frac{\Delta\nu}{F_{T,0}}\right)\xi \quad (6.9)$$

Therefore:

$$q = q_0 \left[1 + \left(\frac{\Delta\nu}{F_{T,0}}\right)\xi\right] \quad (6.10)$$

The concentration of species i is:

$$C_i = \frac{F_i}{q} = \frac{F_{i,0} + \nu_i \xi}{\left[q_0 \left(1 + \left(\frac{\Delta\nu}{F_{T,0}}\right)\xi\right)\right]} \quad (6.11)$$

For the key reactant A, using Equation 6.7:

$$C_A = C_{A,0} \left[\frac{(1 - x_A)}{1 + \left(\frac{\Delta\nu}{F_{T,0}}\right)\xi} \right] \quad (6.12)$$

where $C_{A,0} = F_{A,0}/q_0$ is the inlet concentration of A.

6.3 CSTR Design with Extent of Reaction

6.3.1 Modified Design Equation

For a CSTR at steady state, the material balance on species A is:

$$F_{A,0} - F_A + v_A r V = 0 \quad (6.13)$$

where r is the reaction rate (mol/(L·s)) with magnitude. Using $F_A = F_{A,0} + v_A \xi$:

$$F_{A,0} - (F_{A,0} + v_A \xi) + v_A r V = 0$$

Simplifying:

$$-v_A \xi + v_A r V = 0$$

$$\xi = rV \quad (6.14)$$

Dividing by $F_{A,0}$ and using $\xi = -\left(\frac{F_{A,0}}{v_A}\right) x_A$:

$$x_A = \frac{rV}{[F_{A,0}(-v_A)]} \quad (6.15)$$

Defining space time based on inlet conditions as $\tau_0 = \frac{V}{q_0}$ and noting that $C_{A,0} = \frac{F_{A,0}}{q_0}$:

$$\tau_0 = \frac{x_A C_{A,0}}{[r(-v_A)]} \quad (6.16)$$

The key challenge is expressing r in terms of extent or conversion. For a power-law rate expression $r = kC_A^\alpha$, we must use Equation 6.12 to express C_A in terms of x_A and ξ , accounting for the volumetric flow rate change.

Worked Example 6.1: CSTR with Gas Phase Decomposition

Key Problem:

The first-order gas-phase decomposition $A \rightarrow 2B$ occurs in an isothermal CSTR at 500 K and 2 atm. Pure A is fed at 100 mol/min. The rate constant is $k = 0.5 \text{ min}^{-1}$. Calculate the reactor volume required for 80% conversion of A using the extent of reaction approach.

Solution:

Step 1: Identify stoichiometry and calculate Δv

For the reaction $A \rightarrow 2B$:

$$v_A = -1, v_B = 2$$

$$\Delta v = v_A + v_B = -1 + 2 = 1 \text{ mol per mol of reaction}$$

$$\text{For pure A feed: } F_{T,0} = F_{A,0} = 100 \text{ mol/min}$$

Step 2: Calculate extent of reaction at 80% conversion

$$\text{Using } \xi = -\left(\frac{F_{A,0}}{v_A}\right) x_A:$$

$$\xi = -(100 \text{ mol/min})/(-1) \times 0.8 = 80 \text{ mol/min}$$

Step 3: Calculate exit volumetric flow rate

$$\text{Using } q = q_0 \left[1 + \left(\frac{\Delta v}{F_{T,0}} \right) \xi \right]:$$

first, calculate inlet volumetric flow rate using ideal gas law:

$$q_0 = \frac{F_{A,0}RT}{P} = \frac{(100 \frac{\text{mol}}{\text{min}}) \left(0.08206 \text{ L} \cdot \frac{\text{atm}}{\text{mol} \cdot \text{K}} \right) (500 \text{ K})}{2 \text{ atm}} = 2051.5 \frac{\text{L}}{\text{min}}$$

flow rate at 80% conversion:

$$q = 2051.5 [1 + (1/100) \times 80] = 2051.5 \times 1.8 = 3692.7 \text{ L/min}$$

The volumetric flow rate increases by 80% due to the increase in moles.

Step 4: Calculate exit concentration of A

$$C_{A,0} = \frac{F_{A,0}}{q_0} = 100 \text{ mol/min} / 2051.5 \text{ L/min} = 0.04875 \text{ mol/L}$$

$$\text{Using } C_A = \frac{C_{A,0}(1 - x_A)}{1 + \left(\frac{\Delta v}{F_{T,0}} \right) \xi}:$$

$$C_A = 0.04875(1 - 0.8)/1.8 = 0.00542 \text{ mol/L}$$

Step 5: Calculate reactor volume using design equation

$$\text{For first-order kinetics, } r = kC_A = 0.5 \text{ min}^{-1} \times 0.00542 \text{ mol/L} = 0.00271 \text{ mol/(L}\cdot\text{min)}$$

$$\text{Using } \xi = rV:$$

$$V = \xi/r = 80 \text{ mol/min} / 0.00271 \text{ mol/(L}\cdot\text{min)} = 29,520 \text{ L}$$

Alternatively, using space time:

$$\tau_0 = \frac{V}{q_0} = \frac{x_A C_{A,0}}{[r(-v_A)]}$$

$$\tau_0 = 0.8 \times 0.04875 / [0.00271 \times 1] = 14.39 \text{ min}$$

$$V = \tau_0 q_0 = 14.39 \text{ min} \times 2051.5 \text{ L/min} = 29,520 \text{ L}$$

Answer: The required reactor volume is 29,520 L or 29.5 m³.

6.4 PFR Design with Extent of Reaction

6.4.1 Modified Design Equation

For a PFR, the material balance on species A over a differential volume element gives:

$$\frac{dF_A}{dV} = v_A r \quad (6.17)$$

Since $F_A = F_{A,0} + v_A \xi$, taking the derivative:

$$\frac{dF_A}{dV} = v_A \left(\frac{d\xi}{dV} \right) \quad (6.18)$$

Substituting into the material balance:

$$v_A \left(\frac{d\xi}{dV} \right) = v_A r$$
$$\frac{d\xi}{dV} = r \quad (6.19)$$

This is a remarkably simple result: the rate of change of extent with reactor volume equals the reaction rate. Integrating from inlet ($\xi = 0$) to exit ($\xi = \xi_{exit}$):

$$V = \int_0^{\xi_{exit}} \left(\frac{d\xi}{r} \right) \quad (6.20)$$

The challenge is expressing r in terms of ξ . For species A with rate $r = kC_A^\alpha$, we need C_A as a function of ξ . From Equation 6.11:

$$C_A = \frac{F_{A,0} + v_A \xi}{\left[q_0 \left(1 + \left(\frac{\Delta v}{F_{T,0}} \right) \xi \right) \right]} \quad (6.21)$$

For first-order kinetics ($\alpha = 1$):

$$r = kC_A = \frac{k(F_{A,0} + v_A \xi)}{\left[q_0 \left(1 + \left(\frac{\Delta v}{F_{T,0}} \right) \xi \right) \right]} \quad (6.22)$$

This can be integrated analytically for first-order kinetics, but for higher-order kinetics, numerical integration is typically required.

Worked Example 6.2: PFR with Gas Phase Expansion

Problem:

For the same reaction as Example 6.1 ($A \rightarrow 2B$ with $k = 0.5 \text{ min}^{-1}$), calculate the PFR volume required for 80% conversion with pure A feed at 100 mol/min, 500 K, and 2 atm.

Solution:

Step 1: Set up the design equation

From Example 6.1: $\Delta v = 1$, $F_{T,0} = 100 \text{ mol/min}$, $q_0 = 2051.5 \text{ L/min}$

At 80% conversion: $\xi = 80 \text{ mol/min}$

The concentration expression is:

$$C_A = \frac{(100 - \xi)}{\left[2051.5 \left(1 + \frac{\xi}{100}\right)\right]}$$

$$\text{Rate: } r = 0.5 \times \frac{100 - \xi}{\left[2051.5 \left(1 + \frac{\xi}{100}\right)\right]}$$

Step 2: Integrate numerically

$$V = \int_0^{80} \left\{ \frac{2051.5 \left(1 + \frac{\xi}{100}\right)}{[0.5(100 - \xi)]} \right\} d\xi$$

Using numerical integration (e.g., Simpson's rule or trapezoidal rule):

$$V \approx 9,920 \text{ L}$$

Step 3: Compare with CSTR

From Example 6.1, the CSTR volume was 29,520 L.

The PFR requires only 40% of the CSTR volume for the same conversion, demonstrating the efficiency advantage of plug flow, even with variable density.

Answer: The required PFR volume is approximately 9.9 m^3 .

6.5 Multiple Reactions with Variable Density

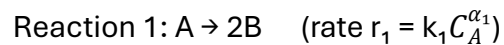
The extent of reaction approach becomes particularly powerful when dealing with multiple reactions. For systems with m independent reactions, we define m independent extents $\xi_1, \xi_2, \dots, \xi_m$. The molar flow rate of any species i is then:

$$F_i = F_{i,0} + \sum_1^m \nu_{ij} \xi_j \quad (6.23)$$

where ν_{ij} is the stoichiometric coefficient of species i in reaction j . This formulation elegantly handles the fact that a species may participate in multiple reactions.

6.5.1 Parallel Reactions

Consider two parallel reactions where reactant A can follow competing pathways:



Using the extent of reaction approach:

For reaction 1: $\nu_{A1} = -1, \nu_{B1} = 2, \nu_{C1} = 0; \Delta\nu_1 = 1$

For reaction 2: $\nu_{A2} = -1, \nu_{B2} = 0, \nu_{C2} = 1; \Delta\nu_2 = 0$

The molar flow rates are:

$$F_A = F_{A,0} - \xi_1 - \xi_2$$

$$F_B = 2\xi_1$$

$$F_C = \xi_2$$

Total molar flow rate:

$$F_T = F_{T,0} + \Delta\nu_1 \xi_1 + \Delta\nu_2 \xi_2 = F_{A,0} + \xi_1 \quad (6.24)$$

Volumetric flow rate:

$$q = \frac{q_0 (F_{A,0} + \xi_1)}{F_{A,0}} \quad (6.25)$$

Concentration of A:

$$C_A = \frac{F_A}{q} = \frac{(F_{A,0} - \xi_1 - \xi_2)}{\left[\frac{q_0(F_{A,0} + \xi_1)}{F_{A,0}} \right]} \quad (6.26)$$

For a CSTR: The design equations are:

$$\xi_1 = r_1 V \quad (6.27)$$

$$\xi_2 = r_2 V \quad (6.28)$$

These two equations must be solved simultaneously. The selectivity of B relative to C is:

$$S = \frac{\text{moles B produced}}{\text{moles C produced}} = \frac{2\xi_1}{\xi_2} = \frac{r_1}{r_2} \quad (6.29)$$

For a PFR: The design equations are:

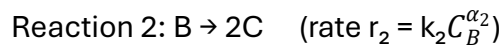
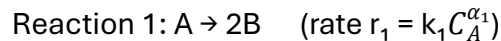
$$d\xi_1/dV = r_1 \quad (6.30)$$

$$d\xi_2/dV = r_2 \quad (6.31)$$

These coupled ordinary differential equations must be integrated numerically with initial conditions $\xi_1(0) = 0$ and $\xi_2(0) = 0$.

6.5.2 Consecutive Reactions

For consecutive (series) reactions:



Stoichiometric coefficients:

$$\text{Reaction 1: } \nu_{A1} = -1, \nu_{B1} = 2, \nu_{C1} = 0; \Delta\nu_1 = 1$$

$$\text{Reaction 2: } \nu_{A2} = 0, \nu_{B2} = -1, \nu_{C2} = 2; \Delta\nu_2 = 1$$

Molar flow rates:

$$F_A = F_{A,0} - \xi_1$$

$$F_B = 2\xi_1 - \xi_2$$

$$F_C = 2\xi_2$$

Total molar flow rate:

$$F_T = F_{A,0} + \xi_1 + \xi_2 \quad (6.32)$$

Concentrations:

$$C_A = \frac{(F_{A,0} - \xi_1)}{\left[\frac{q_0(F_{A,0} + \xi_1 + \xi_2)}{F_{A,0}} \right]} \quad (6.33)$$

$$C_B = \frac{(2\xi_1 - \xi_2)}{\left[\frac{q_0(F_{A,0} + \xi_1 + \xi_2)}{F_{A,0}} \right]} \quad (6.34)$$

For a PFR: The coupled differential equations are:

$$\frac{d\xi_1}{dV} = r_1 = k_1 C_A^{\alpha_1} \quad (6.35)$$

$$\frac{d\xi_2}{dV} = r_2 = k_2 C_B^{\alpha_2} \quad (6.36)$$

These must be solved numerically, updating concentrations at each step using Equations (6.33)-(6.35). The maximum yield of B occurs at the point where $dF_B/dV = 0$, which gives:

$$2r_1 = r_2 \text{ (condition for maximum B yield)} \quad (6.37)$$

Worked Example 6.3: Parallel Reactions in CSTR

Key Problem:

The gas-phase decomposition of A occurs via two competing First-order pathways in an isothermal CSTR at 400 K and 2 atm:

Reaction 1: $A \rightarrow 2B$ ($k_1 = 0.8 \text{ min}^{-1}$, desired)

Reaction 2: $A \rightarrow C$ ($k_2 = 0.2 \text{ min}^{-1}$, undesired)

Pure A is fed at 100 mol/min. Calculate the reactor volume required for a total conversion of 75%, the individual extents of reaction, selectivity of B relative to C, and outlet concentrations using the extent of reaction approach.

Solution:

Step 1: Set up the stoichiometry

Reaction 1: $\Delta v_1 = 1$ (expansion)

Reaction 2: $\Delta v_2 = 0$ (no volume change)

For pure A feed: $F_{A,0} = F_{T,0} = 100$ mol/min

Total conversion: $x_A = \frac{(\xi_1 + \xi_2)}{F_{A,0}} = 0.75$

Therefore: $\xi_1 + \xi_2 = 75$ mol/min

Step 2: Write design equations

Volumetric flow rate: $q = \frac{q_0(100 + \xi_1)}{100}$

Concentration of A: $C_A = \frac{(100 - \xi_1 - \xi_2)}{\left[\frac{q_0(100 + \xi_1)}{100}\right]}$

For First-order kinetics:

$\xi_1 = r_1 V = k_1 C_A V$

$\xi_2 = r_2 V = k_2 C_A V$

Taking the ratio:

$\xi_1/\xi_2 = k_1/k_2 = 0.8/0.2 = 4$

Step 3: Solve for individual extents

From $\xi_1 = 4\xi_2$ and $\xi_1 + \xi_2 = 75$:

$4\xi_2 + \xi_2 = 75$

$\xi_2 = 15$ mol/min

$\xi_1 = 60$ mol/min

Step 4: Calculate reactor volume

Inlet volumetric flow rate:

$q_0 = \frac{F_{A,0}RT}{P} = (100)(0.08206)(400)/(2) = 1641.2$ L/min

Exit concentration of A:

$C_A = (100 - 60 - 15)/[1641.2(100 + 60)/100] = 25/2625.92 = 0.00952$ mol/L

Using $\xi_1 = k_1 C_A V$:

$V = \frac{\xi_1}{k_1 C_A} = 60/(0.8 \times 0.00952) = 7,874$ L

Step 5: Calculate selectivity and outlet compositions

Selectivity: $S = 2\xi_1/\xi_2 = (2 \times 60)/15 = 8.0$ (mol B/mol C)

Exit volumetric flow rate: $q = 1641.2(160/100) = 2625.92$ L/min

Outlet mole fractions:

$$F_A = 25 \text{ mol/min}, y_A = 25/160 = 0.156$$

$$F_B = 2 \times 60 = 120 \text{ mol/min}, y_B = 120/160 = 0.750$$

$$F_C = 15 \text{ mol/min}, y_C = 15/160 = 0.094$$

Answer: $V = 7,874 \text{ L}$, $\xi_1 = 60 \text{ mol/min}$, $\xi_2 = 15 \text{ mol/min}$, $S = 8.0$. The majority of the product is the desired B species due to the higher rate constant for reaction 1.

Worked Example 6.4: Consecutive Reactions in PFR

Problem:

The consecutive first-order gas-phase reactions $A \rightarrow 2B \rightarrow 2C$ occur in a PFR at 450 K and 3 atm with $k_1 = 1.5 \text{ min}^{-1}$ and $k_2 = 0.5 \text{ min}^{-1}$. Pure A is fed at 80 mol/min. Determine the PFR volume required to maximize the production rate of B (mol B/min), and calculate the maximum yield of B production (considering stoichiometry) before loss to species C becomes significant.

We will use extent of reaction (ξ) to formulate this problem. This approach is more fundamental and leads to cleaner design equations.

For a flow reactor, the extent of reaction ξ_j for reaction j has units of mol/time (mol/min).

Define:

- ξ_1 = extent of reaction 1 ($A \rightarrow 2B$)
- ξ_2 = extent of reaction 2 ($2B \rightarrow 2C$)

Step 1: Stoichiometric Relationships

From stoichiometry, all molar flow rates can be expressed in terms of the extents:

Species	Molar Flow Rate
A	$F_A = F_{A0} - \xi_1$
B	$F_B = 2\xi_1 - 2\xi_2$
C	$F_C = 2\xi_2$
Total	$F_T = F_{A0} + \xi_1$

Key insight: The total molar flow $F_T = F_{A0} + \xi_1$ increases with ξ_1 , confirming variable density!

Step 2: Variable Density

Initial conditions:

$$q_0 = F_{A0} \times R \times T / P = 80 \times 0.08206 \times 450 / 3 = 984.72 \text{ L/min}$$

Volumetric flow rate varies with total molar flow:

$$q = q_0 \times \left(\frac{F_T}{F_{T0}} \right) = q_0 \times \left(\frac{F_T}{F_{A0}} \right)$$

$$q = q_0 \times \frac{(F_{A0} + \xi_1)}{F_{A0}}$$

$$q = q_0 \times \left(1 + \frac{\xi_1}{F_{A0}} \right)$$

Step 3: PFR Design Equations

For a PFR, the general design equation for extent is:

$$\frac{d\xi_j}{dV} = r_j$$

Or in terms of space time $\tau = V/q_0$:

$$\frac{d\xi_j}{d\tau} = q_0 \times r_j$$

The reaction rates are:

$$r_1 = k_1 C_A = k_1 \times \frac{F_A}{q}$$

$$r_2 = k_2 C_B = k_2 \times \frac{F_B}{q}$$

Substituting and simplifying:

$$\frac{d\xi_1}{d\tau} = q_0 \times k_1 \times \frac{F_A}{q} = q_0 \times k_1 \times \frac{F_{A0} - \xi_1}{\left[\frac{q_0 (F_{A0} + \xi_1)}{F_{A0}} \right]}$$

DESIGN EQUATIONS (Extent of Reaction)

$$\frac{d\xi_1}{d\tau} = k_1 \times F_{A0} \times \frac{(F_{A0} - \xi_1)}{(F_{A0} + \xi_1)}$$

$$\frac{d\xi_2}{d\tau} = 2k_2 \times F_{A0} \times \frac{(\xi_1 - \xi_2)}{(F_{A0} + \xi_1)}$$

Note: The denominator $(F_{A0} + \xi_1)$ accounts for variable density. This is much cleaner than tracking individual molar flows!

Step 4: Initial Conditions and Solution

Initial conditions (pure A feed, no reaction yet):

$$\xi_1(0) = 0$$

$$\xi_2(0) = 0$$

We solve these ODEs numerically to find τ that maximizes:

$$F_B = 2\xi_1 - 2\xi_2 = 2(\xi_1 - \xi_2)$$

RESULT

OPTIMAL REACTOR DESIGN

Required PFR Volume: $V = 1,135 \text{ L}$

Maximum Production Rate: $F_{B,\max} = 71.11 \text{ mol/min}$

Maximum Yield of B: 63.16%

Extents of Reaction at Optimum

Extent	Value
$\xi_1 (A \rightarrow 2B)$	56.30 mol/min
$\xi_2 (2B \rightarrow 2C)$	20.74 mol/min

Complete System State at Optimum

Parameter	Value
Optimal space time, τ_{opt}	1.153 min
Conversion of A, $X_A = \xi_1/F_{A0}$	70.37%
Molar flow of A: $F_A = F_{A0} - \xi_1$	23.70 mol/min
Molar flow of B: $F_B = 2(\xi_1 - \xi_2)$	71.11 mol/min
Molar flow of C: $F_C = 2\xi_2$	41.48 mol/min
Total molar flow: $F_T = F_{A0} + \xi_1$	136.30 mol/min

Volumetric flow rate, v 1,678 L/min

Volume expansion +70.4% from inlet

Yield Calculation

The yield of B is the fraction of A converted that ends up as B:

$$\begin{aligned} \text{Yield} &= (\text{moles of B produced}) / (\text{max possible moles of B}) \\ &= (2\xi_1 - 2\xi_2) / (2\xi_1) \\ &= (\xi_1 - \xi_2) / \xi_1 \\ &= 1 - \xi_2/\xi_1 \end{aligned}$$

At optimum:

$$\text{Yield} = (56.30 - 20.74) / 56.30 = \mathbf{0.6316 = 63.16\%}$$

Physical Interpretation

What do the extents tell us?

Extent $\xi_1 = 56.30$ mol/min:

- This is the rate at which A is being consumed
- Equivalently, it is the rate at which reaction 1 proceeds
- If reaction 2 did not occur, we would have $F_B = 2\xi_1 = 112.6$ mol/min

Extent $\xi_2 = 20.74$ mol/min:

- This is the rate at which reaction 2 proceeds
- It consumes B and produces C
- The net production of B is reduced by $2\xi_2 = 41.48$ mol/min

Net result:

$$F_B = 2\xi_1 - 2\xi_2 = 112.6 - 41.48 = 71.11 \text{ mol/min}$$

6.6 Practice Problems

Problem 6.1: CSTR with Reversible Reaction and Volume Change

The reversible gas-phase reaction $A \rightleftharpoons 2B$ occurs at 500 K and 3 atm with forward rate constant $k_1 = 2.0 \text{ min}^{-1}$ and equilibrium constant $K_{eq} = 4.0$ (concentration basis). Pure A is fed at 150 mol/min to a CSTR. Calculate: (a) the extent of reaction at equilibrium, (b) the reactor volume required for 70% of equilibrium conversion, and (c) the outlet concentrations of A and B.

Problem 6.2: PFR with Second-Order Kinetics

The gas-phase dimerization $2A \rightarrow B$ follows second-order kinetics ($r = kC_A^2$) with $k = 0.8 \text{ L}/(\text{mol}\cdot\text{min})$ at 400 K and 2 atm. Pure A is fed at 120 mol/min. Determine the PFR volume required for 85% conversion using the extent of reaction approach, and compare the concentration profile with the constant density assumption.

Problem 6.3: Three Parallel Reactions

In a gas-phase CSTR at 450 K, reactant A can follow three competing pathways: $A \rightarrow 2B$ ($k_1 = 1.2 \text{ min}^{-1}$), $A \rightarrow C + D$ ($k_2 = 0.8 \text{ min}^{-1}$), and $A \rightarrow 3E$ ($k_3 = 0.4 \text{ min}^{-1}$). All reactions are first-order. Pure A is fed at 100 mol/min at 3 atm. For a reactor volume of 200 L, calculate the three extents of reaction ξ_1 , ξ_2 , ξ_3 , the total conversion, and the selectivities of each product pathway.

Problem 6.4: Optimizing Yield in Consecutive Reactions

For the consecutive gas phase reactions $A \rightarrow 3B \rightarrow 2C$ with first-order rate constants $k_1 = 3.0 \text{ min}^{-1}$ and $k_2 = 1.0 \text{ min}^{-1}$ occurring in a PFR at 500 K and 2 atm, determine the PFR volume that maximizes the yield of B when pure A is fed at 100 mol/min. Calculate the maximum production rate of B (mol/min) and the corresponding conversions of A and B.

Problem 6.5: Effect of Pressure on Selectivity

The parallel reactions $A \rightarrow 2B$ ($k_1 = 1.5 \text{ min}^{-1}$) and $A \rightarrow C$ ($k_2 = 0.5 \text{ min}^{-1}$) occur in a CSTR at 400 K. Pure A is fed at 80 mol/min. Investigate how varying the operating pressure from 1 to 10 atm affects: (a) the selectivity of B relative to C at 80% total conversion, (b) the required reactor volume, and (c) the outlet concentration of B. Explain the trends using the extent of reaction framework.

Chapter 6 Summary: What You Should Have Learned

1. **Extent of reaction ξ :** A fundamental variable that quantifies how many times a reaction has occurred. For any species i : $F_i = F_{i,0} + \nu_i \xi$.
2. **Variable density:** Gas-phase reactions with $\Delta \nu \neq 0$ experience volumetric expansion or contraction. The volumetric flow rate is $q = q_0 \left[1 + \left(\frac{\Delta \nu}{F_{T,0}} \right) \xi \right]$.
3. **CSTR design:** For a single reaction, $\xi = rV$. Concentration must account for volumetric changes using $C_i = F_i/q$.
4. **PFR design:** The elegant relationship $d\xi/dV = r$ allows direct integration. Numerical methods are typically required when concentrations depend nonlinearly on ξ .
5. **Multiple reactions:** Define m extents for m reactions. Each species' flow rate is $F_i = F_{i,0} + \sum_j \nu_{ij} \xi_j$. This naturally handles complex networks.
6. **Parallel reactions:** Solve coupled equations (algebraic for CSTR, differential for PFR) to find individual extents ξ_1, ξ_2, \dots . Selectivity is determined by the ratio of extents.
7. **Consecutive reactions:** Maximum intermediate concentration occurs when the rate of formation equals the rate of consumption. For $A \rightarrow B \rightarrow C$, maximum B occurs when $2r_1 = r_2$.
8. **Volumetric effects:** Total volumetric change is $F_T = F_{T,0} + \Sigma(\Delta \nu_j \xi_j)$, accounting for all reactions. This affects concentration calculations throughout the reactor.

Chapter 7: Unsteady-State Reactors

Learning Objectives

After completing this chapter, you should be able to:

- Formulate and solve transient material balances for CSTRs, recognizing that accumulation terms become important during startup, shutdown, and disturbances, and understanding how reactor time constants determine the rate of approach to steady state.
- Derive and analyze coupled transient material and energy balances for non-isothermal reactors, predicting temperature and conversion trajectories during transients and identifying potential safety issues such as temperature overshoot or runaway during startup.
- Calculate characteristic time constants for CSTRs and determine the time required to reach a specified percentage of the final steady-state value, applying first-order system analysis to reactor dynamics and control.
- Analyze transient behavior in plug flow reactors, understanding that PFRs exhibit wave propagation of disturbances with time delays related to residence time, and distinguishing between the fundamentally different dynamic responses of CSTRs and PFRs.
- Design safe startup and shutdown procedures for exothermic reactors, considering factors such as feed temperature ramping, flow rate scheduling, and cooling system capacity to avoid thermal runaway or incomplete conversion during transients.
- Evaluate reactor response to various disturbances including feed composition changes, temperature disturbances, and flow rate variations, predicting the magnitude and duration of transient deviations from steady state and designing appropriate control strategies.

Nomenclature

The following symbols are introduced in this chapter and supplement the comprehensive nomenclature in Appendix B:

Roman Letters

t	Time (s, min, or h)
t_{ss}	Time to reach steady state (s, min, or h)

Greek Letters

τ_c	Characteristic time constant (s, min, or h)
ξ	Fractional approach to steady state (dimensionless)

7.1 Introduction to Unsteady-State Operation

Throughout Chapters 4 through 6, we focused on steady-state reactor design—conditions where all variables remain constant with time. While steady-state analysis is essential for sizing reactors and predicting long-term performance, real reactors spend significant time operating under transient conditions:

- **Startup:** From empty or filled with inerts to operating conditions
- **Shutdown:** From operating conditions to safe, non-reactive state
- **Disturbances:** Feed composition changes, temperature fluctuations, flow rate variations
- **Grade transitions:** Changing product specifications or feedstocks
- **Control actions:** Deliberate changes to maintain desired operation

Understanding transient behavior is critical for several reasons:

- **Safety:** Exothermic reactions can exhibit temperature overshoot during startup, potentially leading to runaway or equipment damage.
- **Product quality:** Off-specification product produced during transients may need to be discarded or reprocessed.
- **Economics:** Faster, smoother transitions minimize downtime and waste.
- **Control design:** Transient response characteristics determine controller settings and achievable performance.
- **Environmental compliance:** Emissions during startups and upsets must be controlled.

The key difference from steady-state analysis is that accumulation terms in material and energy balances are no longer zero. For a CSTR:

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

becomes a differential equation in time rather than an algebraic equation. This chapter develops the mathematical framework for analyzing transient reactor behavior and applies it to startup, shutdown, and disturbance scenarios for both isothermal and non-isothermal systems.

7.2 Isothermal CSTR Transient Behavior

7.2.1 Transient Material Balance

For an isothermal CSTR, the transient material balance on species A is:

$$V \frac{dC_A}{dt} = q_0 C_{A,0} - q C_A + V r_A \quad (7.1)$$

For constant density ($q = q_0$) and defining space time $\tau = V/q_0$:

$$\frac{dC_A}{dt} = \frac{C_{A,0} - C_A}{\tau} + r_A \quad (7.2)$$

For a first-order reaction ($r_A = -kC_A$):

$$\frac{dC_A}{dt} = \frac{C_{A,0} - C_A}{\tau} - kC_A \quad (7.3)$$

Rearranging:

$$\frac{dC_A}{dt} + \left(\frac{1}{\tau} + k\right) C_A = \frac{C_{A,0}}{\tau} \quad (7.4)$$

This is a first-order linear ODE. The solution depends on initial conditions and exhibits exponential approach to steady state with characteristic time constant:

$$\tau_c = \frac{1}{\frac{1}{\tau} + k} \quad (7.5)$$

7.2.2 Startup from Empty Reactor

Consider a CSTR initially empty ($C_A(0) = 0$) when feed is introduced at $t = 0$. The solution to Equation 7.4 is:

$$C_A(t) = C_{A,ss}[1 - \exp(-t/\tau_c)] \quad (7.6)$$

where $C_{A,ss}$ is the steady-state concentration:

$$C_{A,ss} = \frac{C_{A,0}}{1 + k\tau} \quad (7.7)$$

The fractional approach to steady state is:

$$\xi = \frac{C_A}{C_{A,ss}} = 1 - \exp(-t/\tau_c) \quad (7.8)$$

Key observations:

At $t = \tau_c$: $\xi = 0.632$ (63.2% of steady state)

At $t = 3\tau_c$: $\xi = 0.950$ (95% of steady state)

At $t = 5\tau_c$: $\xi = 0.993$ (99.3% of steady state)

Practically, steady state is reached after **3-5 time constants**.

Worked Example 7.1: CSTR Startup Dynamics

Problem:

A first-order liquid-phase reaction is carried out isothermally in a 500 L CSTR with rate constant $k = 0.20$ per min. Feed concentration is 2.0 mol per L at 100 L per min. The reactor is initially filled with pure solvent. (a) Calculate the steady-state concentration and conversion. (b) Determine the characteristic time constant. (c) Calculate the time required to reach 95% of steady-state conversion. (d) Plot concentration versus time during startup.

Solution:

Model (startup from pure solvent)

For a constant-volume CSTR with first-order consumption,

$$\frac{dC_A}{dt} = \frac{q}{V}(C_{A0} - C_A) - kC_A$$

$$\text{Given } V = 500 \text{ L, } q = 100 \text{ L/min} \Rightarrow q/V = 0.20 \text{ min}^{-1}$$

$$k = 0.20 \text{ min}^{-1}, C_{A0} = 2.0 \text{ mol/L, and } C_A(0) = 0.$$

(a) Steady-state concentration and conversion

At steady state, $dC_A/dt = 0$:

$$C_{A,ss} = \frac{(q/V) C_{A0}}{(q/V) + k} = \frac{0.20 \cdot 2.0}{0.20 + 0.20} = 1.0 \text{ mol/L}$$

$$X_{ss} = \frac{C_{A0} - C_{A,ss}}{C_{A0}} = \frac{2.0 - 1.0}{2.0} = 0.50$$

$$C_{A,ss} = 1.0 \text{ mol/L, } X_{ss} = 0.50$$

(b) Characteristic time constant

The linear system has decay rate $\lambda = (q/V) + k = 0.40 \text{ min}^{-1}$, so

$$\tau_c = \frac{1}{\lambda} = \frac{1}{0.40} = 2.5 \text{ min}$$

(c) Time to reach 95% of steady-state conversion (startup)

With $C_A(0) = 0$, the solution is

$$C_A(t) = C_{A,ss}(1 - e^{-t/\tau_c})$$

So reaching 95% of the steady-state *value* corresponds to $C_A(t) = 0.95C_{A,ss}$:

$$0.95 = 1 - e^{-t/\tau_c} \Rightarrow t_{95} = -\tau_c \ln(0.05)$$

$$t_{95} = -(2.5) \ln(0.05) = 7.49 \text{ min}$$

$$t_{95} \approx 7.49 \text{ min}$$

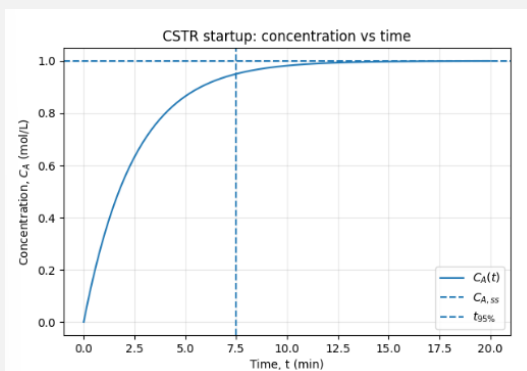
(At that time $C_A \approx 0.95 \text{ mol/L}$ and $X \approx (2 - 0.95)/2 = 0.525$, i.e. conversion is still slightly above its steady 0.50 because C_A is still slightly below 1.0.)

(d) Plot: concentration vs time during startup

The curve is

$$C_A(t) = 1.0(1 - e^{-t/2.5}) \text{ mol/L}$$

and the plotted startup trajectory (with t_{95} marked) is shown above in the generated figure.



7.3 Non-Isothermal CSTR Transient Behavior

7.3.1 Coupled Transient Balances

For a non-isothermal CSTR, both material and energy balances contain time derivatives. The coupled system is:

Material balance:

$$\frac{dC_A}{dt} = \frac{(C_{A0} - C_A)}{\tau} + r_A(C_A, T) \quad (7.9)$$

Energy balance:

$$\rho C_p \frac{dT}{dt} = \frac{\rho C_p (T_0 - T)}{\tau} + (-\Delta H_{rxn}) r_A + \frac{U A_{HT} (T_c - T)}{V} \quad (7.10)$$

These coupled nonlinear ODEs require numerical solution. The system can exhibit complex dynamics including:

Temperature overshoot: Temperature temporarily exceeds steady-state value during startup

Oscillations: Damped oscillations around steady state

Multiple time scales: Different rates of approach for concentration and temperature

Instability: Potential for thermal runaway if cooling is insufficient

Worked Example 7.2: Non-Isothermal CSTR Startup with Temperature Overshoot

Problem:

An exothermic first-order reaction is carried out in a 1000 L CSTR. Initially at 300 K with pure solvent. At $t = 0$, feed begins at 100 L per min, 2.0 mol per L, 300 K. Reaction data: $k_0 = 1.0 \times 10^{10}$ per min, $E_a = 75$ kJ per mol, $\Delta H = -350$ kJ per mol. Mixture: $\rho = 1000$ kg per m^3 , $C_p = 4.0$ kJ per kg K. Cooling: $U = 800$ W per m^2 K, $A = 3$ m^2 , $T_c = 290$ K. (a) Calculate steady-state temperature and concentration. (b) Set up the transient equations. (c) Describe expected temperature overshoot behavior. (d) What temperature is required for the solvent initially for reaching the high conversion steady state?

Given:

$$V = 1000 \text{ L}, q_0 = 100 \text{ L/min}, C_{A0} = 2.0 \text{ mol/L}, T_0 = 300 \text{ K}$$

$$k_0 = 1.0 \times 10^{10} \text{ min}^{-1}, E_a = 75 \text{ kJ/mol}$$

$$\Delta H_{rxn} = -350 \text{ kJ/mol (highly exothermic)}$$

$$\rho = 1000 \text{ kg/m}^3, C_p = 4.0 \text{ kJ/(kg}\cdot\text{K)}$$

$$U = 800 \text{ W/(m}^2\cdot\text{K)}, A = 3 \text{ m}^2, T_c = 290 \text{ K}$$

$$UA = 2400 \text{ J/(s}\cdot\text{K)} = 144 \text{ kJ/(min}\cdot\text{K)}$$

$$\text{Coolant } T_c = 290 \text{ K}$$

Useful heat-capacity rates:

$$\text{Flow: } q\rho C_p = 100 \cdot 4 = 400 \text{ kJ/(min}\cdot\text{K)}$$

$$\text{Reactor thermal capacitance: } \rho C_p V = 4 \cdot 1000 = 4000 \text{ kJ/K}$$

(a) Steady-state temperature and concentration

CSTR species balance (steady)

$$0 = \frac{q}{V}(C_{A0} - C_A) - k(T)C_A \Rightarrow C_A(T) = \frac{C_{A0}}{1 + k(T)\tau}$$

CSTR energy balance (steady)

$$0 = q\rho C_p(T_0 - T) + (-\Delta H)V k(T)C_A(T) - UA(T - T_c)$$

Solving the coupled equations gives **three steady states** (two stable, one unstable):

Branch	T_{ss} (K)	$k(T_{ss})$	$(C_{A,ss})$ (mol/L)	$X_{ss} = 1 - \frac{C_A}{C_{A0}}$
Low (stable)	298.29	7.35×10^{-4}	1.985	0.00729 (0.73%)
Middle (unstable)	351.89	7.36×10^{-2}	1.152	0.4239 (42.4%)
High (stable)	423.81	5.70	0.0345	0.9828 (98.3%)

So, there is a **high-conversion steady state** available, but only if the reactor “ignites” past the unstable middle branch.

(b) Transient startup equations

Initial conditions (pure solvent at 300 K):

$$C_A(0) = 0, T(0) = 300 \text{ K}$$

Kinetics:

$$k(T) = k_0 \exp\left(-\frac{E_a}{RT}\right)$$

Species ODE

$$\frac{dC_A}{dt} = \frac{q}{V}(C_{A0} - C_A) - k(T)C_A$$

$$\frac{dC_A}{dt} = 0.1(2.0 - C_A) - k(T)C_A$$

Energy ODE

$$\rho C_p V \frac{dT}{dt} = q\rho C_p(T_0 - T) + (-\Delta H)V k(T)C_A - UA(T - T_c)$$

Divide by $\rho C_p V$:

$$\frac{dT}{dt} = \frac{q}{V}(T_0 - T) + \frac{-\Delta H}{\rho C_p} k(T)C_A - \frac{UA}{\rho C_p V}(T - T_c)$$

Here: $\frac{q}{V} = 0.1$

$$\frac{-\Delta H}{\rho C_p} = \frac{350}{4} = 87.5 \text{ K/mol}$$

$$\frac{UA}{\rho C_p V} = \frac{144}{4000} = 0.036$$

So:

$$\frac{dT}{dt} = 0.1(300 - T) + 87.5 k(T)C_A - 0.036(T - 290)$$

(c) Expected temperature overshoot behavior

Because the system has two stable steady states separated by an unstable one:

Starting at 300 K, you are well below the unstable branch (~352 K). The reaction rate is initially small, and cooling pulls T downward. As C_A builds from 0 toward ~2 mol/L, heat generation increases somewhat, but not enough to “ignite.”

Expected outcome: approach the low stable state near 298.3 K with ~0.7% conversion.

You might see a minor transient “wobble,” but no large upward overshoot.

If the contents are started hot enough, Arrhenius feedback makes $k(T)$ large, heat generation jumps, and the reactor ignites toward the high stable state (~424 K). During ignition, a temperature overshoot above 424 K is possible (common in exothermic CSTR startups) before settling back, depending on thermal inertia and how quickly reactant is replenished.

(d) Initial solvent temperature needed to reach the high-conversion steady state

To end up on the high-conversion branch, the initial condition must be on the “hot side” of the unstable steady state, which acts like a threshold.

$$T_{init} \gtrsim 352 \text{ K ("about " 351.9" K"}$$

If $T(0) < 351.9 \text{ K} \rightarrow$ trajectory goes to the low stable state.

If $T(0) > 351.9 \text{ K}$ (or you otherwise perturb above it) \rightarrow ignition to the high stable state.

Prompted Example 7.1: CSTR Response to Feed Concentration Disturbance

Problem:

A CSTR operating at isothermal steady state with first-order kinetics suddenly experiences a 20 percent increase in feed concentration. The reactor has space time of 8 minutes and rate constant of 0.15 per minute. Initial steady-state conversion is 55 percent. (a) Determine the new steady-state concentration and conversion. (b) Calculate how long it takes to reach 90 percent of the new steady state. (c) Analyze the transient conversion profile. (d) If this disturbance occurs repeatedly, discuss implications for product quality control.

Approach: My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the fundamental assumptions in the modelling by asking me questions and wait for my answer to each question.

7.4 Plug Flow Reactor Transient Behavior

7.4.1 Fundamental Differences from CSTR

PFR transient behavior differs fundamentally from CSTRs:

Wave propagation: Disturbances propagate through the reactor as waves

Time delay: Exit responds after residence time delay

Distributed dynamics: Each position has different time constant

The transient PFR material balance is:

$$\frac{\partial C_A}{\partial t} + q \frac{\partial C_A}{\partial V} = r_A \quad (7.11)$$

where q is volumetric flow and V is Volume. This partial differential equation shows concentration depending on both time and position.

7.4.2 Transient Energy Balance for PFR

General Transient Energy Balance

For a plug flow reactor with heat exchange, the transient energy balance is:

$$\rho C_p \left(\frac{\partial T}{\partial t} + q \cdot \frac{\partial T}{\partial V} \right) = -\Delta H_{rxn} \cdot r_A + UA(T_c - T) \quad (7.12)$$

Where:

First term ($\partial T/\partial t$): Accumulation of thermal energy

Second term ($u \cdot \partial T/\partial z = q \partial T/\partial V$): Convective transport of thermal energy

Third term ($-\Delta H_{rxn} \cdot r_A$): Heat generation from reaction

Fourth term (UA)($T_c - T$): Heat exchange with surroundings

With:

U = overall heat transfer coefficient [$W/(m^2 \cdot K)$]

A = heat transfer area per unit volume [m^2/m^3]

T_c = coolant/jacket temperature [K]

Steady-State PFR Energy Balance

At steady state ($\partial T/\partial t = 0$), the energy balance simplifies to:

$$\rho C_p \cdot q \cdot \frac{dT}{dV} = -\Delta H_{rxn} \cdot r_A + UA(T_c - T) \quad (7.13)$$

This ODE must be solved simultaneously with the material balance:

$$q \cdot \frac{dC_A}{dV} = r_A \quad (7.14)$$

Special Cases

1. Adiabatic PFR (No Heat Exchange)

When $UA = 0$ (perfectly insulated):

$$\rho C_p \cdot q \cdot \frac{dT}{dV} = -\Delta H_{rxn} \cdot r_A \quad (7.15)$$

For first-order reaction:

$$\frac{dT}{dC_A} = \frac{(-\Delta H_{rxn})}{(\rho C_p)} \quad (7.16)$$

Integration gives:

$$T(z) = T_0 + \frac{(-\Delta H_{rxn})}{(\rho C_p)} (C_{A0} - C_A) = T_0 + \Delta T x_A \quad (7.17)$$

2. Isothermal PFR (Perfect Heat Exchange)

When heat exchange is sufficient to maintain constant temperature:

$$T(z) = T_0 \text{ (constant)}$$

Required heat duty per unit volume:

$$Q(z) = (-\Delta H_{rxn}) \cdot r_A \quad (7.18)$$

3. Non-Adiabatic, Non-Isothermal PFR (General Case)

The solution must be solved numerically with:

Coupled material and energy balances in equations (7.11) and (7.12)

Temperature-dependent reaction rate: $k(T) = k_0 \exp(-E_a/RT)$

Boundary conditions: $C_A(0) = C_{A0}, T(0) = T_0$

Possible formation of hot spots in highly exothermic reactions.

Prompted Example 7.2: PFR Startup and Wave Propagation

Problem:

A tubular reactor 20 meters long operates with average velocity of 0.5 meters per second. Initially filled with inert solvent. At $t = 0$, reactant feed begins with concentration 3.0 mol per L. First-order reaction with $k = 0.05$ per second. (a) Calculate the residence time and when exit first sees reactant. (b) Describe the concentration wave propagation through the reactor. (c) Determine steady-state exit concentration. (d) Compare startup time to equivalent CSTR.

Approach: My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the fundamental assumptions in the modelling by asking me questions and wait for my answer to each question.

7.5 Startup and Shutdown Procedures

7.5.1 Safe Startup Strategies

For exothermic reactions, careful startup prevents thermal runaway:

Cold start: Begin with cold feed, allow temperature to rise gradually

Hot start: Preheat reactor before introducing reactants

Ramped feed: Gradually increase reactant concentration

Staged cooling: Increase cooling capacity as reaction accelerates

7.5.2 Shutdown Procedures

Safe shutdown considerations:

Feed cutoff: Stop reactant feed, allow reactor to purge

Cooling continuation: Maintain cooling until temperature drops sufficiently

Inert purging: Flush with inert to prevent residual reaction

Emergency procedures: Rapid quenching, dump systems, inhibitor injection

7.6 Advanced Practice Problems

Problem 7.1: CSTR Startup with Catalyst Deactivation

A catalytic CSTR operates with first-order kinetics but the catalyst slowly deactivates. Initial activity $a = 1$, deactivation follows first-order decay with rate constant $k_d = 0.001$ per hour. Feed: $C_{A,0} = 4.0$ mol per L at 80 L per min. Reactor: $V = 800$ L. Initial $k = 0.25$ per min.

(a) Write coupled transient equations for CA and catalyst activity a . (b) During startup from empty reactor, calculate concentration profiles for first 2 hours. (c) Determine when conversion drops to 80 percent of initial steady-state value. (d) Design a catalyst replacement schedule to maintain conversion above 85 percent of fresh catalyst performance. (e) Compare total catalyst usage for continuous operation versus periodic complete replacement. (f) Analyze economic trade-offs between catalyst cost and off-spec product.

Problem 7.2: Non-Isothermal CSTR Multiple Steady States and Stability

An exothermic reaction in a CSTR exhibits three steady states: low conversion stable, intermediate unstable, high conversion stable. Rate parameters allow analytical determination of steady states. Operating at high conversion steady state, various disturbances occur.

(a) For a step decrease in coolant temperature of 10 K, solve transient response. Does reactor remain at high conversion state? (b) For a pulse increase in feed temperature (spike to T_0 plus 20 K for 2 minutes then return), determine if reactor blows out to low conversion state. (c) Design control strategy to reject disturbances and maintain high conversion operation. (d) Calculate minimum cooling capacity required to guarantee stability. (e) Analyze startup procedure: should reactor be preheated to operating temperature or started cold? (f) Develop emergency shutdown procedure if cooling fails.

Problem 7.3: Series CSTR Train Dynamics

Three equal-volume CSTRs in series process a first-order reaction. Each reactor $V = 500$ L, total feed 150 L per min, $C_{A,0} = 2.5$ mol per L, $k = 0.15$ per min, isothermal at 350 K.

(a) Calculate steady-state concentrations in each reactor. (b) Starting from empty reactors, solve coupled transient equations for all three reactors simultaneously. (c) Compare time to reach steady state for first, second, and third reactors. (d) Introduce step change in feed concentration to 3.0 mol per L at $t = 30$ min. Plot transient

response of all three reactors. (e) Compare dynamic response to equivalent single CSTR of total volume 1500 L. Which configuration responds faster to disturbances? (f) Design optimal startup procedure: fill all simultaneously or sequentially?

Additional Practice Problems (Hand Calculations)

The following problems are designed to be solved with hand calculations to reinforce fundamental concepts.

Problem 7.4: Characteristic Time Constant Calculation

A first-order reaction with $k = 0.10$ per min is carried out in a CSTR with space time of 12 minutes. (a) Calculate the characteristic time constant. (b) How long does it take to reach 63.2 percent, 90 percent, and 99 percent of steady state? (c) If space time is doubled to 24 minutes with same rate constant, how does the characteristic time constant change? (d) For the original reactor, if rate constant is doubled to 0.20 per min, calculate the new characteristic time constant.

Problem 7.5: Startup Concentration Profile

A CSTR starts from empty with first-order kinetics $k = 0.25$ per min, $\tau = 8$ min, $C_{A,0} = 3.0$ mol per L. (a) Calculate steady-state concentration and conversion. (b) Find characteristic time constant. (c) Calculate C_A at $t = 2, 4, 6, 8, 10,$ and 15 minutes using Equation 7.6. (d) At what time does conversion reach 50 percent of steady-state conversion?

Problem 7.6: Step Change Response

A CSTR at steady state with $C_A = 1.5$ mol per L experiences step increase in feed concentration from $C_{A,0} = 2.0$ to 2.4 mol per L. First-order reaction $k = 0.20$ per min, $\tau = 6$ min. (a) Calculate the new steady-state concentration. (b) Determine characteristic time constant. (c) Calculate the concentration change magnitude ΔC_A . (d) How long until C_A reaches 1.8 mol per L (90 percent of the way to new steady state)?

Chapter 7 Summary: What You Should Have Learned

1. Formulate and solve transient material balances for CSTRs.
2. Derive and analyze coupled transient material and energy balances for non-isothermal reactors.
3. Calculate characteristic time constants for CSTRs.

4. Analyze transient behavior in plug flow reactors.
5. Design safe startup and shutdown procedures for exothermic reactors.

Chapter 8: Multiple Reactions and Selectivity

Learning Objectives

After completing this chapter, you should be able to:

- Classify multiple reaction systems as parallel (competitive), series (consecutive), or complex networks, and recognize how reaction stoichiometry and kinetics interact to determine product distribution.
- Define and calculate selectivity and yield for multiple reaction systems, distinguishing between instantaneous and overall selectivity, and apply these metrics to evaluate reactor performance.
- Determine optimal reactor types (CSTR, PFR, or combinations) for parallel reaction systems by analyzing how concentration profiles affect the ratio of desired to undesired reaction rates based on relative reaction orders.
- Determine optimal reactor types for series reaction systems by analyzing intermediate concentration profiles and recognizing that PFRs generally minimize overreaction to undesired final products.
- Apply temperature optimization strategies for multiple reactions by comparing activation energies to maximize selectivity toward desired products while maintaining acceptable conversion.
- Design combined reactor systems (CSTRs in series, PFR-CSTR combinations, recycle configurations) to achieve selectivity targets that cannot be met with a single ideal reactor.
- Develop and solve species mole balance equations for multiple reaction systems in ideal CSTRs and PFRs, incorporating selectivity constraints and conversion targets.
- Analyze trade-offs between conversion and selectivity, recognizing that maximum conversion and maximum selectivity rarely occur under the same conditions, requiring process optimization based on economic considerations.

Nomenclature

The following symbols are introduced in this chapter and supplement the comprehensive nomenclature in Appendix B:

Roman Letters

C_i	Concentration of species i (mol/L or mol/m ³)
D	Desired product
E_a	Activation energy (J/mol or kJ/mol)
F_i	Molar flow rate of species i (mol/s)

k	Reaction rate constant (units depend on reaction order)
r_i	Rate of formation of species i per unit volume (mol/(L·s) or mol/(m ³ ·s))
R	Universal gas constant, 8.314 J/(mol·K)
$S_{D/U}$	Selectivity of desired product D relative to undesired product U (dimensionless)
T	Temperature (K)
U	Undesired product
V	Reactor volume (L or m ³)
X_A	Fractional conversion of reactant A (dimensionless)
Y_D	Yield of desired product D (dimensionless)

Greek Letters

α	Reaction order with respect to a species (dimensionless)
τ	Space time (s, min, or h)

Subscripts

0	Initial condition or inlet
D	Desired product
U	Undesired product
1, 2	Reaction indices

8.1 Introduction: The Challenge of Multiple Reactions

In industrial practice, chemical reactions rarely occur in isolation. Most reaction systems involve multiple reactions proceeding simultaneously, creating competition for reactants and producing both desired and undesired products. The challenge facing the reaction engineer is not merely to achieve high conversion of reactants, but to maximize the production of desired products while minimizing waste and byproducts.

Consider the partial oxidation of ethylene to ethylene oxide, a critical industrial process. The desired reaction produces valuable ethylene oxide, while the undesired complete oxidation to CO₂ and H₂O wastes both reactant and energy. Even small improvements in selectivity toward ethylene oxide—from 80% to 85%—can translate into millions of dollars of annual savings for a large-scale plant.

The reactor type, operating conditions (particularly temperature and concentration), and configuration profoundly influence product distribution. Unlike single-reaction systems where the primary concern is achieving target conversion efficiently, multiple reaction

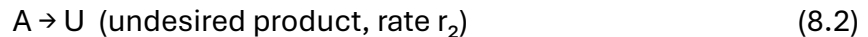
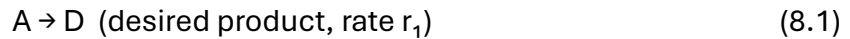
systems require simultaneous optimization of conversion and selectivity. These objectives often conflict: conditions favoring high conversion may reduce selectivity, and vice versa.

This chapter develops systematic approaches to reactor selection and design for multiple reaction systems. We examine how reaction kinetics, reactor type, and operating conditions interact to determine product distribution, and learn to design reactor systems that achieve optimal economic performance.

8.2 Classification of Multiple Reaction Systems

8.2.1 Parallel (Competitive) Reactions

Parallel reactions involve a common reactant forming different products through competing pathways:



The product distribution depends on the relative rates of the competing reactions. If both reactions are first-order in A:

$$r_1 = k_1 C_A \quad (8.3)$$

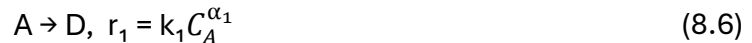
$$r_2 = k_2 C_A \quad (8.4)$$

The instantaneous selectivity—the ratio of desired to undesired product formation rates—is:

$$S_{D/U} = \frac{r_1}{r_2} = \frac{k_1}{k_2} \quad (8.5)$$

For parallel reactions with the same reaction order, selectivity is determined solely by the ratio of rate constants and is independent of reactant concentration and reactor type. Temperature becomes the only adjustable parameter, selecting T to maximize k_1/k_2 .

However, when reaction orders differ, concentration profiles strongly affect selectivity. Consider:



The instantaneous selectivity becomes:

$$S_{D/U} = (k_1/k_2) C_A^{(\alpha_1 - \alpha_2)} \quad (8.8)$$

Now selectivity depends on concentration. If $\alpha_1 > \alpha_2$, high concentrations favor the desired product, suggesting use of a PFR or operating conditions that maintain high C_a . If $\alpha_1 < \alpha_2$, low concentrations favor the desired product, suggesting use of a CSTR or dilution strategies.

8.2.2 Series (Consecutive) Reactions

Series reactions involve sequential conversion where the desired product from the first reaction becomes a reactant in a subsequent undesired reaction:



The challenge is to stop the reaction at the intermediate D before it proceeds to the undesired product U. For first-order kinetics:

$$r_1 = k_1 C_A \text{ (formation of D)} \quad (8.10)$$

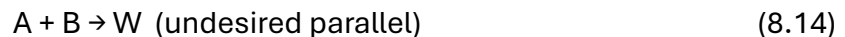
$$r_2 = k_2 C_D \text{ (depletion of D)} \quad (8.11)$$

The concentration of desired intermediate D increases initially as A is consumed, reaches a maximum, then decreases as D converts to U. The key is to design the reactor to achieve high C_D at the outlet while minimizing conversion of D to U.

PFRs generally perform better than CSTRs for series reactions because they maintain the concentration profile needed to maximize D. In a CSTR, all fluid elements experience the same (low) outlet concentration, allowing significant conversion of D to U. In a PFR, the concentration of D builds up along the reactor length, and if we stop at the optimal point, we can harvest D before excessive conversion to U occurs.

8.2.3 Complex Reaction Networks

Many industrial systems involve combinations of parallel and series reactions, creating complex networks:



Such systems require careful analysis of all reaction pathways. Generally, we must balance competing objectives: keeping A concentration high enough for the desired reaction but preventing excessive series reaction of D, while maintaining appropriate B concentration to favor the desired pathway over parallel undesired pathways.

8.3 Selectivity and Yield Definitions

Selectivity quantifies how effectively a reaction system produces desired products relative to undesired products. For a system producing desired product D and undesired product U from reactant A, we define:

Instantaneous selectivity: the ratio of formation rates at a specific point:

$$S_{D/U,inst} = r_D/r_U \quad (8.15)$$

Overall selectivity: the ratio of total amounts produced:

$$S_{D/U,overall} = \frac{\text{moles of D formed}}{\text{moles of U formed}} \quad (8.16)$$

For a CSTR at steady state, instantaneous and overall selectivity are identical because the entire reactor operates at uniform composition. For a PFR or batch reactor, selectivity varies along the reactor length or with time, and overall selectivity represents the integrated result.

Yield measures the effectiveness of converting reactant into desired product:

$$Y_D = \frac{\text{moles of D formed}}{\text{moles of A fed}} \quad (8.17)$$

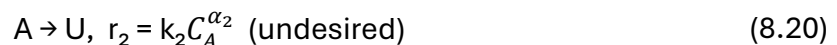
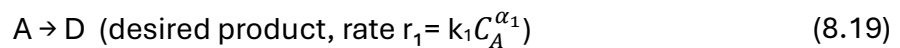
Yield combines both conversion and selectivity effects. We can relate yield to conversion and selectivity:

$$Y_D = \frac{x_A \times S_D}{D+U} \quad (8.18)$$

This relationship shows that maximizing yield requires balancing conversion (favored by more reactor volume or longer residence time) with selectivity (which may decrease with increasing conversion).

8.4 Reactor Selection for Parallel Reactions

The choice between CSTR and PFR for parallel reactions depends critically on the relative reaction orders. Consider parallel reactions:



Case 1: $\alpha_1 > \alpha_2$ (desired reaction has higher order)

High concentrations favor the desired product because $S_{D/U} = (k_1/k_2)C_A^{(\alpha_1-\alpha_2)}$ increases with C_A . Use a PFR or minimize CSTR volume to maintain high C_A . Avoid dilution or high recycle ratios that reduce concentration. Consider semi-batch operation with slow addition of second reactant to keep the first reactant concentration high.

Case 2: $\alpha_1 < \alpha_2$ (desired reaction has lower order)

Low concentrations favor the desired product. Use a CSTR or add inert diluent to reduce concentration. Large recycle ratios can improve selectivity. Semi-batch operation with slow addition of the limiting reactant maintains low concentration.

Case 3: $\alpha_1 = \alpha_2$ (equal reaction orders)

Selectivity $S_{D/U} = k_1/k_2$ is independent of concentration and reactor type. Only temperature affects selectivity through the rate constant ratio. Choose reactor type based on other considerations (heat management, ease of operation, capital cost).

8.5 Reactor Selection for Consecutive Reactions

For consecutive reactions $A \rightarrow D \rightarrow U$, we want to maximize the yield of intermediate D. The concentration profile in a PFR allows D to accumulate to a maximum, then decrease as it converts to U. In contrast, a CSTR operates at the outlet composition throughout, where D has already partially converted to U.

For first-order kinetics ($r_1 = k_1 C_a$, $r_2 = k_2 C_D$), the maximum yield of D in a batch reactor or PFR can be derived analytically. The optimal space time or batch time occurs where $dC_D/dt = 0$, giving:

$$\tau_{optimal} = \left(\frac{1}{k_1 - k_2} \right) \times \ln \left(\frac{k_1}{k_2} \right) \quad (8.21)$$

PFRs should be designed to operate near this optimal residence time. If $k_1 \gg k_2$ (first reaction much faster), a short residence time harvests D before significant conversion to U. If $k_1 \approx k_2$, careful control of residence time is critical.

CSTRs typically achieve lower yields of D for series reactions because the entire reactor volume operates at low C_D . However, CSTRs in series can approach PFR performance by creating a concentration gradient across the reactor train.

8.6 Temperature Effects on Selectivity

Temperature profoundly affects selectivity through the Arrhenius temperature dependence of rate constants. For parallel reactions:

$$S_{D/U} = \left(\frac{k_1}{k_2} \right) = \left(\frac{A_1}{A_2} \right) \exp \left[- \frac{E_1 - E_2}{RT} \right] \quad (8.22)$$

If the desired reaction has higher activation energy ($E_1 > E_2$), selectivity increases with temperature—high temperature favors the desired product. If $E_1 < E_2$, low temperature favors

the desired product. This creates a fundamental trade-off: high temperature increases reaction rates (reducing required reactor volume) but may decrease selectivity.

For series reactions, temperature affects both the rate of D formation and its rate of depletion. If the second reaction ($D \rightarrow U$) has higher activation energy, low temperature favors accumulation of D. However, low temperature also slows D formation, requiring larger reactors. The optimal temperature balances these competing effects.

Variable temperature operation—temperature profiles along a PFR or temperature progression in a reactor sequence—can sometimes improve performance beyond isothermal operation. Start at high temperature to achieve rapid initial conversion, then reduce temperature to prevent overreaction of intermediate products.

8.7 Combined Reactor Systems

Complex reaction networks often require combined reactor systems to achieve acceptable selectivity:

8.7.1 CSTRs in Series

Multiple CSTRs in series create concentration gradients that approach PFR behavior while retaining the temperature control advantages of CSTRs. For N equal-volume CSTRs in series, performance approaches a PFR as N increases. Two or three CSTRs often provide most of the selectivity benefit at reasonable capital cost.

8.7.2 PFR-CSTR Combinations

For reactions where concentration must be kept high initially but low finally, a PFR followed by a CSTR can be optimal. The PFR provides high initial conversion at high selectivity, while the CSTR completes conversion at acceptable selectivity.

8.8 Worked Examples

Worked Example 8.1: Parallel Reactions with Different Orders

Problem:

The liquid-phase reactions occur in parallel:

$A \rightarrow D$ (desired), $r_1 = 2.0 C_A^2 \text{ mol}/(\text{L}\cdot\text{min})$

$A \rightarrow U$ (undesired), $r_2 = 1.0 C_A \text{ mol}/(\text{L}\cdot\text{min})$

Feed concentration is $C_{A0} = 4.0 \text{ mol}/\text{L}$, flow rate 100 L/min. Compare the overall selectivity $S_{D/U}$ achieved in: (a) a CSTR achieving 80% conversion, and (b) a PFR achieving 80% conversion.

Solution:

Analysis: The desired reaction is second-order while the undesired is first-order. Since $\alpha_1 > \alpha_2$, high concentrations favor the desired product. We expect the PFR to give better selectivity.

(a) CSTR:

At 80% conversion: $X_A = 0.80$, so $C_A = C_{A0}(1 - X_A) = 4.0(1 - 0.80) = 0.8 \text{ mol/L}$

Rates at CSTR outlet (and throughout CSTR):

$$r_1 = 2.0(0.8)^2 = 1.28 \text{ mol/(L}\cdot\text{min)}$$

$$r_2 = 1.0(0.8) = 0.80 \text{ mol/(L}\cdot\text{min)}$$

Instantaneous selectivity:

$$S_{D/U} = r_1/r_2 = 1.28/0.80 = 1.60$$

For a CSTR, overall selectivity equals instantaneous selectivity: **$S_{D/U} = 1.60$**

(b) PFR:

For a PFR, we must integrate along the reactor length. The mole balance for A:

$$\frac{dF_A}{dV} = -(r_1 + r_2) = -(2.0C_A^2 + 1.0C_A)$$

The mole balances for D and U:

$$\frac{dF_D}{dV} = r_1 = 2.0C_A^2$$

$$\frac{dF_U}{dV} = r_2 = 1.0C_A$$

For liquid phase with constant volumetric flow rate q_0 :

$$q_0 dC_A/dV = -(2.0C_A^2 + 1.0C_A)$$

Integrating numerically from $C_A = 4.0$ to $C_A = 0.8 \text{ mol/L}$ while tracking D and U formation:

$$\text{Total D formed: } \int r_1 dV/q_0 = \int 2.0C_A^2 dC_A/(-2.0C_A^2 - 1.0C_A)$$

$$\text{Total U formed: } \int r_2 dV/q_0 = \int 1.0C_A dC_A/(-2.0C_A^2 - 1.0C_A)$$

Numerical integration gives:

$$C_{D,\text{out}} \approx 2.54 \text{ mol/L}$$

$$C_{U,\text{out}} \approx 0.66 \text{ mol/L}$$

$$\mathbf{S_{D/U} = 2.54/0.66 = 3.85}$$

Conclusion: The PFR achieves selectivity of 3.85 compared to 1.60 for the CSTR—a 140% improvement. This confirms that high concentrations favor the higher-order desired reaction. The PFR maintains high C_A through most of its length, enhancing r_1 relative to r_2 .

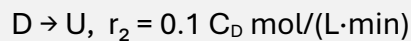
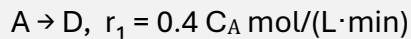
8.7.3 Recycle Reactors

Product or unconverted reactant recycle can improve selectivity by controlling concentration. Recycle dilutes the feed, reducing concentration if that favors selectivity. Alternatively, recycling intermediate products can allow them to react further under controlled conditions.

Worked Example 8.2: Series Reactions - Optimal Reactor Size

Problem:

A valuable intermediate D is produced by series reactions:



Pure A is fed at $C_{A,0} = 2.0 \text{ mol/L}$, $q_0 = 50 \text{ L/min}$ to a PFR. Determine the reactor volume that maximizes the exit concentration of D. What is the maximum C_D achieved?

Solution:

Analysis: For first-order series reactions in a PFR, C_D increases initially as A converts to D, reaches a maximum, then decreases as D converts to U. We seek the space time or volume where $dC_D/dV = 0$.

Mole balances for liquid-phase PFR:

$$dC_A/d\tau = -r_1 = -0.4 C_A$$

$$dC_D/d\tau = r_1 - r_2 = 0.4 C_A - 0.1 C_D$$

where $\tau = V/q_0$ is the space time.

Solving the first equation:

$$C_A = C_{A,0} \exp(-0.4\tau) = 2.0 \exp(-0.4\tau)$$

Substituting into the second equation:

$$dC_D/d\tau + 0.1 C_D = 0.4(2.0)\exp(-0.4\tau) = 0.8 \exp(-0.4\tau)$$

This is a first-order linear ODE. The solution with $C_D = 0$ at $\tau = 0$:

$$C_D = (0.8/(0.4-0.1))[\exp(-0.1\tau) - \exp(-0.4\tau)]$$

$$C_D = (8/3)[\exp(-0.1\tau) - \exp(-0.4\tau)]$$

To find maximum, set $dC_D/d\tau = 0$:

$$dC_D/d\tau = (8/3)[-0.1 \exp(-0.1\tau) + 0.4 \exp(-0.4\tau)] = 0$$

$$-0.1 \exp(-0.1\tau) + 0.4 \exp(-0.4\tau) = 0$$

$$0.4 \exp(-0.4\tau) = 0.1 \exp(-0.1\tau)$$

$$4 = \exp(0.3\tau)$$

$$\tau_{opt} = \ln(4)/0.3 = 4.62 \text{ min}$$

$$\text{Optimal reactor volume: } V = q_0 \times \tau_{opt} = 50 \times 4.62 = 231 \text{ L}$$

Maximum C_D :

$$C_{D,max} = (8/3)[\exp(-0.1 \times 4.62) - \exp(-0.4 \times 4.62)]$$

$$C_{D,max} = (8/3)[0.632 - 0.159] = (8/3)(0.473)$$

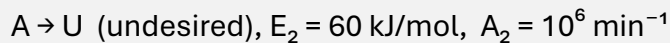
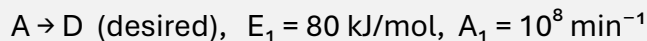
$$C_{D,max} = 1.26 \text{ mol/L}$$

Conclusion: A 231 L PFR operating at 4.62 min space time maximizes D concentration at 1.26 mol/L (63% of initial A concentration). Operating longer converts more D to undesired U; operating shorter leaves too much unreacted A. This demonstrates the critical importance of proper reactor sizing for series reactions.

Worked Example 8.3: Temperature Optimization for Parallel Reactions

Problem:

Consider the parallel reactions in a CSTR:



Both reactions are first-order in A. You want 90% conversion of A. Should you operate at high or low temperature for maximum selectivity? Calculate the selectivity at 350 K and 400 K. If the reactor volume required at 350 K is 1000 L, what volume is needed at 400 K for 90% conversion?

Solution:

Analysis: Since both reactions are first-order, selectivity $S_{D/U} = k_1/k_2$ depends only on temperature, not reactor type or concentration. The desired reaction has higher activation energy (80 vs 60 kJ/mol), so high temperature favors the desired product.

Rate constants at $T = 350 \text{ K}$:

$$k_1 = 10^8 \exp(-80,000/(8.314 \times 350)) = 10^8 \exp(-27.48) = 1.15 \cdot 10^{-4} \text{ min}^{-1}$$

$$k_2 = 10^6 \exp(-60,000/(8.314 \times 350)) = 10^6 \exp(-20.61) = 1.11 \cdot 10^{-3} \text{ min}^{-1}$$

$$S_{D/U} (350 \text{ K}) = k_1/k_2 = 0.104$$

Rate constants at $T = 400 \text{ K}$:

$$k_1 = 10^8 \exp(-80,000/(8.314 \times 400)) = 10^8 \exp(-24.05) = 3.57 \cdot 10^{-3} \text{ min}^{-1}$$

$$k_2 = 10^6 \exp(-60,000/(8.314 \times 400)) = 10^6 \exp(-18.04) = 1.46 \cdot 10^{-2} \text{ min}^{-1}$$

$$S_{D/U} (400 \text{ K}) = k_1/k_2 = 3.57/14.6 = 0.244$$

Selectivity improves from 0.104 to 0.244 (132% increase) when temperature increases from 350 to 400 K. Higher temperature strongly favors the desired product.

Reactor volume calculation:

For first-order reactions in a CSTR achieving $x_A = 0.90$:

$$\tau = x_A / [(k_1 + k_2)(1 - x_A)]$$

At 350 K:

$$\tau_{350} = 0.90 / [(1.15 + 11.1) \cdot 10^{-4} (1 - 0.90)] = 0.90 / (12.25 \cdot 10^{-4} \times 0.10) = 7350 \text{ min}$$

If $V = 1000 \text{ L}$ at 350 K, then $q_0 = V/\tau = 1000/7350 = 0.136 \text{ L/min}$

At 400 K:

$$\tau_{400} = 0.90 / [(3.57 + 14.6) \cdot 10^{-3} (1 - 0.90)] = 0.90 / (0.01818 \times 0.10) = 495 \text{ min}$$

$$V_{400} = 1000 \cdot \frac{k_{1,350} + k_{2,350}}{k_{1,400} + k_{2,400}} = 67.4 \text{ L}$$

Conclusion: Operating at 400 K rather than 350 K provides: (1) 132% better selectivity (0.244 vs 0.104), and (2) 95% smaller reactor volume (67.4 L vs 1000 L). This demonstrates the powerful benefits of high-temperature operation when the desired reaction has higher activation energy. The economic advantage is substantial despite higher energy costs.

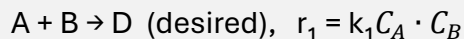
8.9 Prompted Examples

The following problems are designed to help you understand the fundamental assumptions in multiple reaction systems.

Prompted Example 8.1: Reactor Selection for Parallel Reactions

Problem:

In a liquid-phase system, reactant A undergoes two parallel reactions:



The feed contains equimolar amounts of A and B at 1.0 mol/L each. You must achieve 85% conversion of A. Should you use a CSTR or PFR to maximize selectivity toward D? Consider also how you might feed the reactants (premixed vs. separate addition).

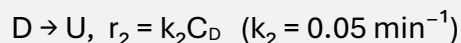
Guidance approach: My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the

fundamental assumptions in the modelling by asking me questions and wait for my answer to each question.

Prompted Example 8.2: Series Reaction Network

Problem

A pharmaceutical intermediate D is produced through series reactions:



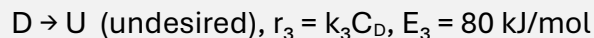
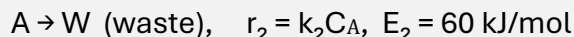
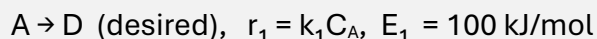
You have three 100-L CSTRs available. Compare: (a) using all three CSTRs in series, (b) using a single 300-L CSTR, and (c) using a single 100-L CSTR. Feed concentration is $C_{A,0} = 3.0 \text{ mol/L}$ at 80 L/min. Which configuration maximizes C_D at the outlet?

Guidance approach: My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the fundamental assumptions in the modelling by asking me questions and wait for my answer to each question.

Prompted Example 8.3: Complex Network with Temperature Effects

Problem:

A complex reaction network occurs in a PFR:



You want to maximize yield of D. The reactor can operate isothermally at any temperature from 320–380 K, or you can implement a temperature profile (high inlet temperature, lower outlet temperature). Discuss the trade-offs and propose an optimal temperature strategy. At 350 K, the rate constants are: $k_1 = 2.0 \text{ min}^{-1}$, $k_2 = 4.0 \text{ min}^{-1}$, $k_3 = 0.5 \text{ min}^{-1}$.

Guidance approach: My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the fundamental assumptions in the modelling by asking me questions and wait for my answer to each question.

8.10 Practice Problems

Simple Problems (Hand Calculations)

8.1 Selectivity in Parallel Reactions

Two parallel reactions occur: $A \rightarrow D$ ($r_1 = 5C_A^2 \text{ mol}/(\text{L}\cdot\text{s})$) and $A \rightarrow U$ ($r_2 = 2C_A \text{ mol}/(\text{L}\cdot\text{s})$). If $C_A = 0.5 \text{ mol}/\text{L}$ in a CSTR, calculate the instantaneous selectivity $S_{D/U}$. What happens to selectivity if C_A is doubled to $1.0 \text{ mol}/\text{L}$?

8.2 Temperature Effect on Selectivity

For parallel first-order reactions $A \rightarrow D$ ($E_1 = 120 \text{ kJ}/\text{mol}$, $A_1 = 10^{10} \text{ s}^{-1}$) and $A \rightarrow U$ ($E_2 = 90 \text{ kJ}/\text{mol}$, $A_2 = 10^8 \text{ s}^{-1}$), calculate the selectivity $S_{D/U}$ at 300 K and 400 K. Which temperature gives better selectivity?

8.3 Yield and Selectivity

In a CSTR, 100 mol/min of A is fed. At the outlet, you measure $F_D = 60 \text{ mol}/\text{min}$ and $F_U = 20 \text{ mol}/\text{min}$. Calculate: (a) the conversion of A, (b) the overall selectivity $S_{D/U}$, and (c) the yield of D.

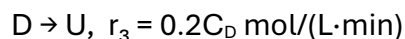
8.4 CSTR vs. PFR for Series Reactions

For series reactions $A \rightarrow D \rightarrow U$ with $k_1 = 0.4 \text{ min}^{-1}$ and $k_2 = 0.1 \text{ min}^{-1}$, explain qualitatively (without detailed calculations) why a PFR generally gives higher yield of D than a CSTR for the same space time. Sketch concentration profiles of A, D, and U vs. space time for a PFR.

Advanced Problems

8.5 Optimal Reactor Configuration for Complex Kinetics

A liquid-phase reaction system involves parallel and series reactions:

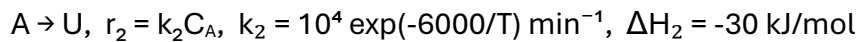
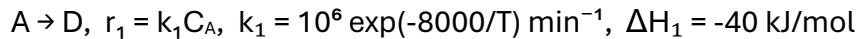


Feed: $C_{A,0} = 2.5 \text{ mol}/\text{L}$, $q_0 = 200 \text{ L}/\text{min}$. Design a reactor system to maximize the outlet concentration of D. Consider: (a) a single PFR, (b) a single CSTR, (c) two CSTRs in series of

equal volume, and (d) a PFR followed by a CSTR. For each configuration, determine the total volume needed to achieve $C_D \geq 1.5$ mol/L at the outlet, and compare the amount of undesired products formed.

8.6 Non-Isothermal PFR with Multiple Reactions

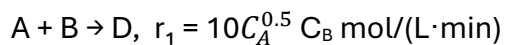
Parallel exothermic reactions occur in an adiabatic PFR:



Feed: $C_{A,0} = 3.0$ mol/L, $T_0 = 320$ K, $q_0 = 150$ L/min. Heat capacity $C_P = 3.5$ kJ/(L·K). Solve the coupled energy and mole balance equations to determine: (a) the PFR volume needed to achieve 80% conversion, (b) the outlet temperature, (c) the overall selectivity S_D/U , and (d) whether isothermal operation at 340 K would improve selectivity (explain using activation energies).

8.7 Recycle Reactor Optimization

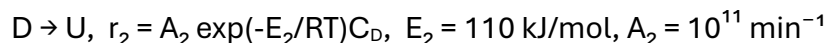
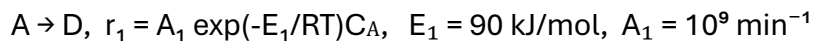
A PFR with product recycle is used for parallel reactions:



Fresh feed: $F_{A,0} = 100$ mol/min at $C_A = 2.0$ mol/L, $F_{B,0} = 100$ mol/min at $C_B = 2.0$ mol/L. A fraction R of the outlet stream is recycled and mixed with fresh feed. The recycle ratio R can be varied from 0 (no recycle) to 0.8. Determine: (a) how the recycle ratio affects the inlet concentration to the reactor, (b) how it affects selectivity, (c) the optimal recycle ratio to maximize S_D/U while achieving at least 75% conversion of A, and (d) the required reactor volume for this optimal condition.

8.8 Temperature Profile Optimization

Series reactions in a 500-L PFR:



Feed: $C_{A,0} = 4.0$ mol/L, $q_0 = 100$ L/min. Compare three operating strategies: (a) isothermal at 360 K, (b) isothermal at 380 K, (c) temperature profile starting at 380 K for the first 60% of reactor length, then reducing linearly to 340 K. For each strategy, calculate the outlet concentrations of A, D, and U, and the yield of D. Explain why the variable temperature profile might be superior using the concept of activation energy differences and concentration evolution along the reactor.

Chapter 8 Summary: What You Should Have Learned

After completing this chapter, you should be able to:

1. Classify multiple reaction systems
2. Define selectivity and yield for multiple reactions
3. Analyze parallel and series reactions
4. Understand temperature effects on selectivity
5. Design reactors for complex reaction networks

Chapter 9: Equilibrium-Limited Processes

Learning Objectives

After completing this chapter, you should be able to:

- Recognize reversible reactions and understand that equilibrium limitations prevent complete conversion, requiring different design strategies than irreversible reactions to maximize product yield.
- Derive and apply equilibrium relationships for reversible reactions, calculating the equilibrium constant K_e from thermodynamic data and relating it to equilibrium conversion as a function of temperature and composition.
- Construct equilibrium conversion curves (x_e vs. T) for reversible reactions, recognizing that exothermic reactions favor lower temperatures while endothermic reactions favor higher temperatures at equilibrium.
- Design isothermal reactors for reversible reactions by incorporating equilibrium limitations into the design equations, understanding that conversion is bounded by $x_e(T)$ and cannot exceed equilibrium regardless of reactor size.
- Apply energy balances to adiabatic reactors with reversible reactions, constructing x - T trajectories and identifying optimal operating points where the trajectory intersects the equilibrium curve for maximum conversion.
- Analyze and design multi-stage reactor systems including tanks in series, adiabatic beds with interstage cooling, and cold-shot cooling configurations to overcome equilibrium limitations and approach higher overall conversions.
- Construct and interpret x - T diagrams with rate contours for different reaction types (irreversible, reversible endothermic, reversible exothermic), using these diagrams to identify optimal temperature trajectories and reactor configurations.

Nomenclature

The following symbols are introduced in this chapter and supplement the comprehensive nomenclature in previous chapters:

Roman Letters

C_p	Heat capacity ($J/(\text{mol}\cdot\text{K})$ or $J/(\text{g}\cdot\text{K})$)
K_c	Equilibrium constant (concentration basis), units vary with reaction order
K_e	Equilibrium constant (general), dimensionless or with units
K_p	Equilibrium constant (pressure basis), units vary with reaction order
k_f	Forward reaction rate constant
k_r	Reverse reaction rate constant
r_{net}	Net reaction rate (forward minus reverse) ($\text{mol}/(\text{L}\cdot\text{s})$)
T_C	Coolant or inlet temperature (K or $^\circ\text{C}$)

x_e Equilibrium conversion, dimensionless

Greek Letters

ΔG° Standard Gibbs free energy change (J/mol or kJ/mol)

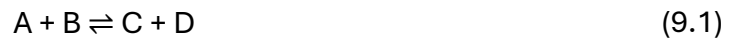
ΔH_{rxn}^0 Standard enthalpy of reaction (J/mol or kJ/mol)

ΔS° Standard entropy change (J/(mol·K))

ξ Extent of reaction (mol)

9.1 Introduction to Reversible Reactions

In previous chapters, we assumed reactions proceed irreversibly to complete conversion given sufficient reactor volume and residence time. However, many industrially important reactions are reversible, meaning both forward and reverse reactions occur simultaneously:



At equilibrium, the forward and reverse reaction rates are equal, and no net change in composition occurs even with infinite residence time. This equilibrium limitation fundamentally alters reactor design strategy, as conversion cannot exceed the equilibrium value x_e regardless of reactor size.

Important industrial examples of reversible reactions include:

Ammonia synthesis: $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (exothermic, $\Delta H_{rxn}^0 = -92$ kJ/mol) - This reaction is equilibrium-limited, favoring lower temperatures but requiring higher temperatures for acceptable rates.

Methanol synthesis: $CO + 2H_2 \rightleftharpoons CH_3OH$ (exothermic, $\Delta H_{rxn}^0 = -90$ kJ/mol) - Operates at high pressure to shift equilibrium toward products.

Steam reforming: $CH_4 + H_2O \rightleftharpoons CO + 3H_2$ (endothermic, $\Delta H_{rxn}^0 = +206$ kJ/mol) - High temperatures favor products but pose materials challenges.

Ester hydrolysis: $RCOOR' + H_2O \rightleftharpoons RCOOH + R'OH$ (typically $\Delta H_{rxn}^0 \approx 0$) - Controlled by removing water or alcohol products.

The fundamental challenge with reversible reactions is that thermodynamics and kinetics pull in opposite directions. For exothermic reactions, equilibrium favors low temperatures (Le Chatelier's principle), but reaction rates increase with temperature (Arrhenius equation). This creates an optimization problem that requires careful consideration of temperature management and reactor configuration.

9.2 Equilibrium Relationships for Reversible Reactions

9.2.1 Thermodynamic Equilibrium Constant

For a general reversible reaction:



The equilibrium constant based on activities is related to standard Gibbs free energy:

$$\Delta G^\circ = -RT \ln(K_e) \quad (9.3)$$

The standard Gibbs free energy can be calculated from:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9.4)$$

Combining these relationships gives:

$$\ln(K_e) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (9.5)$$

For practical calculations with concentration-based equilibrium constants:

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (9.6)$$

For gas-phase reactions, pressure-based constants are often more convenient:

$$K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b} \quad (9.7)$$

The concentration-based equilibrium constant equals the thermodynamic equilibrium constant K_e when the activity coefficients equal unity and pressure based constant $K_p = K_e$ for ideal gases.

9.2.2 Temperature Dependence - Van't Hoff Equation

The van't Hoff equation describes how equilibrium constant varies with temperature:

$$\frac{d(\ln K_e)}{dT} = \frac{\Delta H_{rxn}^\circ}{RT^2} \quad (9.8)$$

Integrating this expression (assuming ΔH_{rxn}° is approximately constant):

$$\ln\left(\frac{K_2}{K_1}\right) = -\left(\frac{\Delta H_{rxn}^\circ}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (9.9)$$

This equation reveals critical behavior:

For exothermic reactions ($\Delta H_{rxn}^\circ < 0$): K_e decreases with increasing temperature, meaning equilibrium favors reactants at high temperatures.

For endothermic reactions ($\Delta H_{rxn}^0 > 0$): K_e increases with increasing temperature, meaning equilibrium favors products at high temperatures.

9.2.3 Relating Equilibrium Constant to Conversion

For the reaction $A \rightleftharpoons B$ with equimolar feed (stoichiometric ratio), the equilibrium conversion can be expressed as:

$$K_C = \frac{C_B}{C_A} = \frac{(C_{A,0} \cdot x_e)}{C_{A,0}(1-x_e)} = \frac{x_e}{1-x_e} \quad (9.10)$$

Solving for equilibrium conversion:

$$x_e = \frac{K_C}{1 + K_C} \quad (9.11)$$

For more complex stoichiometry like $A + B \rightleftharpoons C + D$ with feed ratio $\Theta_B = C_{B,0}/C_{A,0}$:

$$K_C = \frac{x_e^2}{(1-x_e)(\Theta_B - x_e)} \quad (9.12)$$

9.3 The Equilibrium Conversion Curve

9.3.1 Construction of the Equilibrium Curve

The equilibrium curve is a plot of equilibrium conversion x_e versus temperature T . This curve represents the maximum achievable conversion at any given temperature and serves as an upper bound for reactor performance.

To construct the equilibrium curve:

1. Obtain thermodynamic data (ΔH_{rxn}^0 , ΔS°) for the reaction
2. Calculate K_e at various temperatures using Equation 9.5 or 9.9
3. Convert K_e to x_e using the appropriate stoichiometric relationship (Equation 9.11 or 9.12)
4. Plot x_e versus T to obtain the equilibrium curve

9.3.2 Properties of the Equilibrium Curve

For exothermic reactions ($\Delta H_{rxn}^0 < 0$):

The equilibrium curve slopes downward (x_e decreases with increasing T), reflecting that high temperatures drive the reaction backward. Low temperatures thermodynamically favor high conversion, but kinetics may be prohibitively slow. An optimal temperature exists where rate and equilibrium considerations balance.

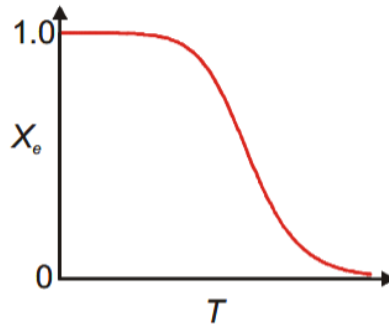


Figure 9-1 Equilibrium curve for an exothermic reversible reaction

For endothermic reactions ($\Delta H_{rxn}^0 > 0$):

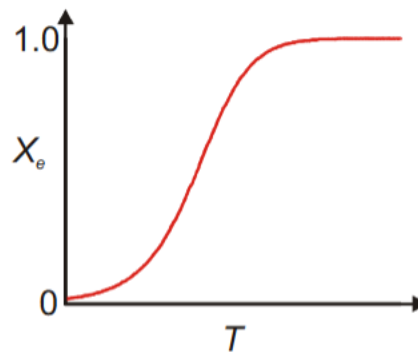


Figure 9-2 Equilibrium curve for an endothermic reversible reaction

The equilibrium curve slopes upward (x_e increases with increasing T), meaning both thermodynamics and kinetics favor high temperatures. The challenge becomes finding materials that withstand these temperatures and supplying the necessary heat.

The equilibrium curve has several important uses:

Feasibility check: Any operating point (x, T) must lie on or below the equilibrium curve.

Optimal temperature identification: For isothermal operation, identifies the temperature that maximizes conversion while maintaining acceptable rates.

Adiabatic operation analysis: The intersection of the adiabatic trajectory with the equilibrium curve determines maximum achievable conversion. The temperature will increase with conversion for an exotherm reaction and decrease with conversion for an endotherm adiabatic reaction.

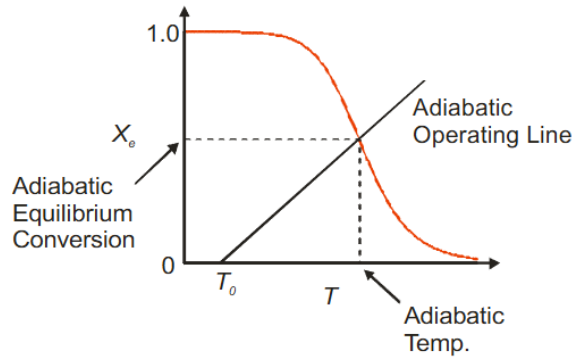


Figure 9-3 The maximum achievable conversion for an exothermic equilibrium reaction

9.4 Isothermal Reactor Design with Equilibrium Limitations

For isothermal operation, the reactor operates at constant temperature T , which fixes the equilibrium conversion $x_e(T)$. The design equation must account for the net rate, which approaches zero as conversion approaches equilibrium.

9.4.1 Net Reaction Rate

The net reaction rate for a reversible reaction $A \rightleftharpoons B$ is:

$$r_{\text{net}} = r_{\text{forward}} - r_{\text{reverse}} = k_f \cdot C_A - k_r \cdot C_B \quad (9.13)$$

At equilibrium, $r_{\text{net}} = 0$, which gives:

$$K_C = \frac{k_r}{k_f} = \frac{C_{B,e}}{C_{A,e}} \quad (9.14)$$

The net rate can be rewritten using the equilibrium constant:

$$r_{\text{net}} = k_f \cdot C_A \left(1 - \frac{C_B}{K_C \cdot C_A}\right) = k_f \cdot C_{A,0} (1-x) \left(1 - \frac{x}{x_e}\right) \quad (9.15)$$

This form clearly shows that the rate approaches zero as $x \rightarrow x_e$.

9.4.2 PFR Design Equation for Reversible Reactions

For a PFR with reversible first-order reaction:

$$\frac{V}{F_{A,0}} = \int_0^x \left(\frac{1}{r_{\text{net}}}\right) dx = \int_0^x \frac{1}{k_f C_{A,0} (1-x) \left(1 - \frac{x}{x_e}\right)} dx \quad (9.16)$$

Integration term reformulateds: $\int_0^x \frac{x_e}{(1-x)(x_e-x)} dx$

$$k_f \cdot \tau = \left(\frac{x_e}{1-x_e}\right) \cdot \ln \left[\frac{x_e(1-x)}{x_e-x}\right] \quad (9.17)$$

As x approaches x_e , the required volume approaches infinity - a characteristic of equilibrium-limited reactions.

9.4.3 CSTR Design Equation for Reversible Reactions

For a CSTR:

$$\frac{V}{F_{A,0}} = \frac{x}{r_{net}} = \frac{x}{k_f \cdot C_{A,0}(1-x) \left(1 - \frac{x}{x_e}\right)} \quad (9.18)$$

Rearranging:

$$k_f \cdot \tau = \frac{x}{(1-x)(x_e-x)} \quad (9.19)$$

9.5 Adiabatic Reactor Design with Equilibrium Limitations

9.5.1 Energy Balance for Adiabatic Operation

For an adiabatic reactor with no shaft work and negligible kinetic/potential energy changes, the energy balance gives:

$$T = T_0 + \frac{-\Delta H_{rxn}^0 x}{\rho \cdot C_P} \quad (9.20)$$

This can be written more generally as:

$$T = T_0 + \Delta T_{ad} \cdot x \quad (9.21)$$

where the adiabatic temperature rise is:

$$\Delta T_{ad} = \frac{-\Delta H_{rxn}^0}{\rho \cdot C_P} \quad (9.22)$$

The sign of ΔT_{ad} depends on the reaction type:

Exothermic reactions: $\Delta T_{ad} > 0$, temperature increases with conversion

Endothermic reactions: $\Delta T_{ad} < 0$, temperature decreases with conversion

9.5.2 The x-T Trajectory

Equation 9.21 defines a straight line in the X-T plane called the adiabatic trajectory or energy balance line. This line starts at $(x=0, T=T_0)$ with slope ΔT_{ad} .

For adiabatic operation, the system must simultaneously satisfy:

The energy balance (adiabatic trajectory): $T = T_0 + \Delta T_{ad} \cdot x$

The material balance (design equation with temperature-dependent rate)

The equilibrium constraint: $x \leq x_e(T)$

The achievable conversion is determined by where the adiabatic trajectory intersects the equilibrium curve. Three scenarios arise:

Exothermic reversible reactions: The adiabatic line has positive slope while the equilibrium curve has negative slope. They intersect at an equilibrium point that limits conversion. Higher inlet temperature T_0 shifts the trajectory upward, potentially reducing the equilibrium-limited conversion.

Endothermic reversible reactions: The equilibrium curve has positive slope, but the adiabatic line has negative slope without external heating and temperature drop limits conversion. Heat must be supplied to maintain temperature and achieve higher conversion.

Irreversible reactions: No equilibrium limitation; conversion continues until reactant is depleted or rate becomes negligibly slow.

9.6 Simplified Heat Balance Models

For non-adiabatic operation, we can incorporate simplified heat removal or addition terms into the energy balance:

$$\rho \cdot C_p \cdot q_0 \cdot (T - T_0) = (-\Delta H_{rxn}^0) \cdot F_{A,0} \cdot X - UA(T - T_C) \quad (9.23)$$

where U is the overall heat transfer coefficient, A is the heat transfer area, and T_C is the coolant temperature.

Rearranging:

$$T = T_0 + \frac{\Delta T_{ad} \cdot X - UA(T - T_C)}{\rho \cdot C_p \cdot q_0} \quad (9.24)$$

This equation shows that the temperature trajectory curves rather than following a straight line, allowing better control over the temperature profile.

9.7 The x-T Diagram and Rate Contours

9.7.1 Construction of Rate Contours

The x-T diagram plots conversion versus temperature and can include:

Equilibrium curve: $x_e(T)$ - the upper bound for reversible reactions

Adiabatic trajectories: straight lines with slope ΔT_{ad} for various T_0

Rate contours: curves of constant reaction rate $r(x,T)$

Rate contours are constructed by calculating the reaction rate at various (X,T) points:

$$r(x, T) = k(T) \cdot f(C_A) = A \cdot \exp\left(-\frac{Ea}{RT}\right) \cdot C_{A,0}^n \cdot (1-x)^n \quad (9.25)$$

For reversible first order reactions:

$$r(x, T) = k_f(T) \cdot C_{A,0} \cdot (1-x) \cdot \left(1 - \frac{x}{x_e(T)}\right) \quad (9.26)$$

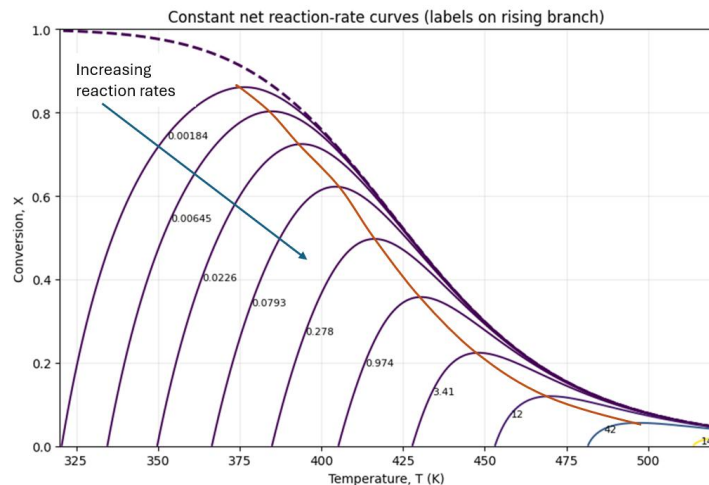


Figure 9-4 Iso reaction rate curves with locus of maximum reaction rates

9.7.2 Interpreting x-T Diagrams for Different Reaction Types

Irreversible Exothermic Reactions:

No equilibrium curve (x can approach 1.0 at any temperature). Rate contours show maximum rate at high T and high remaining reactant (low x). The optimal trajectory moves quickly to high temperature for fast rates. Risk of thermal runaway if heat removal is insufficient.

Reversible Exothermic Reactions:

Equilibrium curve slopes downward (x_e decreases with T). Rate contours show complex behavior: high T gives fast kinetics but poor equilibrium; low T gives good equilibrium but slow kinetics. Optimal path: start at high T for rapid initial reaction, then cool to follow equilibrium curve downward. This is the principle behind interstage cooling configurations.

Reversible Endothermic Reactions:

Equilibrium curve slopes upward (x_e increases with T). Both kinetics and thermodynamics favor high temperature. Rate contours show increasing rate with both T and $(1-X)$. Challenge is supplying heat while maintaining high temperature. Often limited by materials constraints rather than equilibrium.

9.7.3 Using x-T Diagrams for Reactor Design

The x-T diagram enables visualization of different operating strategies:

- Single adiabatic reactor: straight line from $(0, T_0)$ with slope ΔT_{ad} , stopping at equilibrium curve
- Isothermal operation: horizontal line at constant T , can achieve $x_e(T)$ with infinite reactor volume
- Interstage cooling: staircase pattern alternating between adiabatic sections (diagonal) and cooling (vertical drops)
- Cold shot: diagonal sections connected by cooling + dilution (diagonal drops to the left)
- The optimal trajectory maximizes time spent in high-rate regions while respecting equilibrium constraints.

9.8 Optimizing Reversible Reactions - Multiple Reactor Configurations

Single adiabatic reactors often cannot achieve high conversions for equilibrium-limited reactions due to unfavorable temperature profiles. Multiple reactor configurations overcome this limitation by manipulating the temperature trajectory.

9.8.1 Tanks in Series

Multiple CSTRs in series approach plug flow behavior while allowing temperature control at each stage. For exothermic equilibrium-limited reactions, operating each tank at progressively lower temperatures can maximize overall conversion. Each tank operates at the maximum reaction rate corresponding to each conversion.

For N tanks in series with individual temperatures T_i :

$$\tau_i = \frac{x_i - x_{i-1}}{r_{net}(x_i, T_i)} \quad (9.27)$$

Each tank operates below its equilibrium conversion: $x_i < x_e(T_i)$. By decreasing temperature from tank to tank, we can follow the equilibrium curve downward, achieving higher overall conversion than a single adiabatic stage.

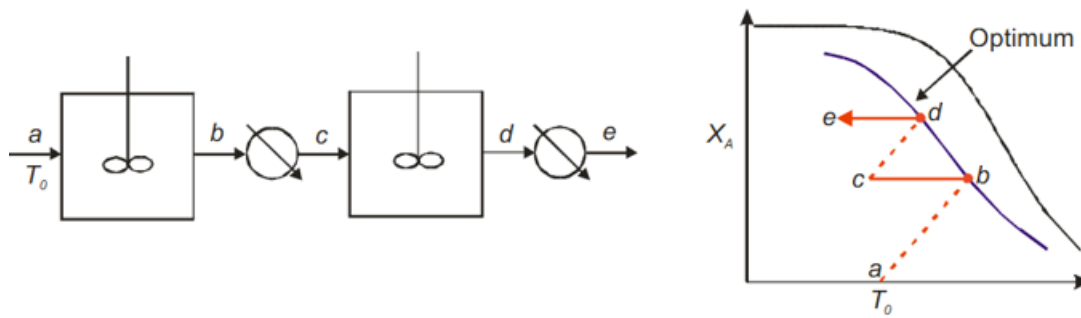


Figure 9-5 Optimal design of CSTR:s in series

9.8.2 Adiabatic Layers with Interstage Cooling

For exothermic reactions, a common industrial configuration uses multiple adiabatic beds with intercoolers between stages. Each adiabatic layer follows an upward-sloping trajectory (T increases with X), and the intercooler drops the temperature back down without changing conversion.

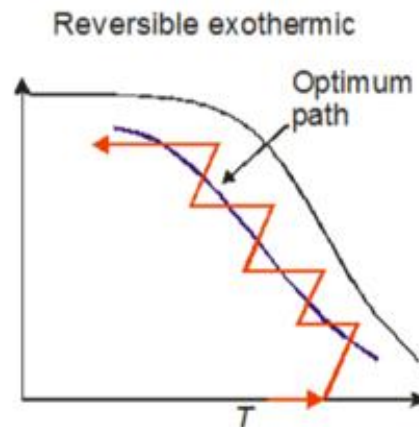


Figure 9-6 Optimal adiabatic layers with interstage cooling

The x-T path follows a staircase pattern:

1. Adiabatic reaction in bed 1: conversion increases along $T = T_0 + \Delta T_{ad} \cdot X$ until approaching equilibrium
2. Cooling: temperature drops at constant X
3. Adiabatic reaction in bed 2: conversion increases again along the new trajectory
4. Repeat cooling and reaction steps

The optimal interstage temperatures are chosen to maximize conversion while maintaining driving force (staying below equilibrium). The optimal trajectory becomes a zigzag path

around the maximal reaction rate at each layer. Typically, each bed is designed to approach but not reach equilibrium, with 3-5 beds common in industrial practice.

9.8.3 Cold Shot Cooling (Split Feed)

Cold shot cooling introduces cold feed between reactor stages, simultaneously cooling the mixture and adding fresh reactant. This configuration is particularly attractive because it avoids external heat exchangers.

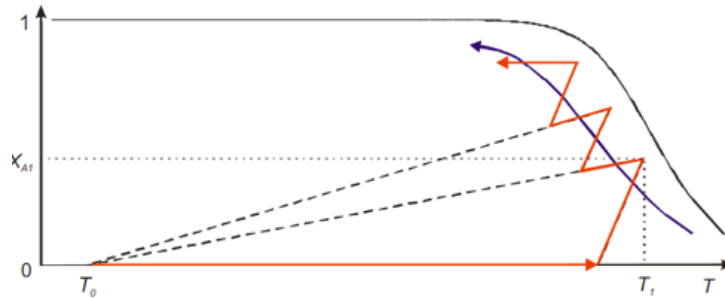


Figure 9-7 Optimal design of cooling with fresh input

For a two-stage system with fraction α of feed to the first stage:

First stage receives $\alpha F_{A,0}$ at T_0 , operates adiabatically to conversion X_1 and temperature T_1 :

$$T_1 = T_0 + \Delta T_{ad} \cdot X_1 \quad (9.28)$$

Cold feed $(1-\alpha)F_{A,0}$ at T_0 mixes with the first stage exit, giving:

$$T_{2,in} = \alpha \cdot T_1 + (1-\alpha) \cdot T_0 \quad (9.29)$$

$$X_{2,in} = \alpha \cdot X_1 \quad (9.30)$$

The second stage then operates adiabatically from this new initial condition. The split ratio α is optimized to maximize final conversion.

9.9 Worked Examples

Example 9.1: Equilibrium Curve Construction and Isothermal PFR Design

Problem Statement:

Consider the reversible gas-phase reaction $A \rightleftharpoons B$ with the following data:

$$\Delta H_{rxn}^0 = -20,000 \text{ J/mol (exothermic)}$$

$$\Delta S^\circ = -50 \text{ J/(mol}\cdot\text{K)}$$

$$k_f = 2.0 \times 10^8 \exp(-8000/T) \text{ min}^{-1} \text{ (T in K)}$$

Feed: Pure A at $C_{A,0} = 2.0 \text{ mol/L}$, $T_0 = 500 \text{ K}$

Tasks: (a) Calculate the equilibrium constant and equilibrium conversion at 400 K, 500 K, and 600 K. (b) Construct the equilibrium curve. (c) For isothermal operation at 500 K in a PFR, calculate the space time required to achieve 80% of the equilibrium conversion.

Solution:

Part (a): Calculate K_e and x_e at different temperatures

Using Equation 9.5: $\ln(K_e) = -\Delta H^\circ/(RT) + \Delta S^\circ/R$

At $T = 400 \text{ K}$:

$$\ln(K_e) = -(-20,000)/(8.314 \times 400) + (-50)/8.314$$

$$\ln(K_e) = 6.014 - 6.014 = 0$$

$$K_e = 1.0$$

Using Equation 9.11: $x_e = K_e/(1 + K_e) = 1.0/(1 + 1.0) = 0.50$ or 50%

At $T = 500 \text{ K}$:

$$\ln(K_e) = -(-20,000)/(8.314 \times 500) + (-50)/8.314 = -1.203$$

$$K_e = 0.300$$

$$x_e = 0.300/(1 + 0.300) = 0.231$$
 or 23.1%

At $T = 600 \text{ K}$:

$$\ln(K_e) = -(-20,000)/(8.314 \times 600) + (-50)/8.314$$

$$\ln(K_e) = 4.009 - 6.014 = -2.005$$

$$K_e = 0.135$$

$$x_e = 0.135/(1 + 0.135) = 0.119$$
 or 11.9%

Part (b): Equilibrium curve

The equilibrium curve shows x_e decreasing with temperature (exothermic reaction):

$$400 \text{ K} \rightarrow x_e = 50.0\%$$

$$500 \text{ K} \rightarrow x_e = 23.1\%$$

$$600 \text{ K} \rightarrow x_e = 11.9\%$$

Part (c): PFR space time for $X = 0.8 \times x_e$ at 500 K

Target conversion: $X = 0.8 \times 0.231 = 0.185$

Calculate forward rate constant at 500 K:

$$k_f = 2.0 \times 10^8 \exp(-8000/500) = 2.0 \times 10^8 \times 1.125 \times 10^{-7} = 22.5 \text{ min}^{-1}$$

Using Equation 9.17 with $x_e = 0.231$ and $x = 0.185$:

$$\tau = (1/k_f) \cdot (x_e/(x_e - 1)) \cdot \ln[(x_e - x)/(x_e(1 - x))]$$

$$\tau = (1/22.5) \cdot (0.231/(0.231-1)) \cdot \ln[(0.046)/(0.188)]$$

$$\tau = (0.0444) \cdot (-0.300) \cdot (-1.409) = 0.0188 \text{ min}$$

$$\tau = 0.0188 \text{ min} = 1.13 \text{ seconds}$$

Example 9.2: Adiabatic Reactor with Equilibrium Limitation

Problem Statement:

An exothermic reversible reaction $A \rightleftharpoons 2B$ is carried out adiabatically in a PFR. Given:

$$\Delta H_{rxn}^0 = -80 \text{ kJ/mol}$$

$$\Delta S^\circ = 100 \text{ J/(mol}\cdot\text{K)}$$

Feed: Pure A, $C_{A,0} = 1.5 \text{ mol/L}$, $T_0 = 350 \text{ K}$

$$\rho C_P = 2000 \text{ J/(L}\cdot\text{K)}$$

Calculate: (a) the adiabatic temperature rise per unit conversion ΔT_{ad} , (b) the equilibrium constant at T_0 , (c) the maximum achievable conversion where the adiabatic trajectory intersects the equilibrium curve.

Solution:

Part (a): Adiabatic temperature rise

Using Equation 9.22:

$$\Delta T_{ad} = (-\Delta H_{rxn}^0) \cdot C_{A,0} / (\rho \cdot C_P)$$

$$\Delta T_{ad} = (-(-80,000 \text{ J/mol})) \cdot (1.5 \text{ mol/L}) / (2000 \text{ J/(L}\cdot\text{K)})$$

$$\Delta T_{ad} = 60 \text{ K per unit conversion}$$

Part (b): Equilibrium constant at 350 K

$$\ln(K_e) = -\Delta H^\circ / (RT) + \Delta S^\circ / R$$

$$\ln(K_e) = -(-80,000) / (8.314 \times 350) + (100) / (8.314)$$

$$\ln(K_e) = 27.48 + 12.03 = 39.51$$

$$K_e = 1.38 \times 10^{17} \text{ (very large - reaction strongly favors products at 350 K)}$$

Part (c): Maximum achievable conversion

The adiabatic trajectory is: $T = 350 + 60x$

For the stoichiometry $A \rightleftharpoons 2B$, with pure A feed:

$$K_C = C_B^2 / C_A = [2C_{A,0} \cdot x]^2 / [C_{A,0}(1-x)] = 4C_{A,0} \cdot x^2 / (1-x)$$

$$\text{At equilibrium: } x_e^2 = K_C(1-x_e) / (4C_{A,0})$$

We need to find where the adiabatic line intersects equilibrium curve. This requires solving:

$$\ln(K_e(T)) = -(-80,000)/(8.314 \cdot T) + 100/8.314 \text{ with } T = 350 + 60x$$

This is transcendental and requires iteration. Let's try $x = 0.5$:

$$T = 350 + 60(0.5) = 380 \text{ K}$$

$$\ln(K_e) = 80,000/(8.314 \times 380) + 12.03 = 25.32 + 12.03 = 37.35$$

$$K_e = 1.31 \times 10^{16}$$

Check if $x = 0.5$ satisfies equilibrium:

$$K_C = 4(1.5)(0.5)^2/(1-0.5) = 3.0$$

This is much less than K_e , so we can achieve higher conversion. Given the very large K_e values, the reaction essentially goes to completion ($x \rightarrow 1.0$) before equilibrium becomes limiting. The practical limit would be kinetics or temperature constraints rather than equilibrium. The low exothermic heat of reaction and large positive ΔS° explains the very large equilibrium constant.

Maximum conversion $\approx 0.95-0.99$ (nearly complete)

Example 9.3: Two-Stage System with Interstage Cooling

Problem Statement:

A reversible exothermic reaction $A \rightleftharpoons B$ is conducted in two adiabatic PFR stages with interstage cooling. Given:

Stage 1: $T_{in,1} = 600 \text{ K}$, exits at equilibrium with $x_e(600\text{K}) = 0.15$

Intercooler: cools to $T_{in,2} = 500 \text{ K}$ at constant conversion

Stage 2: operates adiabatically from ($x=0.15, T=500\text{K}$)

Additional data: $\Delta T_{ad} = 100 \text{ K}$, $x_e(500\text{K}) = 0.30$

Calculate: (a) the exit temperature from stage 2, (b) the final conversion if stage 2 reaches equilibrium, (c) compare total conversion to a single adiabatic stage starting at 600 K.

Solution:

Part (a): Exit temperature from stage 2

Stage 2 starts at $x = 0.15, T = 500 \text{ K}$

The adiabatic trajectory from this point:

$$T = T_{in,2} + \Delta T_{ad}(x - x_{in,2}) = 500 + 100(x - 0.15)$$

If stage 2 reaches equilibrium at $x_e = 0.30$:

$$T_{exit,2} = 500 + 100(0.30 - 0.15) = 500 + 15 = 515 \text{ K}$$

Part (b): Final conversion

Stage 2 can reach equilibrium at 515 K. We need to verify $x_e(515\text{K})$:

Using the van't Hoff equation to estimate between 500 K and 600 K, the equilibrium conversion at 515 K would be by linear approximation:

$$x_e(515\text{K}) \approx 0.30 - (515-500)/(600-500) \times (0.30-0.15) \approx 0.28$$

The adiabatic line from (0.15, 500K) would intersect the equilibrium curve at approximately:

$$X=0.28$$

Part (c): Comparison to single stage

Single adiabatic stage starting at 600 K reaches $x = 0.15$ (given)

Two-stage system with interstage cooling achieves $x \approx 0.28$

Improvement: $(0.28 - 0.15)/0.15 = 87\%$ increase in conversion

This demonstrates the significant benefit of interstage cooling for exothermic equilibrium-limited reactions.

9.10 Guided Learning Examples

The following examples use a guided problem-solving approach. Do not solve the problems directly. Instead, I will ask you questions to help you understand the fundamental assumptions and guide you toward the solution.

Guided Example 9.1: Cold Shot Cooling Design

Problem Statement:

A reversible exothermic reaction $A \rightleftharpoons B$ is to be carried out in a two-stage PFR system with cold shot cooling. The first stage receives 60% of the total feed ($\alpha = 0.6$) at $T_0 = 550$ K and operates adiabatically to $x_1 = 0.20$. The remaining 40% of feed at $T_0 = 550$ K is mixed with the first stage exit before entering the second adiabatic stage. Given $\Delta T_{ad} = 80$ K and $x_e(500\text{K}) = 0.35$, $x_e(550\text{K}) = 0.20$, determine the conditions entering the second stage and estimate the final achievable conversion.

Approach: My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the fundamental assumptions in the modelling by asking me questions and wait for my answer to each question.

Guided Example 9.2: Endothermic Reversible Reaction

Problem Statement:

Consider an endothermic reversible reaction $A \rightleftharpoons B$ with $\Delta H_{\text{rxn}}^{\circ} = +50 \text{ kJ/mol}$. The reaction is to be carried out in an adiabatic reactor with feed at $T_0 = 600 \text{ K}$, $C_{A,0} = 2.0 \text{ mol/L}$, and $\rho C_P = 3000 \text{ J/(L}\cdot\text{K)}$. The equilibrium constant follows $\ln(K_e) = 50,000/(RT) - 5$. Analyze the feasibility of this adiabatic operation and determine what happens as the reaction proceeds.

Approach: My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the fundamental assumptions in the modelling by asking me questions and wait for my answer to each question.

Guided Example 9.3: Optimal Temperature Progression in Multi-Stage System

Problem Statement:

A reversible exothermic reaction is to be conducted in three isothermal CSTR stages in series. Each stage has the same volume and operates at progressively lower temperatures: $T_1 = 550 \text{ K}$, $T_2 = 500 \text{ K}$, $T_3 = 450 \text{ K}$. The equilibrium conversions are $x_e(550\text{K}) = 0.20$, $x_e(500\text{K}) = 0.35$, $x_e(450\text{K}) = 0.55$. The forward rate constant is $k_f = 1 \times 10^{10} \exp(-10,000/T) \text{ min}^{-1}$. For a total residence time of 15 minutes, determine how to distribute the residence time among the three reactors to maximize overall conversion.

Approach: My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the fundamental assumptions in the modelling by asking me questions and wait for my answer to each question.

9.11 Practice Problems

Advanced Exercises

Exercise 9.1: For the ammonia synthesis reaction $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$, derive the expression for equilibrium conversion as a function of temperature, pressure, and inert mole fraction. Given $\Delta H^\circ_{\text{rxn}} = -92 \text{ kJ/mol}$, $\Delta S^\circ = -198 \text{ J/(mol}\cdot\text{K)}$, feed ratio $\text{H}_2:\text{N}_2 = 3:1$ with 20% inerts, calculate and plot the equilibrium conversion versus temperature (300-700 K) at pressures of 10, 50, 100, and 200 bar. Discuss why industrial processes operate at high pressure despite the increased capital and operating costs.

Exercise 9.2: Design a three-stage adiabatic reactor system with interstage cooling for an exothermic reversible reaction $\text{A} \rightleftharpoons \text{B}$. Given: $\Delta H^\circ_{\text{rxn}} = -60 \text{ kJ/mol}$, $\Delta S^\circ = -80 \text{ J/(mol}\cdot\text{K)}$, $k_f = 5 \times 10^7 \exp(-7500/T) \text{ s}^{-1}$, $C_{\text{A},0} = 3.0 \text{ mol/L}$, $\rho C_p = 2500 \text{ J/(L}\cdot\text{K)}$, $T_0 = 580 \text{ K}$, total flow rate 100 L/min. Determine: (a) the conversion and exit temperature from each stage assuming each reaches 90% of equilibrium, (b) the required volume of each stage, (c) the intercooler duties, (d) the overall conversion and compare to a single adiabatic stage. Optimize the number of stages and interstage temperatures to maximize conversion.

Exercise 9.3: Construct a complete x - T diagram for the reversible exothermic reaction $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$ with $\Delta H^\circ_{\text{rxn}} = -40 \text{ kJ/mol}$, $\Delta S^\circ = -60 \text{ J/(mol}\cdot\text{K)}$, equimolar feed at $C_{\text{A},0} = 2.0 \text{ mol/L}$, $\rho C_p = 2200 \text{ J/(L}\cdot\text{K)}$. The forward rate follows $k_f = 1 \times 10^8 \exp(-8500/T) \text{ L/(mol}\cdot\text{min)}$. On the same diagram, plot: (a) the equilibrium curve from 350-650 K, (b) adiabatic trajectories for $T_0 = 400, 500, \text{ and } 600 \text{ K}$, (c) rate contours for $r = 0.1, 0.5, 1.0, 2.0, \text{ and } 5.0 \text{ mol/(L}\cdot\text{min)}$, (d) the optimal temperature trajectory for maximum production rate. Explain how to use this diagram to design an optimal multi-stage system.

Exercise 9.4: Analyze a cold-shot cooling configuration with three stages for the reaction $\text{A} \rightleftharpoons 2\text{B}$. Feed fractions are $\alpha_1 = 0.5$, $\alpha_2 = 0.3$, $\alpha_3 = 0.2$ entering stages 1, 2, and 3 respectively, all at $T_0 = 550 \text{ K}$. Each stage operates adiabatically with $\Delta T_{\text{ad}} = 120 \text{ K}$. The equilibrium relationship is $x_e = 0.8 - 0.001T$ (T in K). Derive expressions for the inlet temperature and conversion to each stage as functions of the conversions achieved in previous stages. Calculate the overall conversion and compare to: (a) a single adiabatic stage, (b) a two-stage system with $\alpha_1 = 0.6$, $\alpha_2 = 0.4$, (c) three equal stages with interstage cooling to 500 K. Discuss the trade-offs between cold-shot and interstage cooling configurations.

Simple Hand-Calculation Exercises

Exercise 9.5: A reversible reaction $\text{A} \rightleftharpoons \text{B}$ has equilibrium constants $K_e = 2.0$ at 400 K and $K_e = 0.5$ at 500 K. Assuming $\Delta H^\circ_{\text{rxn}}$ is constant, calculate: (a) $\Delta H^\circ_{\text{rxn}}$, (b) the equilibrium constant

at 450 K, (c) the equilibrium conversion at 450 K for pure A feed. Would this reaction be classified as endothermic or exothermic?

Exercise 9.6: For an adiabatic reactor with reversible reaction $A \rightleftharpoons B$, the feed enters at $T_0 = 500$ K and $C_{A,0} = 1.0$ mol/L. If $\Delta T_{ad} = 50$ K and the equilibrium conversion at 500 K is $x_e = 0.40$, determine: (a) the temperature if conversion reaches $X = 0.30$, (b) the equilibrium conversion at this temperature if the equilibrium curve has slope $dx_e/dT = -0.004$ K⁻¹, (c) whether $X = 0.30$ is achievable or if equilibrium will limit conversion to a lower value.

Exercise 9.7: A CSTR operates isothermally at 480 K with mean residence time $\tau = 10$ min for the reversible reaction $A \rightleftharpoons B$. Given $k_f = 0.15$ min⁻¹, $K_e = 1.5$, and $C_{A,0} = 2.0$ mol/L, use Equation 9.19 to calculate the conversion achieved in the reactor. What is the maximum possible conversion at this temperature? If the reactor were operated at 450 K where $K_e = 3.0$ and $k_f = 0.08$ min⁻¹, would the conversion increase or decrease?

Exercise 9.8: A two-stage system operates with the first stage reaching $X_1 = 0.25$ at $T_1 = 550$ K. An intercooler reduces the temperature to $T_2 = 480$ K. If the second stage operates adiabatically with $\Delta T_{ad} = 60$ K and reaches equilibrium at $x_e = 0.45$, calculate: (a) the exit temperature from stage 2, (b) the temperature rise in stage 2, (c) the incremental conversion achieved in stage 2. Verify that the final conversion does not exceed the equilibrium value at the final temperature.

Chapter 9 Summary: What You Should Have Learned

After completing this chapter, you should be able to:

1. Understand thermodynamic equilibrium limitations
2. Calculate equilibrium conversion for reversible reactions
3. Design systems to overcome equilibrium limitations
4. Apply Le Chatelier's principle to optimize conditions
5. Design optimal temperature profiles for reversible reactions

Chapter 10: Residence Time Distribution and Non-Ideal Reactors

Learning Objectives

After completing this chapter, you should be able to:

- Understand the concept of residence time distribution (RTD) and recognize that real reactors exhibit a distribution of residence times rather than uniform residence time, which significantly impacts reactor performance and product quality.
- Conduct and interpret RTD measurements using both step input (tracer injection) and pulse input (instantaneous tracer injection) experiments, analyzing the resulting concentration-time curves to characterize reactor mixing behavior.
- Derive the RTD functions $E(t)$ and $F(t)$ for ideal plug flow reactors (PFRs) and continuous stirred tank reactors (CSTRs), understanding that PFRs have delta function RTDs while CSTRs exhibit exponential decay distributions.
- Apply the tanks-in-series model to describe real reactors as a series of N equal-volume CSTRs, calculating the number of tanks N from variance analysis and predicting conversion for different reaction orders.
- Utilize the axial dispersion model to characterize non-ideal flow in tubular reactors by determining the Péclet number (Pe) or Bodenstein number (Bo) from RTD data and solving the dispersion equation for conversion predictions.
- Calculate reactor conversion using RTD data for first-order, second-order, and zero-order reactions, integrating the RTD function with the appropriate kinetic expression to predict real reactor performance.

Nomenclature

The following symbols are introduced in this chapter and supplement the comprehensive nomenclature in previous chapters:

Roman Letters

Bo	Bodenstein number, dimensionless dispersion parameter ($Bo = uL/D$)
$C(t)$	Tracer concentration at time t (mol/L or g/L)
C_0	Initial tracer concentration for step input (mol/L or g/L)
D	Axial dispersion coefficient (m^2/s or cm^2/s)
$E(t)$	Residence time distribution function (1/s or 1/min)
$E(\theta)$	Normalized RTD function, dimensionless
$F(t)$	Cumulative distribution function, dimensionless
L	Reactor length (m)
M	Total mass of tracer injected (g or mol)

N	Number of tanks in series, dimensionless
Pe	Péclet number ($Pe = uL/D$)
t	Time (s or min)
u	Superficial velocity (m/s or cm/s)
V	Reactor volume (L or m ³)

Greek Letters

σ^2	Variance of RTD (s ² or min ²)
σ_θ^2	Dimensionless variance
τ	Mean residence time (s or min), $\tau = V/v_0$
θ	Dimensionless time, $\theta = t/\tau$

10.1 Introduction to Non-Ideal Reactors

In previous chapters, we developed reactor design equations based on two idealized flow patterns: the continuous stirred tank reactor (CSTR) with perfect mixing and the plug flow reactor (PFR) with no axial mixing. While these models provide valuable insights and reasonable predictions for many systems, real reactors often deviate significantly from these ideal behaviors.

Real reactors exhibit non-ideal flow due to several factors:

Channeling and bypassing: Some fluid elements may find preferential paths through the reactor, spending less time than the theoretical average residence time. This is particularly problematic in packed bed reactors where non-uniform packing creates flow channels.

Recirculation and dead zones: Stagnant regions or recirculation patterns can cause some fluid to remain in the reactor much longer than expected. Baffled reactors and stirred tanks with poor agitation often exhibit these characteristics.

Axial dispersion: In tubular reactors, molecular diffusion and turbulent mixing cause some degree of back-mixing, deviating from ideal plug flow behavior. The extent of dispersion depends on flow velocity, reactor geometry, and fluid properties.

10.2 The Residence Time Distribution (RTD)

The residence time distribution (RTD) provides a powerful diagnostic tool for characterizing real reactor behavior. Rather than assuming all molecules spend exactly the same time $\tau = V/q_0$ in the reactor, the RTD describes the statistical distribution of residence times. This distribution directly affects conversion, especially for reactions other than first-order where the relationship between concentration and rate is nonlinear.

Understanding RTD enables us to:

Diagnose flow problems: Identify channeling, dead zones, or excessive dispersion from RTD measurements.

Compare reactor performance: Benchmark actual reactors against ideal models.

Predict conversion: Use RTD data with kinetic models to estimate reactor performance for different reactions.

Design improvements: Guide modifications to approach ideal behavior.

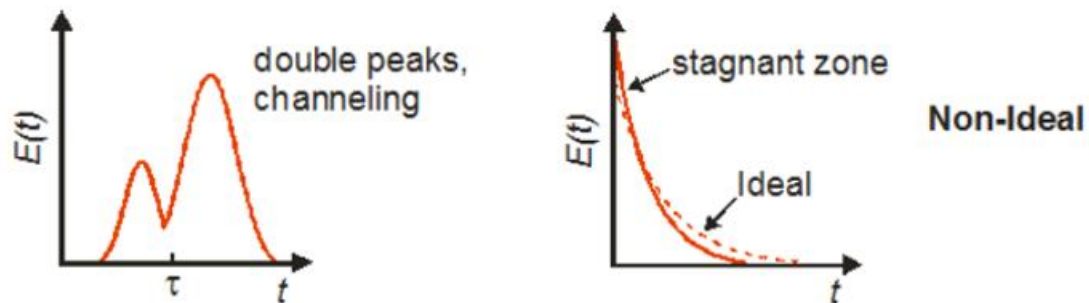


Figure 10-1 Pulse experiments for analyzing reactor behavior. Left packed bed. Right stirred tank

10.2.1 Pulse Input Experiment

The pulse input method involves injecting a known quantity of inert tracer instantaneously at the reactor inlet and measuring the tracer concentration at the outlet as a function of time. An ideal pulse is a Dirac delta function, though in practice the injection occurs over a very short time interval.

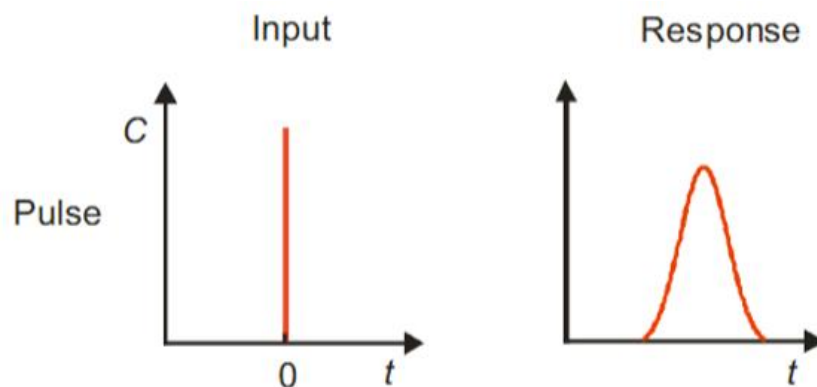


Figure 10-2 Pulse experiments in a packed bed

For a pulse injection of mass M at $t = 0$, the RTD function $E(t)$ is defined such that $E(t)dt$ represents the fraction of material leaving the reactor with residence time between t and $t + dt$. The tracer concentration at the outlet $C(t)$ is directly related to $E(t)$:

$$E(t) = \frac{C(t)}{\int_0^{\infty} C(t)dt} \quad (10.1)$$

Since the integral of $E(t)$ over all time must equal unity (all material eventually exits), we can normalize the concentration curve:

$$\int_0^{\infty} E(t)dt = 1 \quad (10.2)$$

The mean residence time τ can be calculated from the first moment of the distribution:

$$\tau = \int_0^{\infty} t \cdot E(t)dt \quad (10.3)$$

The variance σ^2 , which measures the spread of the distribution, is given by the second central moment:

$$\sigma^2 = \int_0^{\infty} (t - \tau)^2 E(t)dt = \int_0^{\infty} t^2 E(t)dt - \tau^2 \quad (10.4)$$

10.2.2 Step Input Experiment

In a step input experiment, the tracer concentration in the feed is suddenly changed from zero to C_0 at $t = 0$ and maintained at this level. The outlet concentration $C(t)$ gradually increases from zero to C_0 as tracer-containing fluid displaces tracer-free fluid.

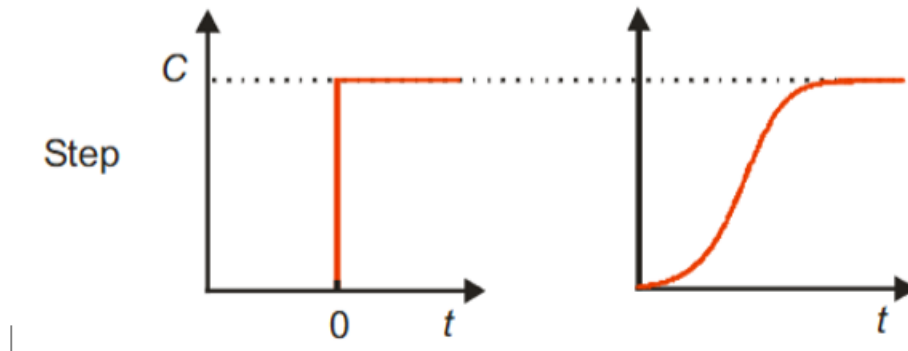


Figure 10-3 Step input experiments

The cumulative distribution function $F(t)$ represents the fraction of exit stream with age less than t :

$$F(t) = \frac{C(t)}{C_0} \quad (10.5)$$

The RTD function $E(t)$ is the derivative of $F(t)$:

$$E(t) = \frac{dF(t)}{dt} \quad (10.6)$$

Step experiments are often more practical than pulse experiments as they require less precise timing and are easier to implement in industrial settings.

10.3 RTD for Ideal Reactors

10.3.1 Plug Flow Reactor (PFR)

In an ideal PFR, all fluid elements have identical residence times equal to $\tau = V/v_0$. This corresponds to a Dirac delta function:

$$E(t) = \delta(t - \tau) \quad (10.7)$$

For a step input, the cumulative distribution function is:

$$F(t) = 0 \text{ for } t < \tau, F(t) = 1 \text{ for } t \geq \tau \quad (10.8)$$

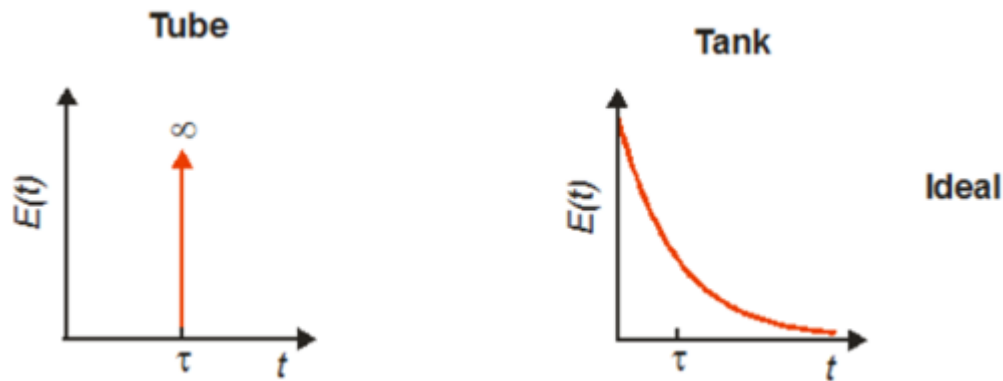


Figure 10-4 RTD for an ideal tube (left) and an ideal tank reactor (right)

The variance of an ideal PFR is zero, reflecting the absence of any distribution in residence times.

10.3.2 Continuous Stirred Tank Reactor (CSTR)

For an ideal CSTR with perfect mixing, the RTD follows an exponential decay:

$$E(t) = (1/\tau) \cdot \exp(-t/\tau) \quad (10.9)$$

This can be expressed in dimensionless form using $\theta = t/\tau$:

$$E(\theta) = \exp(-\theta) \quad (10.10)$$

The cumulative distribution function is:

$$F(t) = 1 - \exp(-t/\tau) \quad (10.11)$$

The variance for a CSTR is:

$$\sigma^2 = \tau^2 \quad (10.12)$$

The dimensionless variance is therefore $\sigma_0^2 = \sigma^2/\tau^2 = 1$ for an ideal CSTR.

10.4 The Zero Parameter Model

The zero parameter model, also known as the *segregation model* or *batch reactor model*, provides the simplest approach to predicting conversion from RTD data. This model requires no adjustable parameters—hence the name “zero parameter model”—and assumes perfect segregation of fluid elements.

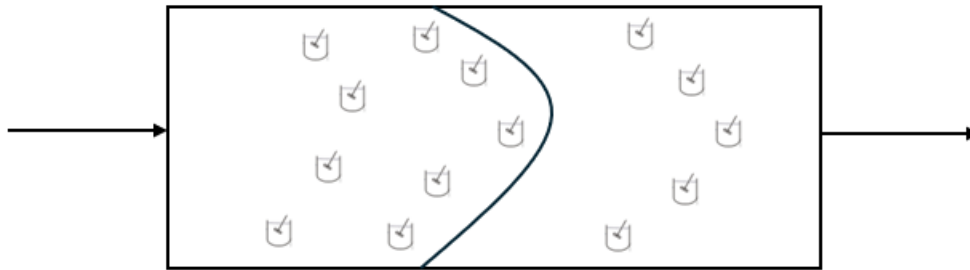


Figure 10-5 Illustration of the segregation model

10.4.1 Fundamental Assumptions

The zero parameter model is based on two key assumptions:

- **Perfect segregation:** Each fluid element travels through the reactor without mixing with other fluid elements. This means that molecules that enter the reactor stay together as a cohort throughout their residence in the reactor.
- **Batch reactor behavior:** Each fluid element behaves as a tiny batch reactor for the duration of its residence time in the reactor. The conversion achieved by each element depends only on its residence time and the reaction kinetics.

These assumptions lead to the fundamental equation for the zero parameter model. The overall conversion X is obtained by integrating the conversion of individual fluid elements, weighted by the fraction of fluid with each residence time:

$$x = \int_0^{\infty} X(t)E(t)dt \quad (10.13)$$

where $X(t)$ is the conversion that would be achieved in a batch reactor after time t , and $E(t)$ is the residence time distribution function. The batch reactor conversion $X(t)$ depends on the reaction order and rate constant, as shown in Table 10-1.

10.4.2 Applications to Different Reaction Orders

For common reaction orders, the batch reactor conversion $X(t)$ can be expressed analytically. Table 10-1 summarizes the key relationships for zero-order, first-order, and second-order reactions.

Table 10-1: Batch Reactor Conversions for the Zero Parameter Model

Reaction Order	Rate Expression	Batch Conversion $X(t)$
Zero-order	$r = k$	$X(t) = kt/C$ (for $t \leq C/k$), = 1 otherwise
First-order	$r = kC$	$X(t) = 1 - \exp(-kt)$
Second-order	$r = kC^2$	$X(t) = C_0kt/(1 + C_0kt)$

For first-order reactions, the zero parameter model integration becomes particularly straightforward. Substituting the first-order batch conversion into Equation (10.12) :

$$x = \int_0^{\infty} [1 - \exp(-kt)]E(t)dt = 1 - \int_0^{\infty} \exp(-kt) E(t)dt \quad (10.14)$$

This integration requires only the RTD function $E(t)$ from experimental measurements and the rate constant k from kinetic studies, with no additional adjustable parameters.

10.4.3 Practical Implementation and Model Limitations

In practice, RTD measurements provide discrete data points rather than continuous functions. The integral in Equation (9.13) is therefore evaluated numerically using the trapezoidal rule or Simpson's rule:

$$X \approx \sum_{i=1}^n X(t_i)E(t_i)\Delta t \quad (10.15)$$

where n is the number of data points and Δt is the time interval between measurements. For first-order reactions, $X(t) = 1 - \exp(-kt)$, and $E(t)$ is calculated from the normalized concentration data using Equation (10.1).

The zero parameter model has important strengths and limitations:

- **Strengths:** Requires no parameter fitting, making it objective and free from optimization uncertainties. The model provides a conservative estimate of conversion, as perfect segregation typically represents a lower bound on performance compared to scenarios with beneficial micromixing.

- Limitations:** The assumption of perfect segregation is rarely exact in real reactors, where molecular diffusion and turbulent mixing create some degree of micromixing between fluid elements. For reactions other than first-order, micromixing effects can significantly influence conversion, making the zero parameter model less accurate.

The zero parameter model is particularly useful as a benchmark. Comparing its predictions with actual reactor performance can reveal whether micromixing effects are important for a given reaction system. If measured conversion significantly exceeds the zero parameter model prediction for a second-order or higher-order reaction, this indicates beneficial micromixing is occurring. Conversely, close agreement suggests the segregation assumption is adequate, simplifying subsequent analysis.

10.5 The Tanks-in-Series Model

The idea behind the Tanks-in-Series Model is that the reacting flow consists of a large number of small batch reactors with different residence times.

10.5.1 Model Development

The tanks-in-series model represents a real reactor as N equal-volume CSTRs connected in series. Each tank has volume V/N and mean residence time τ/N . As N increases, the system approaches plug flow behavior; when $N = 1$, we have a single CSTR.

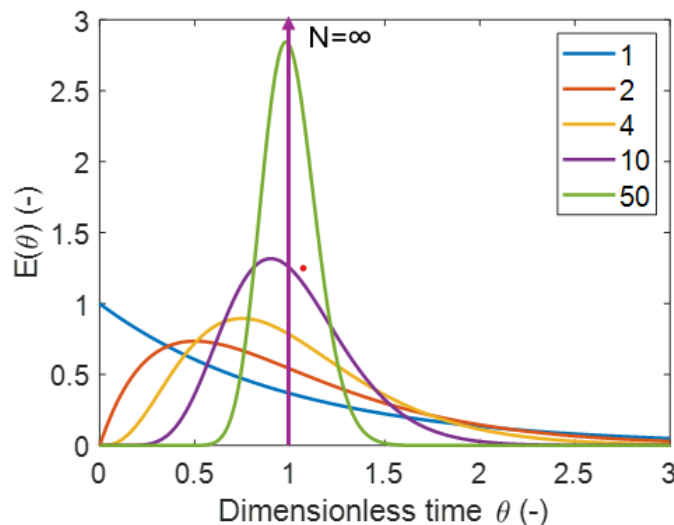


Figure 10-6 Normalized RTD function for the Tank-in-series model and different number of tanks

For N tanks in series, the RTD function is given by:

$$E(t) = (N/\tau) \cdot (Nt/\tau)^{(N-1)} \cdot \frac{\exp\left(-\frac{Nt}{\tau}\right)}{(N-1)!} \quad (10.16)$$

In dimensionless form:

$$E(\theta) = N \cdot (N\theta)^{(N-1)} \cdot \frac{\exp(-N\theta)}{(N-1)!} \quad (10.17)$$

The dimensionless variance for the tanks-in-series model is:

$$\sigma_{\theta}^2 = \frac{1}{N} \quad (10.18)$$

This relationship provides a simple method to determine N from experimental RTD data: measure the variance, calculate the dimensionless variance, and $N = 1/\sigma_{\theta}^2$.

10.5.2 Conversion Predictions

For a first-order reaction $A \rightarrow$ products with rate constant k, the conversion in N tanks in series is:

$$x = 1 - \frac{1}{\left(1 + \frac{k\tau}{N}\right)^N} \quad (10.19)$$

For second-order reactions ($A \rightarrow$ products) with rate $r = kC_A^2$, the analysis becomes more complex. For each tank i:

$$C_{A,i} = \frac{-1 + \sqrt{1 + 4k\tau/NC_{A,i-1}}}{2k\tau/N} \quad (10.20)$$

This requires iterative solution starting from the first tank.

10.6 The Axial Dispersion Model

10.6.1 Model Formulation

The axial dispersion model describes non-ideal tubular reactors by superimposing axial dispersion on plug flow. The model is characterized by the dispersion coefficient D or the dimensionless Péclet number $Pe = uL/D$, where u is the superficial velocity and L is the reactor length.

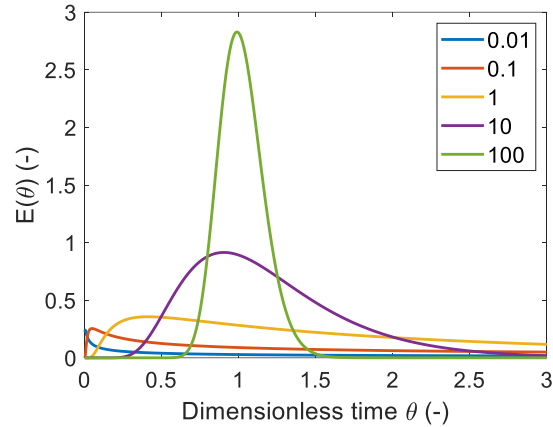


Figure 10-7 Normalized RTD function vs time for different Peclet numbers

The general mass balance with dispersion is:

$$D \cdot \frac{\partial^2 C}{\partial z^2} - u \cdot \frac{\partial C}{\partial z} + r_a = \frac{\partial C}{\partial t} \quad (10.21)$$

For tracer studies at steady state with no reaction, this simplifies to:

$$D \cdot \frac{\partial^2 C}{\partial z^2} = u \cdot \frac{\partial C}{\partial z} \quad (10.22)$$

For vessels with closed-closed boundary conditions (no dispersion at inlet and outlet), the RTD for large Pe is:

$$E(\theta) = \left(\frac{Pe}{4\pi\theta} \right)^{\frac{1}{2}} \cdot \exp \left[-\frac{Pe(1-\theta)^2}{4\theta} \right] \quad (10.23)$$

The dimensionless variance is related to the Péclet number by:

$$\sigma_{\theta}^2 = \frac{2}{Pe} - \frac{2}{Pe^2} \cdot (1 - \exp(-Pe)) \quad (10.24)$$

For large Pe (Pe > 20), this simplifies to:

$$\sigma_{\theta}^2 \approx 2/Pe \quad (10.25)$$

10.6.2 Conversion with Dispersion

For first-order reactions in a dispersed plug flow reactor, the conversion is given by solving:

$$x = 1 - 4a \cdot \frac{\exp\left(\frac{Pe}{2}\right)}{(1+a)^2 \cdot \exp\left(\frac{aPe}{2}\right) - (1-a)^2 \cdot \exp\left(-\frac{aPe}{2}\right)} \quad (10.26)$$

where $a = (1 + 4k\tau/Pe)^{1/2}$.

For small dispersion (large Pe), the conversion approaches that of an ideal PFR. For large dispersion (small Pe), behavior approaches a CSTR.

10.7 Worked Examples

Example 10.1: RTD Analysis from Pulse Experiment

Problem Statement:

A pulse of 10 g of tracer is injected into a reactor with volumetric flow rate $v_0 = 2.0$ L/min. The outlet concentration data are given in the table below. Calculate: (a) the mean residence time, (b) the variance, (c) the dimensionless variance, and (d) determine if the reactor behaves more like a CSTR or PFR.

t (min)	C (g/L)	t (min)	C (g/L)
0	0	6	0.251
1	0.329	8	0.123
2	0.622	10	0.061
4	0.545	12	0.030

Solution:

Step 1: Calculate $E(t)$ using Equation (10.1)

First, we need to find $\int_0^{\infty} C(t) dt$ using numerical integration (trapezoidal rule):

$$\int C(t)dt \approx \sum (C_i + C_{i+1})/2 \times \Delta t$$

With $\Delta t = 2$ min for most intervals and $\Delta t = 1$ min for the first interval:

$$\int C(t)dt = (0+0.329)/2 \times 1 + (0.329+0.622)/2 \times 1 + (0.622+0.545)/2 \times 2 + (0.545+0.251)/2 \times 2 + (0.251+0.123)/2 \times 2 + (0.123+0.061)/2 \times 2 + (0.061+0.030)/2 \times 2 = 3.253 \text{ g} \cdot \text{min/L}$$

Therefore, $E(t) = C(t)/3.253$

Step 2: Calculate mean residence time τ using Equation 10.3

$$\tau = \int_0^{\infty} t \cdot E(t) dt = \int_0^{\infty} t \cdot C(t) dt / \int_0^{\infty} C(t) dt$$

Using numerical integration:

$$\int t \cdot C(t) dt = (0 \times 0 + 1 \times 0.329) / 2 \times 1 + (1 \times 0.329 + 2 \times 0.622) / 2 \times 1 + (2 \times 0.622 + 4 \times 0.545) / 2 \times 2 + (4 \times 0.545 + 6 \times 0.251) / 2 \times 2 + (6 \times 0.251 + 8 \times 0.123) / 2 \times 2 + (8 \times 0.123 + 10 \times 0.061) / 2 \times 2 + (10 \times 0.061 + 12 \times 0.030) / 2 \times 2 = 13.115 \text{ g} \cdot \text{min}^2 / \text{L}$$

$$\tau = 13.115 / 3.253 = 4.03 \text{ min}$$

Step 3: Calculate variance σ^2 using Equation 10.4

$$\sigma^2 = \int_0^{\infty} t^2 E(t) dt - \tau^2$$

First calculate $\int t^2 \cdot C(t) dt$:

$$\int t^2 \cdot C(t) dt = (0^2 \times 0 + 1^2 \times 0.329) / 2 \times 1 + (1^2 \times 0.329 + 2^2 \times 0.622) / 2 \times 1 + (2^2 \times 0.622 + 4^2 \times 0.545) / 2 \times 2 + (4^2 \times 0.545 + 6^2 \times 0.251) / 2 \times 2 + (6^2 \times 0.251 + 8^2 \times 0.123) / 2 \times 2 + (8^2 \times 0.123 + 10^2 \times 0.061) / 2 \times 2 + (10^2 \times 0.061 + 12^2 \times 0.030) / 2 \times 2 = 71.837 \text{ g} \cdot \text{min}^3 / \text{L}$$

$$\int t^2 \cdot E(t) dt = 71.837 / 3.253 = 22.08 \text{ min}^2$$

$$\sigma^2 = 22.08 - (4.03)^2 = 5.83 \text{ min}^2$$

Step 4: Calculate dimensionless variance

$$\sigma_{\theta}^2 = \sigma^2 / \tau^2 = 5.83 / (4.03)^2 = 0.358$$

Step 5: Reactor characterization

For an ideal CSTR: $\sigma_{\theta}^2 = 1.0$

For an ideal PFR: $\sigma_{\theta}^2 = 0$

Our reactor has $\sigma_{\theta}^2 = 0.358$, which is closer to PFR behavior than CSTR. Using the tanks-in-series model: $N = 1 / \sigma_{\theta}^2 = 1 / 0.358 = 2.8$ tanks.

The reactor behaves like 3 CSTRs in series, indicating moderate deviation from plug flow.

Example 10.2: Conversion in Tanks-in-Series Model

Problem Statement:

A non-ideal reactor has been characterized by RTD analysis and found to behave as $N = 3$ tanks in series. The mean residence time is $\tau = 10$ min. A first-order reaction $A \rightarrow B$ with $k = 0.25 \text{ min}^{-1}$ is to be carried out in this reactor. Calculate the expected conversion and compare it to the conversion in an ideal PFR and an ideal CSTR with the same residence time.

Solution:

Step 1: Calculate conversion for $N = 3$ tanks in series

Using Equation (10.19):

$$x = 1 - 1/(1 + k\tau/N)^N$$

$$x = 1 - 1/(1 + 0.25 \times 10/3)^3 = 1 - 0.162$$

$$x = 0.838 \text{ or } 83.8\%$$

Step 2: Calculate conversion for ideal PFR

For first-order reaction in PFR:

$$x = 1 - \exp(-k\tau)$$

$$x_{\text{PFR}} = 1 - \exp(-0.25 \times 10) = 1 - \exp(-2.5)$$

$$x_{\text{PFR}} = 1 - 0.082 = 0.918 \text{ or } 91.8\%$$

Step 3: Calculate conversion for ideal CSTR

For first-order reaction in CSTR: $x = \frac{k\tau}{1 + k\tau}$

$$x_{\text{CSTR}} = (0.25 \times 10)/(1 + 0.25 \times 10) = 2.5/3.5$$

$$x_{\text{CSTR}} = 0.714 \text{ or } 71.4\%$$

Step 4: Comparison

$$x_{\text{PFR}} = 91.8\% > x_{3\text{tanks}} = 83.8\% > x_{\text{CSTR}} = 71.4\%$$

The three-tank model gives intermediate performance between ideal PFR and CSTR, as expected. The conversion is closer to PFR than CSTR, which is consistent with having $N = 3$ tanks (moderate back-mixing).

Example 10.3: Dispersion Model Parameter Estimation

Problem Statement:

A tubular reactor of length $L = 4$ m and diameter $d = 0.1$ m operates with a superficial velocity $u = 0.05$ m/s. A pulse tracer test yields a dimensionless variance $\sigma_{\theta}^2 = 0.08$. Calculate: (a) the Péclet number, (b) the dispersion coefficient D , and (c) the expected conversion for a first-order reaction with $k = 0.2 \text{ s}^{-1}$.

Solution:

Step 1: Calculate Péclet number using Equation (10.25)

For large Pe , $\sigma_{\theta}^2 \approx 2/Pe$

$$Pe = 2/\sigma_{\theta}^2 = 2/0.08 = 25$$

Pe = 25 (large enough to use the approximation)

Step 2: Calculate dispersion coefficient

$Pe = uL/D$, therefore $D = uL/Pe$

$$D = (0.05 \text{ m/s} \times 4 \text{ m})/25 = 0.2/25 = \mathbf{8.0 \times 10^{-3} \text{ m}^2/\text{s}}$$

Step 3: Calculate mean residence time

$$\tau = L/u = 4 \text{ m} / 0.05 \text{ m/s} = 80 \text{ s}$$

Step 4: Calculate conversion using Equation (10.26)

First calculate $k\tau$:

$$k\tau = 0.2 \times 80 = 16$$

Calculate $a = (1 + 4k\tau/Pe)^{(1/2)}$:

$$a = (1 + 4 \times 16/25)^{(1/2)} = (1 + 2.56)^{(1/2)} = (3.56)^{(1/2)} = 1.887$$

Using Equation (10.26):

$$x = 1 - 4a \cdot \exp(Pe/2) / [(1+a)^2 \cdot \exp(aPe/2) - (1-a)^2 \cdot \exp(-aPe/2)]$$

$$x = 1 - 4 \times 1.887 \times \exp(12.5) / [(2.887)^2 \times \exp(23.59) - (-0.887)^2 \times \exp(-23.59)]$$

$x \approx 1.0$ or essentially 100%

For comparison, an ideal PFR would give $X = 1 - \exp(-16) \approx 1.0$, so the dispersion has negligible effect for this high conversion case.

10.8 Guided Learning Examples

The following examples use a guided problem-solving approach. Do not solve the problems directly. Instead, I will ask you questions to help you understand the fundamental assumptions and guide you toward the solution.

Guided Example 10.1: Step Input RTD Analysis

Problem Statement:

A step input of tracer (concentration $C_0 = 2.0 \text{ g/L}$) is introduced to a reactor at $t = 0$. The outlet concentration is measured and reaches 1.0 g/L at $t = 3 \text{ min}$, 1.5 g/L at $t = 6 \text{ min}$, and 1.8 g/L at $t = 10 \text{ min}$. Determine the RTD function $E(t)$ and estimate the mean residence time.

My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the fundamental assumptions in the modelling by asking me questions and wait for my answer to each question.

Guided Example 10.2: Second-Order Reaction in Tanks-in-Series

Problem Statement:

A second-order liquid-phase reaction $2A \rightarrow P$ with $k = 0.15 \text{ L}/(\text{mol}\cdot\text{min})$ is conducted in a non-ideal reactor that behaves as $N = 2$ tanks in series. The feed concentration is $C_{a0} = 3.0 \text{ mol/L}$ and the total mean residence time is $\tau = 8 \text{ min}$. Calculate the outlet concentration and conversion.

My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the fundamental assumptions in the modelling by asking me questions and wait for my answer to each question.

Guided Example 10.3: Comparing Models for Non-Ideal Reactor

Problem Statement:

RTD measurements on a tubular reactor give $\tau = 120 \text{ s}$ and $\sigma^2 = 1800 \text{ s}^2$. The reactor is to be used for a first-order reaction with $k = 0.05 \text{ s}^{-1}$. Compare the predicted conversions using: (a) tanks-in-series model, (b) dispersion model, and (c) ideal PFR assumption. Discuss which model is most appropriate.

My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the fundamental assumptions in the modelling by asking me questions and wait for my answer to each question.

10.9 Practice Problems

Advanced Exercises

Exercise 10.1: A reactor system consists of two CSTRs in series with volumes $V_1 = 100 \text{ L}$ and $V_2 = 150 \text{ L}$. The total volumetric flow rate is 10 L/min . A pulse of 50 g of tracer is injected at the inlet. Derive the expression for the outlet concentration as a function of time and sketch the expected $C(t)$ curve. Calculate the mean residence time and variance of the overall system. How does this compare to a single CSTR of total volume $V_1 + V_2$?

Exercise 10.2: A packed bed reactor of length 2 m exhibits axial dispersion characterized by $D = 0.005 \text{ m}^2/\text{s}$. The superficial velocity is $u = 0.02 \text{ m/s}$. For a consecutive reaction $A \rightarrow B \rightarrow C$ with $k_1 = 0.1 \text{ s}^{-1}$ and $k_2 = 0.05 \text{ s}^{-1}$, derive the differential equations describing the concentration profiles of A, B, and C along the reactor length. What boundary conditions should be applied? Discuss qualitatively how dispersion affects the selectivity to B compared to an ideal PFR.

Exercise 10.3: A bioreactor can be modeled using the tanks-in-series approach with $N = 5$. Cell growth follows Monod kinetics: $r = \mu_{\max} \cdot C_{\text{cells}} \cdot C_{\text{substrate}} / (K_s + C_{\text{substrate}})$. Given $\mu_{\max} = 0.3 \text{ h}^{-1}$, $K_s = 0.5 \text{ g/L}$, initial cell concentration = 0.1 g/L , feed substrate concentration = 10 g/L , and $\tau = 6 \text{ h}$, set up the equations needed to solve for substrate and cell concentrations in each tank. Explain why this problem requires iterative solution and outline a solution strategy.

Exercise 10.5: A reactor exhibits both dead volume (20% of total volume is stagnant) and channeling (30% of flow bypasses the active volume). Develop a compartment model to represent this system and derive the RTD function $E(t)$. If the active volume behaves as an ideal CSTR, what is the effective residence time in the active zone? How would you experimentally distinguish between dead volume and bypassing effects?

Simple Hand-Calculation Exercises

Exercise 10.6: A CSTR has a mean residence time of $\tau = 15 \text{ min}$. Calculate $E(t)$ at $t = 5, 10, 15, 20,$ and 30 minutes. What fraction of the exit stream has spent less than 10 minutes in the reactor? (Hint: Calculate $F(10)$ using Equation 10.11)

Exercise 10.7: A reactor has been characterized as $N = 4$ tanks in series with total $\tau = 20 \text{ min}$. For a first-order reaction with $k = 0.1 \text{ min}^{-1}$, calculate the conversion using Equation (10.19). Compare this to the conversion in a single CSTR with the same total residence time.

Exercise 10.8: From pulse tracer data, the following measurements of $tC(t)$ and $t^2C(t)$ integrals were obtained: $\int tC(t)dt = 450 \text{ g} \cdot \text{min}^2/\text{L}$ and $\int t^2C(t)dt = 3600 \text{ g} \cdot \text{min}^3/\text{L}$, while $\int C(t)dt = 75 \text{ g} \cdot \text{min}/\text{L}$. Calculate the mean residence time τ and the variance σ^2 . Determine the number of tanks N in the tanks-in-series model.

Exercise 10.9: A dispersion model analysis gives $Pe = 50$ for a tubular reactor with $\tau = 60 \text{ s}$. For a first-order reaction with $k = 0.08 \text{ s}^{-1}$, would you expect the dispersion to have a significant effect on conversion? Justify your answer by comparing $k\tau$ and Pe values. (Hint: Dispersion effects are small when $Pe > 20$ and $k\tau < 5$)

Chapter 10 Summary: What You Should Have Learned

After completing this chapter, you should be able to:

1. Understand residence time distribution in non-ideal reactors
2. Measure and characterize RTD using tracer experiments
3. Apply tanks-in-series and dispersion models
4. Predict reactor performance from RTD data
5. Understand causes of non-ideal behavior

Chapter 11: Reactor Stability, Safety, and Risk Management

Learning Objectives

After completing this chapter, you should be able to:

1. Recognize that chemical reactors can exhibit multiple steady states, parametric sensitivity, and unstable operation, understanding that these phenomena arise from the nonlinear coupling between highly temperature-dependent reaction rates and exothermic heat generation.
2. Identify and assess process-related risks in chemical reactor systems, including thermal runaway, overpressure scenarios, equipment failures, human errors, and external hazards, applying systematic risk assessment methodologies.
3. Evaluate chemical hazards associated with reactive systems, including toxicity, flammability, explosivity, and chemical reactivity, using appropriate hazard classification systems and quantitative risk analysis tools.
4. Design and specify appropriate safety systems including pressure relief devices, emergency shutdown systems, detection and alarm systems, and containment strategies based on quantitative risk assessment.
5. Develop mathematical models for CSTR stability analysis by formulating coupled material and energy balance equations, identifying steady states as solutions where all time derivatives equal zero, and analyzing local stability through linearization.
6. Apply phase plane analysis to visualize reactor dynamics, constructing trajectories in concentration-temperature space, identifying nullclines where individual state variables do not change, and interpreting the approach to steady states.
7. Utilize Lyapunov's stability criteria to rigorously determine whether steady states are stable, asymptotically stable, or unstable by analyzing the eigenvalues of the Jacobian matrix at equilibrium points.
8. Implement inherent safety principles in reactor design, following the hierarchy of risk reduction from elimination through substitution, engineering controls, administrative controls, to personal protective equipment as the last resort.
9. Conduct systematic hazard identification studies including HAZOP and FMEA for reactor systems to identify potential hazards and implement appropriate safeguards.
10. Design reactors with multiple layers of protection following the concept of defense-in-depth, recognizing that prevention of incidents through proper design is preferable to relying solely on active protection systems.

Nomenclature

The following symbols supplement the comprehensive nomenclature in previous chapters:

Roman Letters

B	Dimensionless heat transfer parameter, $B = UA/(\rho C_p \cdot q_0)$
Da	Damköhler number, $Da = k \cdot \tau$ (dimensionless)
J	Jacobian matrix
P	Probability (dimensionless)
S	Sensitivity parameter; Severity of consequence
T_c	Coolant temperature (K)
U	Overall heat transfer coefficient ($W/(m^2 \cdot K)$)
$V(x)$	Lyapunov function

Greek Letters

β	Dimensionless activation energy, $\beta = E_a/(RT_c)$
γ	Dimensionless heat of reaction, $\gamma = (-\Delta H_{rxn})C_{A,0}/(\rho C_p \cdot T_c)$
δ	Perturbation from steady state
λ	Eigenvalue
ψ	Dimensionless temperature, $\psi = (T - T_c)/T_c$
ω	Dimensionless concentration, $\omega = C_A/C_{A,0}$

Abbreviations

BLEVE	Boiling Liquid Expanding Vapor Explosion
F	Failure rate (failures per year)
HAZOP	Hazard and Operability Study
LEL	Lower Explosive Limit (vol% or mol%)
LOPA	Layer of Protection Analysis
MAWP	Maximum Allowable Working Pressure (Pa)
MIE	Minimum Ignition Energy (mJ)
PFD	Probability of Failure on Demand
PHA	Process Hazard Analysis
SIL	Safety Integrity Level
TLV	Threshold Limit Value (mg/m^3 or ppm)
UEL	Upper Explosive Limit (vol% or mol%)

11.1 Introduction: From Stability Analysis to Comprehensive Risk Management

Chemical reactors represent complex dynamic systems where concentration and temperature evolve according to material and energy balances. While previous chapters focused on steady-state design for optimal performance, this chapter addresses the critical aspects of stability, safety, and risk management essential for protecting people, property, and the environment. The integration of these topics reflects the modern understanding that reactor design must consider not only what happens during normal operation, but also what can go wrong and how to prevent or mitigate such events.

The chemical industry has learned through painful experience the importance of comprehensive safety analysis. The 1947 Texas City disaster, where ammonium nitrate cargo aboard ships decomposed explosively, killed 581 people and demonstrated the catastrophic potential of thermal runaway in reactive systems. Nearly three decades later, the 1974 Flixborough disaster in the United Kingdom showed how a seemingly minor modification—a temporary bypass pipe installed around a reactor—could lead to massive cyclohexane release, vapor cloud explosion, 28 fatalities, and complete destruction of the plant. This incident particularly highlighted the critical importance of process safety management and rigorous management of change procedures.

The 1984 Bhopal tragedy remains the world's worst industrial disaster. When water entered a storage tank containing methyl isocyanate at a pesticide plant in India, an exothermic reaction caused pressure buildup and release of toxic gas. The immediate death toll exceeded 3,000, with long-term casualties numbering in the tens of thousands. This catastrophe revealed fundamental weaknesses in safety systems, emergency planning, and the consequences of inadequate hazard assessment. More recently, the 2008 explosion at a Bayer CropScience facility in West Virginia resulted from runaway polymerization in a methomyl residue treater, killing two workers. Investigation revealed inadequate understanding of reactive hazards and insufficient emergency relief capacity.

These incidents, among many others, share common underlying causes. In most cases, there was inadequate understanding of process hazards, particularly the potential for exothermic runaway reactions under upset conditions. Engineering controls proved insufficient or improperly designed, often because the full range of credible scenarios had not been considered. Safety systems, where they existed, frequently failed to operate as intended, either due to poor design, inadequate maintenance, or improper testing. Perhaps most importantly, organizational factors—including production pressure, poor safety culture, inadequate training, and weak management systems—allowed hazardous conditions to persist until catastrophe struck.

Modern reactor engineering has evolved to integrate stability analysis, hazard identification, quantitative risk assessment, and defense-in-depth protection strategies from the earliest conceptual design stages. This chapter presents a comprehensive framework that begins with classical mathematical stability theory to understand fundamental reactor dynamics, then expands to encompass broader process risks, chemical hazards, and the design of protective systems. The ultimate goal is to develop reactors that are inherently safer by design, equipped with appropriate layers of protection, and operated with full understanding of potential hazards and their management.

11.2 Fundamental Concepts in Reactor Stability

11.2.1 Defining Stability and Its Implications

Reactor stability refers to the system's response to disturbances from steady-state operation. Consider a reactor operating at a steady state characterized by concentration C_s and temperature T_s . If we introduce a small perturbation δC in concentration and δT in temperature, the subsequent behavior of the system determines its stability classification. In a stable system, the reactor returns to the original steady state (C_s, T_s) as time approaches infinity, with perturbations decaying exponentially. This behavior is desirable because it means the reactor can tolerate small disturbances—inevitable in any real process—without adverse consequences.

The concept of asymptotic stability represents an even stronger condition. An asymptotically stable system not only returns to the steady state but remains there indefinitely, provided no additional disturbances occur. This is the ideal condition for industrial operation, as it ensures that the reactor will maintain desired operating conditions despite minor upsets. In contrast, an unstable system moves away from the original steady state when perturbed. The perturbations grow rather than decay, potentially leading the system to a completely different steady state or even to unbounded behavior where temperature and concentration continue increasing without limit.

A third category, marginal stability, represents an intermediate case where perturbations neither grow nor decay but persist in the form of sustained oscillations. While mathematically interesting, marginally stable operation is generally undesirable in industrial practice because any additional disturbance or nonlinearity can push the system toward instability, and the oscillations themselves complicate process control and may cause mechanical fatigue in equipment.

The consequences of instability in chemical reactors can be dramatic and dangerous. Thermal runaway represents the most feared instability scenario. In this situation, a small temperature increase accelerates the reaction rate through the exponential Arrhenius

temperature dependence, $k = A \cdot \exp(-E_a/RT)$. The faster reaction generates more heat, causing further temperature rise in a self-reinforcing positive feedback loop. If heat removal capacity cannot match the accelerating heat generation, temperature rises rapidly and without bound. The results can include pressure buildup leading to vessel rupture, explosion if flammable materials are present, release of toxic materials, formation of hazardous decomposition products, and complete loss of the intended reaction selectivity.

Multiple steady states present a different but equally important stability challenge. Under identical operating conditions—same feed composition, same flow rate, same coolant temperature—a reactor may have several possible steady-state solutions. Some of these states may be stable while others are unstable. During startup, shutdown, or following a disturbance, the reactor might transition unexpectedly from a desired high-conversion steady state to an undesired low-conversion state, or vice versa. Such transitions can occur suddenly and may be difficult to predict or control without proper stability analysis.

Parametric sensitivity refers to situations where small changes in operating parameters produce disproportionately large changes in reactor behavior. A reactor with high parametric sensitivity might see temperature jump by 50 degrees in response to a 2-degree change in feed temperature, or conversion might drop from 90% to 30% when coolant temperature increases by 5 degrees. Such extreme sensitivity makes the process nearly impossible to control effectively and creates operational risk because parameter variations that would be trivial in other processes can trigger major upsets.

Finally, some reactors exhibit oscillatory behavior where temperature and concentration undergo sustained or growing oscillations even without external forcing. These oscillations can arise from the interaction of reaction kinetics with heat and mass transfer, particularly in systems with recycle or multiple reactors in series. Sustained oscillations complicate quality control, may cause mechanical fatigue in equipment from thermal and pressure cycling, and can eventually trigger safety relief devices if amplitudes become too large.

11.2.2 Process Characteristics That Promote Instability

Certain characteristics of chemical processes make instability more likely. Understanding these factors allows engineers to recognize potential stability problems during process design and to take appropriate preventive measures. The most significant factor is the combination of exothermic reactions with high activation energy. The Arrhenius equation, $k = A \cdot \exp(-E_a / RT)$, shows that reaction rate depends exponentially on temperature. For reactions with high activation energies—typically those exceeding 80 kJ/mol—a modest 10 K temperature increase can double or even triple the reaction rate. When such temperature-sensitive kinetics are coupled with exothermic heat release, where the heat generation rate is $Q_{\text{gen}} = (-\Delta H_{\text{rxn}}) \cdot V \cdot k(T) \cdot f(C)$, a powerful positive feedback mechanism emerges.

Consider what happens when temperature increases slightly in such a system. The higher temperature causes $k(T)$ to increase exponentially, which increases Q_{gen} proportionally. If this additional heat generation is not immediately removed, temperature rises further, causing an even larger increase in reaction rate. The process accelerates in a vicious cycle. The dimensionless activation energy $\beta = E_a/(RT)$ quantifies this temperature sensitivity. When β exceeds approximately 20, the system shows strong temperature dependence and heightened instability risk. Many important industrial reactions fall into this category, including nitrations ($\beta = 25-35$), oxidations ($\beta = 20-30$), polymerizations ($\beta = 15-25$), and hydrogenations ($\beta = 20-28$).

Inadequate heat removal capacity represents the second major factor promoting instability. Heat removal rate from a jacketed reactor typically follows the simple linear relationship $Q_{\text{removed}} = UA(T - T_c)$, where U is the overall heat transfer coefficient, A is the heat transfer area, and T_c is the coolant temperature. This linear dependence on temperature difference contrasts sharply with the exponential dependence of heat generation on temperature. At low temperatures, heat removal easily exceeds generation. As temperature increases, both increase, but at different rates. Eventually, at sufficiently high temperature, the exponential increase in heat generation overtakes the linear increase in heat removal. Beyond this point, the system loses its ability to control temperature through the existing cooling system.

The intersection points of heat generation and removal curves determine the possible steady states, and the relative slopes at these intersections determine stability. If at a given steady state the slope of the heat generation curve exceeds that of the heat removal curve, any small temperature increase causes generation to exceed removal by an increasing margin, leading to instability. Insufficient heat transfer area A , poor overall heat transfer coefficient U (due perhaps to fouling, poor mixing, or phase change complications), or high coolant temperature T_c (limited by available utilities) all reduce heat removal capacity and push the system toward instability.

Several factors affect the overall heat transfer coefficient U and thus the system's heat removal capability. Fouling on heat transfer surfaces, which accumulates over time, acts as insulation and significantly reduces U . A reactor designed with adequate cooling capacity when clean may become unstable as fouling progresses. Vapor formation on hot surfaces creates a vapor blanket with poor thermal conductivity, drastically reducing heat transfer effectiveness. Poor agitation leads to large temperature gradients and hot spots where local heat generation exceeds local removal even though the average reactor temperature appears acceptable. The physical properties of the reaction mixture, particularly viscosity, can change dramatically during reaction, affecting both heat transfer and mixing effectiveness.

Autocatalytic and complex kinetics create inherent instability even under isothermal conditions. In autocatalytic reactions, products accelerate their own formation according to rate expressions like $r = k \cdot C_A \cdot C_B$, where B is both product and catalyst. This creates positive feedback in the concentration domain: as more product forms, the reaction accelerates, forming product even faster. When combined with thermal effects, autocatalytic systems become extraordinarily complex and prone to instability. Chain reactions, common in many industrial processes, involve sequences of initiation, propagation, and termination steps. In branching chain reactions, a single radical can produce multiple radicals, leading to exponential increases in reaction rate. The hydrogen-oxygen system, certain hydrocarbon oxidations, and chlorination reactions exemplify this behavior.

Reactor configuration introduces additional complexity. Recycle streams create feedback loops that can either stabilize or destabilize operation depending on the specifics. When hot reactor effluent is recycled and mixed with fresh feed, any temperature increase in the reactor produces hotter recycle, which increases the feed temperature, which further increases reactor temperature. This positive feedback loop can overcome the stabilizing effects of other process features. Large recycle ratios amplify this effect and can destabilize otherwise stable single-pass configurations. Series reactor configurations, where the output of one reactor feeds the next, create coupled dynamics. Even when individual reactors would be stable in isolation, their coupling can produce oscillatory behavior, limit cycles, or complex chaotic dynamics. The interaction between reactors creates eigenvalues with complex components, indicating oscillatory tendencies not present in single reactors.

11.2.3 Deviations from Design Specifications as Stability Risks

Reactor stability analyses are almost always performed assuming that the reactor operates exactly as designed: feed is uniformly distributed, catalyst activity is homogeneous throughout the bed, heat transfer surfaces are clean, and all equipment performs according to its specification. In reality, deviations from these idealised design conditions are inevitable and can profoundly alter the stability landscape. Recognising how such deviations affect stability is essential for robust reactor design and for diagnosing unexpected instabilities in operating plants.

Maldistribution of flow is one of the most common and consequential deviations from design intent, particularly in fixed-bed reactors. When feed gas or liquid does not distribute uniformly across the bed cross-section, regions of high local velocity coexist with stagnant or slow-moving zones. In the high-velocity channels, contact time between reactant and catalyst is reduced, leading to lower conversion and, for exothermic reactions, lower local heat release. In the slow-moving zones the opposite occurs: reactants spend far longer in contact with the catalyst, local conversion is high, and heat generation per unit volume is

substantially elevated. If the heat generated in these slow zones exceeds the local heat removal capacity, the temperature rises, accelerating the reaction further through Arrhenius kinetics. The result is a “hot spot”—a localised region where temperature significantly exceeds the design operating temperature. Hot spots can lead to catalyst sintering and permanent deactivation, runaway in the affected zone even when the overall reactor appears stable by its exit conditions, local overpressure from enhanced vapour formation, and mechanical damage to reactor internals. Maldistribution arises from poor inlet distributor design, blockage of distributor holes by solids or fouling, non-uniform catalyst loading during packing, catalyst attrition that creates fines migrating to preferential flow paths, and channelling along reactor walls. Design measures that reduce the risk include careful distributor sizing, inlet screens or grids, controlled catalyst loading procedures, and periodic inspection of distributor integrity.

Non-uniform catalyst activity creates analogous problems even when flow distribution is perfect. A freshly loaded catalyst bed is rarely perfectly homogeneous. Variations in pellet size, crushing strength, and impregnation uniformity mean that some zones of the bed are more active than others from the very first day of operation. More significantly, catalyst activity evolves over time in ways that can shift the stability operating point. A newly commissioned reactor loaded with fresh catalyst frequently encounters the challenge of excess initial activity. The catalyst may perform its intended function—for example, selective oxidation or hydrogenation—at significantly higher rates than the design basis assumed. This excess activity generates more heat than the cooling system was sized to remove, pushing the reactor toward the upper stable steady state or, in parametrically sensitive systems, past the ignition point into runaway territory. Operators managing reactor start-up with fresh catalyst must therefore often deliberately reduce feed concentration, lower feed temperature, or increase coolant flow to compensate for the higher-than-design activity, gradually relaxing these protective measures as the catalyst ages toward its design activity level.

Time-dependent changes in catalyst activity affect stability throughout the catalyst lifetime. During the initial break-in period, surface restructuring, removal of protective ligands or solvents, and establishment of steady-state surface species all alter intrinsic activity. Over the operating life, gradual deactivation due to coking, poisoning by trace impurities in the feed, or sintering of the active phase progressively reduces activity. As activity falls, the same feed conditions produce less heat, and the reactor may drift from a previously stable high-conversion steady state toward a lower steady state or even extinction. This drift is insidious because it is slow and may not be apparent from routine measurements until conversion has dropped substantially. For reactors exhibiting multiple steady states, deactivation can cause the reactor to “fall off” the upper steady state branch once activity drops below a critical

threshold, requiring a deliberate restart sequence to restore high-conversion operation. Conversely, periodic catalyst regeneration restores activity, and the reactor must be managed carefully through the transient following regeneration to avoid the same over-activity problems encountered during initial start-up.

Heat transfer deterioration over time is a further time-dependent deviation that compromises stability margins. Fouling on heat transfer surfaces accumulates progressively, reducing the overall heat transfer coefficient U and therefore the rate of heat removal $Q = UA(T - T_c)$. A reactor designed with a cooling capacity margin of, say, 20% above the maximum expected heat generation may see that margin eroded over months of operation as fouling builds up. Stability analyses should therefore be performed not only for clean heat transfer surfaces at the start of a run, but also for worst-case fouled conditions expected at the end of the planned operating cycle. If the analysis reveals instability under fouled conditions, the design must be modified—by increasing heat transfer area, improving flow velocity to reduce fouling tendency, or scheduling more frequent cleaning—before the reactor is commissioned.

The practical implication of these considerations is that stability is not a fixed property of a reactor—it is a property of the reactor in its current physical condition. A thorough stability assessment evaluates the reactor across the full range of realistic operating states: from start-up with fresh, potentially over-active catalyst, through normal mid-life operation, to end-of-run with partially deactivated catalyst and fouled heat transfer surfaces. Operating procedures, catalyst management protocols, and control system tuning must all account for this evolution to ensure that the reactor remains within its stable operating envelope throughout its entire service life.

11.2.3 Pressure Relief: Temperature-Pressure Coupling and the Need for Smooth Depressurisation

Pressure and temperature in a reacting system are not independent variables; they are coupled through thermodynamic relationships that create hazards unique to reactive systems and that fundamentally shape the design requirements for pressure relief devices. Understanding this coupling is essential for engineers who size relief systems and specify operating procedures for reactors and associated vessels.

For a closed or partially closed system containing a volatile liquid, the relationship between temperature and pressure is governed by the vapour-liquid equilibrium and, at its simplest, approximated by the Clausius-Clapeyron equation: the vapour pressure of a liquid rises exponentially with temperature. In a reactor or storage vessel, any heat source—whether an exothermic reaction, external fire exposure, or steam jacket failure—that raises the liquid

temperature simultaneously raises the equilibrium vapour pressure and therefore the system pressure. The two variables rise together. This coupling means that a thermal upset is always also a pressure upset, and vice versa. A reactor experiencing incipient thermal runaway will simultaneously approach its maximum allowable working pressure (MAWP) from both directions: the temperature is rising, and the pressure is rising in lockstep. This is why pressure relief devices are a critical component of thermal protection systems even for reactions that do not generate non-condensable gases.

When a pressure relief device opens, the coupling creates a dangerous feedback mechanism if relief is not managed carefully. As vapour is vented from the vessel, the liquid loses its most energetic molecules and cools slightly—a process called flash cooling or auto-refrigeration. In a non-reacting system this is beneficial, since the cooling reduces vapour pressure and tends to arrest further venting. In an exothermic reacting system, however, the situation is more complex. The reaction continues to generate heat even as the liquid cools from flashing. If the heat generation rate exceeds the flash cooling rate, the net effect of opening the relief device may be negligible or even counterproductive: venting removes vapour (reducing pressure temporarily), but the ongoing reaction raises temperature and pressure again, potentially causing the relief device to cycle rapidly—a phenomenon known as “chattering.” Chattering causes mechanical fatigue and damage to valve seats, can prevent the valve from reseating properly, and may lead to uncontrolled release far larger than the designed relief flow.

The most severe consequence of sudden, uncontrolled pressure release in a system containing a liquid near or above its atmospheric-pressure boiling point is a Boiling Liquid Expanding Vapour Explosion (BLEVE). If vessel integrity is suddenly lost—by catastrophic structural failure rather than controlled relief—the pressure drops to atmospheric in milliseconds. The liquid, which was stable under pressure at a temperature far above its normal boiling point, is now massively superheated relative to its new environment. It undergoes explosive, instantaneous vaporisation across the entire liquid volume simultaneously, not just at the liquid surface. The resulting vapour expansion is so rapid that it generates a destructive pressure wave and propels vessel fragments as projectiles. The consequences of a BLEVE are catastrophic even at substantial distances from the event. The fundamental lesson is that pressure must always be reduced gradually and in a controlled manner, never suddenly; and that the liquid temperature must be reduced below its normal boiling point before any rapid depressurisation is attempted.

Two-phase flow during relief is a further complication that is frequently underestimated in relief system design. Classical relief system sizing methods assume that only vapour is discharged through the relief device. In practice, runaway reactions generate heat faster

than vapour can be produced, causing the liquid to swell and froth. The relief device then discharges a two-phase mixture of vapour and entrained liquid droplets. The two-phase mixture has a much lower specific volume than pure vapour, so the volumetric flow rate for a given mass flow rate is far lower—meaning that a relief device sized for vapour-only flow may be significantly undersized for two-phase flow. The DIERS (Design Institute for Emergency Relief Systems) methodology, developed specifically to address this problem, provides the tools to size relief devices correctly for two-phase discharge. Reactors handling runaway-prone reactions should always be evaluated using DIERS or equivalent methods rather than classical vapour-only sizing, and the relief device discharge must be directed to a vapour-liquid separator or knockout drum rather than directly to a vent pipe or scrubber to prevent liquid carryover from causing secondary hazards.

The design philosophy for pressure relief in reactive systems therefore requires smooth, controlled depressurisation that accounts for the thermal-hydraulic coupling. Relief devices should be sized for the worst credible scenario including two-phase flow and maximum heat generation rate; set pressures should provide adequate margin below the vessel MAWP; back-pressure effects from the downstream disposal system must not prevent full opening of the device; and operating procedures must ensure that temperature is not allowed to approach or exceed the boiling point of the process fluid at relief pressure without adequate justification and protective measures in place. Where practical, inherently safer approaches—such as reducing operating pressure and temperature through process intensification or solvent substitution—are always preferable to relying solely on relief system protection.

11.3 Risk Assessment Framework for Reactor Systems

11.3.1 Fundamentals of Process Risk

Risk in chemical reactor systems combines two essential elements: the likelihood that an unwanted event will occur, and the severity of consequences if it does occur. This fundamental relationship, ***Risk = f(Probability, Consequence)***, provides the foundation for rational decision-making about safety investments and design choices. However, both probability and consequence require careful definition and quantification. Probability can range from nearly certain events that occur multiple times per year to extremely rare events that might happen once in a million years of operation. Consequences span from minor equipment damage and brief production interruptions to multiple fatalities, major environmental disasters, and catastrophic business losses.

In reactor safety analysis, we must consider consequences across multiple dimensions. Personnel safety concerns injuries to workers and, in worst cases, fatalities. Environmental impact includes releases of hazardous materials that may persist in soil, water, or air for extended periods. Asset damage encompasses not just the reactor itself but associated equipment, the surrounding facility, and sometimes neighboring properties. Business continuity addresses production losses during shutdowns for repairs, potential permanent loss of operating permits, and reputational damage that affects future business prospects. Insurance and legal costs can dwarf the immediate physical damage, particularly when third parties suffer harm.

Quantitative risk assessment attempts to assign numerical values to both probability and consequence, enabling mathematical comparison of different scenarios and evaluation of risk reduction measures. A major reactor rupture might have a probability of 10^{-5} per year (once in 100,000 years) but consequences measured in hundreds of millions of dollars and multiple fatalities. A minor leak might occur once every few years (probability near 0.1 per year) but cause only local contamination and brief production interruptions. The product of probability and consequence for these two scenarios might be similar, suggesting they deserve comparable attention in safety design despite their vastly different characteristics.

Risk matrices provide a semi-quantitative approach that has gained wide acceptance in industry. These matrices typically use five levels for both probability and consequence. Probability levels might be defined as: rare (less than once in 10,000 years), unlikely (once in 1,000 to 10,000 years), possible (once in 100 to 1,000 years), likely (once in 10 to 100 years), and almost certain (more than once in 10 years). Consequence levels typically range from negligible (minor first aid injury, minimal environmental impact, small financial loss under \$10,000) to catastrophic (multiple fatalities, major long-term environmental damage, financial losses exceeding \$10 million and potentially threatening business survival).

The multiplication or combination of these probability and severity rankings produces risk scores ranging from low (acceptable without additional controls) through medium (requiring review and practical risk reduction measures) to high (requiring immediate action before operations continue) and extreme (activities should not proceed without major risk reduction). This structured approach ensures consistent evaluation of diverse scenarios and helps prioritize safety improvement efforts based on actual risk rather than subjective concerns or recent incidents that may not represent the most significant hazards.

Understanding risk tolerance is crucial for making appropriate safety decisions. No industrial activity can be made completely risk-free; the question is always what level of residual risk is acceptable. Society generally accepts higher risks for voluntary activities than for involuntary exposures. Workers who choose to work in chemical plants accept some

level of occupational risk, but that acceptance has limits, and nearby communities have not consented to exposure from potential accidents. This asymmetry means that off-site consequences typically demand more stringent protection than on-site risks to trained workers wearing protective equipment.

Risk tolerance criteria often distinguish between individual risk (the probability that a specific person will be harmed) and societal risk (the probability of events affecting multiple people simultaneously). A hazard that might kill one person with probability 10^{-4} per year could be acceptable, while a hazard that might kill 100 people with the same probability would not, even though the expected fatalities per year are similar (0.0001 versus 0.01). This reflects society's particular aversion to catastrophic events that kill many people at once, as opposed to the same number of deaths spread over time in separate incidents. This societal concern drives requirements for especially robust protection against scenarios with potential for large-scale harm.

11.3.2 Risks to the Surrounding Community and Land-Use Planning

The consequences of major accidents at chemical reactor installations extend far beyond the plant boundary. Toxic gas clouds, vapour cloud explosions, and BLEVEs can cause fatalities and serious injuries to members of the surrounding community who have had no involvement in the process and no opportunity to take protective action. This fundamental asymmetry—the community bears risk without consent—is the primary driver behind regulatory requirements for consequence modelling, safety distances, and land-use planning around hazardous installations. Quantifying and managing off-site risk is therefore not merely a legal obligation but an ethical imperative for engineers who design and operate reactor systems.

Consequence modelling for credible accident scenarios defines a set of concentric hazard zones around the installation. The innermost zone extends to the distance at which the most severe credible accident would cause immediately life-threatening conditions: concentrations above the IDLH (Immediately Dangerous to Life or Health) for toxic releases, overpressures above approximately 14 kPa for explosions, or thermal radiation fluxes above 12.5 kW/m^2 for fires. Beyond this lies an injury zone where acute but potentially survivable harm is possible, and further out an alert zone where irritation and mild effects might occur but fatalities are unlikely. Under European SEVESO III legislation and equivalent national regulations elsewhere, operators of major hazard establishments must calculate and report these zones, and competent authorities must take them into account in local land-use plans.

Land-use planning around hazardous chemical installations reflects the principle that incompatible activities should not be co-located in space. Within the danger zone, no

permanent human occupancy is permitted: residential housing, schools, hospitals, shopping centres, and other places where vulnerable people congregate are prohibited. In the injury zone, high-density residential development is excluded; existing homes may remain but no new residential planning permission is granted. Light industrial activities—warehousing, logistics, manufacturing that does not involve large numbers of workers in vulnerable locations—may be permissible if workers can be rapidly evacuated and if the activity does not introduce additional ignition sources. In the alert zone, normal industrial and commercial activities are generally permitted, though particularly sensitive uses such as schools and care homes may still be restricted. The exact boundaries and permitted activities vary between jurisdictions, but the underlying logic is consistent: the consequence severity at each distance determines the acceptability of each type of land use.

11.3.3 Systematic Hazard Identification: HAZOP Methodology

Process Hazard Analysis (PHA) encompasses a family of systematic techniques for identifying what can go wrong in chemical processes and determining how to prevent or mitigate such events. The Hazard and Operability Study, universally known as HAZOP, represents the most widely used PHA methodology, particularly for complex continuous processes like reactor systems. HAZOP achieves its systematic character through disciplined application of guide words to process parameters, ensuring that analysts consider a comprehensive range of deviations from design intent.

The HAZOP methodology begins by dividing the process into discrete nodes, each representing a meaningful portion of the system. For a reactor system, typical nodes might include the reactor vessel itself, the feed preparation system, the cooling system, the product separation and recovery section, and relief and emergency systems. Each node is then examined thoroughly by applying guide words to relevant process parameters. The guide words—NO or NOT, MORE, LESS, AS WELL AS, PART OF, REVERSE, and OTHER THAN—systematically generate deviations from intended operation.

Consider applying these guide words to reactor feed flow rate. NO flow means complete loss of feed to the reactor, for example due to pump failure, a closed isolation valve, or a blocked line. MORE flow means a feed rate above the design value, perhaps from a control valve that has failed open, an operator error in setpoint, or a pump delivering above its rated capacity. LESS flow indicates a flow rate below design, which might result from partial blockage, a pump running on a degraded impeller, a control valve failing partially closed, or upstream supply pressure falling. REVERSE flow is particularly serious for reactor feed lines: backflow can occur if downstream pressure exceeds upstream pressure, for example during a reactor pressure surge, and may drive reactive material into feed systems not designed to handle it. AS WELL AS flow might indicate simultaneous deviation in a second parameter alongside

flow—for example, feed flow changing at the same time as feed composition changes. PART OF flow could represent maldistribution within a multi-inlet reactor, where some inlets receive correct flow while others are starved. OTHER THAN flow might mean a different fluid flowing through the line than intended, such as the wrong component being routed through a shared feed header.

For each meaningful deviation identified, the HAZOP team determines credible causes. MORE flow in the reactor feed could result from several mechanisms. A flow control valve may have failed open due to actuator failure, instrument signal failure, or loss of instrument air pressure. The upstream supply pressure may have increased, for example if a pressure-reducing valve upstream has failed open. An operator may have inadvertently entered an incorrect setpoint into the flow controller. A parallel feed line that should have been isolated may have been left open. Pump speed may have increased if a variable-speed drive malfunctions at maximum output. Any of these causes produces the same deviation—feed flow above design—and the team must evaluate the consequences irrespective of the specific cause, while also considering whether particular causes are more likely than others given the specific plant configuration.

After identifying causes, the team evaluates consequences of each deviation. MORE flow in the reactor feed increases the molar supply rate of reactants to the reactor. For an exothermic reaction in a CSTR, the increased reactant concentration at steady state drives a higher reaction rate and therefore higher heat generation; if cooling capacity is not proportionally increased, reactor temperature rises, potentially triggering thermal runaway. In a PFR, higher flow reduces residence time, which lowers conversion per pass; the product stream will contain more unreacted feed material, which may itself be hazardous or may cause downstream processing problems. If the reaction is incomplete and reactants pass through to downstream equipment not designed for reactive service, secondary reactions, corrosion, or safety events may follow. For NO flow or LESS flow, conversion in the reactor may rise toward equilibrium if the reactor is undersized for the lower velocity, potentially causing overheating in the early section of a fixed bed. If feed flow stops entirely while heating or exothermic reaction continues, the reactor contents heat without replenishment and without the cooling effect of cold incoming feed, accelerating temperature rise. In a CSTR, NO flow also means the reactor contents are no longer being diluted or replaced, so conversion approaches its maximum and heat release reaches its peak value.

The HAZOP team then examines existing safeguards that might prevent the deviation or mitigate its consequences. For a MORE flow deviation, safeguards might include a flow control loop that normally maintains flow at setpoint and will resist disturbances, a high-flow alarm that alerts the operator when measured flow exceeds a defined limit, a flow

interlock that reduces or stops feed if flow exceeds a high-high setpoint, a downstream reactor temperature measurement that provides indirect indication of excess feed (since excess reactant increases heat generation), and a pressure relief system that protects the reactor against the overpressure consequences of runaway even if the flow deviation itself is not directly detected. For a NO flow or LOW flow deviation, safeguards include a low-flow alarm, a low-flow trip that initiates safe shutdown if feed is lost, reactor temperature monitoring that detects the rising temperature caused by loss of cold feed dilution, and automatic isolation of heat sources (steam, jacket heating) on loss of feed flow.

If existing safeguards are inadequate, the team recommends additional protective measures. For flow deviations, recommendations might include installation of a dedicated flow transmitter with independent high-flow and low-flow alarms separate from the control transmitter, so that instrument failure does not simultaneously disable control and detection. A redundant flow measurement using a different measurement principle—for example, a vortex meter as backup to an orifice plate—provides independence. Valve position feedback on the feed control valve allows operators to verify that the valve is responding correctly to control signals and has not failed in an unexpected position. For REVERSE flow, a check valve on the feed line prevents backflow mechanically; the HAZOP team should verify that the check valve is rated for the maximum credible backpressure and that it is included in a preventive maintenance programme. Where the consequence of flow deviation is particularly severe, a safety-rated flow transmitter and interlock, classified to the appropriate Safety Integrity Level, may be required in addition to the basic alarm and control system.

The power of HAZOP lies in its systematic nature. By methodically considering each parameter at each node with each guide word, the study team identifies hazards that might be missed by less structured brainstorming approaches. The multidisciplinary team—typically including process engineers, operations personnel, maintenance staff, safety professionals, and often representatives from projects and technical service—brings diverse perspectives that catch issues any single viewpoint might miss. Documentation of the study creates a permanent record of hazards considered and decisions made, supporting future safety reviews and modifications.

However, HAZOP has limitations that engineers must recognize. The quality of a HAZOP depends heavily on team member expertise and the facilitator's skill in managing the discussion. Studies can become lengthy and expensive, sometimes requiring many days of team time for complex processes. The systematic approach ensures coverage but can become mechanical, with team members going through the motions rather than truly thinking about the process. Most importantly, HAZOP identifies only deviations that the team

can imagine based on the guide word combinations; truly novel failure mechanisms may still escape detection.

11.3.4 Failure Mode and Effects Analysis for Equipment

While HAZOP focuses on process deviations, Failure Mode and Effects Analysis (FMEA) complements it by examining how individual equipment failures propagate through the system. FMEA proceeds component by component, asking "How can this item fail?" and "What happens when it does?" This bottom-up approach effectively captures equipment reliability issues that might be less obvious in process-focused HAZOP studies. For reactor systems, FMEA typically examines pumps, agitators, heat exchangers, control valves, instruments, vessels, and piping.

Consider a cooling water circulation pump that supplies the reactor jacket. Several failure modes exist. The pump may fail to start when called upon, perhaps due to motor failure, electrical supply problems, or mechanical issues such as seized bearings. The pump may start but deliver insufficient flow due to cavitation, impeller damage, or system blockage. The pump may run but in the wrong direction if electrical phases are reversed during maintenance. The pump may develop seal leakage, allowing cooling water to escape and potentially creating a pool or spray that could reach electrical equipment. The pump may suffer catastrophic mechanical failure with rapid loss of cooling.

For each failure mode, FMEA assesses three factors. Severity ranks the seriousness of consequences if the failure occurs, typically on a scale of 1 (negligible effect) to 10 (catastrophic effect with safety implications). Loss of cooling water circulation in an exothermic reactor might rate severity of 9 because it could lead to temperature runaway, pressure rise, and potential reactor rupture. Occurrence probability rates how often the failure might happen, from 1 (extremely unlikely, less than once in the equipment lifetime) to 10 (almost certain to occur frequently). A well-maintained centrifugal pump might rate 3 or 4 for failure to start on demand, occurring perhaps once every few years. Detection evaluates how likely the failure is to be detected before causing harm, from 1 (automatically detected with alarm) to 10 (undetectable until accident occurs). Pump failure in a system with flow measurement and low-flow alarm might rate 2 or 3 for detection, while a system without flow monitoring might rate 8.

The Risk Priority Number, calculated as $RPN = \text{Severity} \times \text{Occurrence} \times \text{Detection}$, provides a comparative ranking for prioritizing corrective actions. An RPN of $9 \times 3 \times 8 = 216$ indicates a relatively high-risk failure mode that should receive attention despite moderate occurrence probability, because high severity combined with poor detection creates unacceptable risk. Teams typically establish threshold RPN values above which corrective action is mandatory. Actions might include design modifications to prevent the failure,

additional monitoring and alarms to improve detection, redundant equipment to provide backup capability, or enhanced maintenance programs to reduce occurrence probability.

For the cooling pump example, several risk reduction measures might be considered. A standby pump with automatic start-on-low-flow provides redundancy, dramatically reducing both occurrence probability (two pumps must fail simultaneously) and detection difficulty (the failure of the primary pump is detected by the control system that starts the backup). Continuous flow monitoring with low-flow alarm improves detection even without automatic backup. Temperature monitoring provides secondary detection as reactor temperature would increase if cooling fails. Thermal runaway prevention might include temperature interlocks that stop reaction or add quench if temperature rises despite cooling efforts. Emergency procedures ensure operators know how to respond if pump failure is detected.

FMEA proves particularly valuable for equipment-intensive systems where hardware reliability significantly affects safety. The systematic examination of each component and each failure mode creates confidence that important failure scenarios have not been overlooked. However, FMEA shares some limitations with HAZOP. It requires significant time and expertise to complete thoroughly. The scoring of severity, occurrence, and detection can be subjective, leading different teams to reach different conclusions about the same system. Most critically, FMEA focuses on single component failures and may miss accident scenarios that involve multiple failures, common cause failures affecting multiple components simultaneously, or complex interactions between process and equipment failures.

11.3.5 Layer of Protection Analysis and Quantitative Methods

Layer of Protection Analysis (**LOPA**) bridges the gap between qualitative hazard identification techniques like HAZOP and fully quantitative risk assessment. LOPA provides a semi-quantitative method for evaluating whether existing protective layers provide adequate risk reduction for identified hazards. The methodology begins with a scenario identified in HAZOP or FMEA, determines an acceptable risk level based on consequence severity, estimates the frequency of the initiating event, and then evaluates what risk reduction is provided by existing independent protection layers.

Consider a scenario where cooling water flow to a reactor is lost, leading to temperature runaway and potential pressure vessel failure. We must first estimate how often the initiating event—cooling water flow loss—might occur. Historical industry data suggests that loss of cooling water occurs perhaps once every ten years at a typical facility due to various causes including pump failures, valve operations, supply system problems, and maintenance

activities. This gives an initiating event frequency of approximately 0.1 per year or 10^{-1} per year.

Next we establish the consequence category. Vessel failure due to overpressure could release large quantities of toxic material, potentially causing off-site impact and multiple fatalities. For such major off-site impact scenarios, risk tolerance criteria typically require that event frequency be less than 10^{-5} per year, or once in 100,000 years. This reflects the severe consequences and the involuntary nature of off-site exposure. Given an initiating event frequency of 10^{-1} per year and a required final frequency of less than 10^{-5} per year, the necessary risk reduction factor is $10^{-1} / 10^{-5} = 10^4$, or 10,000-fold reduction.

We now evaluate what risk reduction is provided by independent protection layers (IPLs). Each IPL must be independent, meaning it operates separately from other layers and is unaffected by the failure that initiated the sequence. The basic process control system (BPCS) that normally controls cooling water flow cannot be considered independent, since the loss of cooling is the initiating event. However, several other IPLs might exist.

A high temperature alarm might alert the operator, who could take corrective action within a specified time frame. Operator response to alarms is generally credited with a Probability of Failure on Demand (PFD) of about 0.1, meaning the operator successfully responds 9 times out of 10. This provides a 10-fold risk reduction. A safety instrumented system (SIS) with high-high temperature trip that automatically stops reactant feed and activates emergency cooling might provide PFD of 0.01, giving 100-fold risk reduction. A pressure relief valve properly sized for the worst-case scenario might provide PFD of 0.01, another 100-fold risk reduction. Finally, the inherent design might include sufficient heat capacity in the vessel contents that, even with complete cooling loss, temperature rises slowly enough for other protective layers to act before pressure reaches the relief valve set point. This inherent characteristic might contribute a factor of 10 to overall protection.

The total risk reduction from these IPLs multiplies: $10 \times 100 \times 100 \times 10 = 10,000,000$ or 10^7 . This exceeds the required 10^4 risk reduction by three orders of magnitude, suggesting adequate protection even accounting for uncertainties in the analysis. If the calculated risk reduction were insufficient, the team would need to consider additional IPLs such as redundant cooling systems, upgraded SIS to higher Safety Integrity Level, or redesign using inherently safer chemistry or operating conditions.

LOPA's power lies in its structured approach to evaluating protection adequacy without requiring the extensive effort of full quantitative risk assessment. By focusing on one scenario at a time and considering only major protective layers, LOPA keeps the analysis tractable while still incorporating quantitative thinking about probabilities and

consequences. The methodology forces teams to think clearly about independence between layers, ensuring that credit is not taken for protective features that might fail for the same reason as the initiating event.

11.3.6 Tree Analysis

For scenarios requiring more detailed analysis, full quantitative risk assessment techniques become appropriate. **Event tree analysis** maps out the sequence of events following an initiating event, with each branch point representing a success or failure of some protective feature or response. For the cooling loss scenario, an event tree would show branches for: Does the BPCS attempt to restore cooling? If not, does the operator respond to alarms? If not, does the SIS trip feed and activate emergency cooling? If not, does temperature rise to the relief valve set point? If so, does the relief valve open? If so, can the relief system handle the required flow? Each branch has an associated probability, and terminal nodes represent different outcomes ranging from safe recovery to catastrophic failure. The probability of each outcome is calculated by multiplying probabilities along the path from initiation to that outcome.

Fault tree analysis works in the opposite direction, starting with an undesired top event such as "reactor vessel rupture" and working backward to identify all combinations of basic events that could cause it. Boolean logic gates (AND gates requiring multiple events to occur simultaneously, OR gates where any single event suffices) connect events in a tree structure. Solving the fault tree identifies minimal cut sets—the smallest combinations of basic events that lead to the top event—and calculates the overall frequency of the top event based on frequencies of basic events. This approach proves especially valuable for understanding complex systems where many different failure combinations might lead to the same adverse outcome.

Both event trees and fault trees require substantial data on component failure rates, human error probabilities, and common cause failure factors. Industry databases, equipment manufacturer information, and plant-specific operating experience all contribute to these estimates, but significant uncertainties remain. Sensitivity analysis explores how uncertainties in input parameters affect conclusions, helping identify which parameters most strongly influence overall risk and therefore deserve the most attention in data collection and uncertainty reduction.

11.4 Chemical Hazards in Reactor Systems

11.4.1 Toxicity and Exposure Limits

Chemical toxicity represents one of the most significant hazards in reactor systems, as nearly all industrial chemical reactions involve materials that present some degree of hazard to human health. Understanding toxicity requires more than simply knowing that a material is "toxic" or "safe"—quantitative knowledge of dose-response relationships and exposure limits is essential for proper risk assessment and protective system design. Toxicologists express the fundamental relationship as "the dose makes the poison," recognizing that nearly any substance can cause harm at sufficiently high concentrations or exposure durations, while even very toxic materials may be handled safely with appropriate controls.

Threshold Limit Values (TLVs) form the primary framework for occupational exposure limits. The TLV-TWA (Time-Weighted Average) represents the concentration to which nearly all workers may be repeatedly exposed for an 8-hour workday over a working lifetime without adverse effects. This value integrates the understanding that toxic effects generally depend on both concentration and duration. A worker exposed to the TLV-TWA for an entire shift receives the same toxic dose as one exposed to twice the TLV for 4 hours or ten times the TLV for 48 minutes.

However, some materials cause acute effects at concentrations that might be acceptable if averaged over 8 hours, so TLV-STEL (Short-Term Exposure Limit) defines the concentration to which workers can be exposed for short periods—typically 15 minutes—without suffering irritation, chronic or irreversible tissue damage, or narcosis sufficient to increase accident risk. Usually set at levels 3 to 5 times the TLV-TWA, the STEL ensures that even brief peak exposures remain below immediately hazardous levels. For materials with particularly acute effects, TLV-C (Ceiling) limits establish concentrations that must never be exceeded even momentarily.

The IDLH (Immediately Dangerous to Life or Health) concentration defines the most critical exposure limit. This represents the maximum concentration from which a person could escape within 30 minutes without experiencing any effects that would impair escape or cause irreversible health effects. IDLH values guide respirator selection and emergency planning, as workers must be able to evacuate if they encounter such concentrations. For highly toxic materials like phosgene (COCl_2), the IDLH of 2 ppm lies barely above the TLV-TWA of 0.1 ppm, leaving very little margin for error. In contrast, materials like ammonia have an IDLH of 300 ppm compared to TLV-TWA of 25 ppm, providing more warning time and greater opportunity for protective response.

Consider practical examples. Chlorine, widely used in chlorination reactions and water treatment, has a TLV-TWA of 0.5 ppm, STEL of 1 ppm, and IDLH of 10 ppm. These low values reflect chlorine's irritant and corrosive properties, which can cause severe respiratory damage. Even concentrations well below IDLH cause painful irritation that warns workers of exposure, but this warning property is insufficient protection given the rapid onset of serious injury at higher concentrations. Hydrogen sulfide presents a different hazard profile, with TLV-TWA of 10 ppm, STEL of 15 ppm, and IDLH of 100 ppm. While these limits are higher than for chlorine, hydrogen sulfide's notorious characteristic is that it deadens the sense of smell at concentrations around 50-100 ppm, eliminating the warning property just as concentrations approach IDLH. This makes hydrogen sulfide particularly insidious and demands continuous monitoring rather than reliance on odor detection.

Carbon monoxide, a common byproduct in many processes and a feedstock in carbonylation reactions, illustrates the importance of duration in toxicity. With TLV-TWA of 50 ppm and IDLH of 1200 ppm, carbon monoxide does not cause immediate dramatic effects at moderate concentrations. However, it binds strongly to hemoglobin, gradually reducing the blood's oxygen-carrying capacity. An 8-hour exposure at the TLV produces carboxyhemoglobin levels around 8-10%, causing mild headache but no severe effects in healthy individuals. Exposure to 200 ppm for 8 hours produces carboxyhemoglobin levels around 30%, causing severe headache, nausea, and impaired judgment. At IDLH concentrations, loss of consciousness occurs within minutes, and death follows if exposure continues.

Assessing the consequences of accidental releases requires understanding how much material is available, how quickly it might be released, and how it will disperse in the environment. A reactor containing 1000 kg of a material with TLV of 1 ppm represents vastly more hazard than one containing 10 kg. If released, this mass of toxic material creates a vapor cloud that dispersion models can predict will extend to specified downwind distances before dilution reduces concentrations below hazardous levels. Population density in areas that might be affected determines the number of people potentially exposed. Emergency planning zones are established based on these dispersion calculations, with inner zones where immediate evacuation might be ordered and outer zones where shelter-in-place might be more appropriate.

Engineering controls for toxicity begin with containment. Closed systems with welded piping, well-maintained gaskets, and shaft seals minimize routine emissions. Ventilation systems ensure that any releases are captured and directed to scrubbers or other treatment before atmospheric discharge. For particularly toxic materials, double containment may be appropriate, with the primary container surrounded by a secondary containment vessel or

enclosure that can capture any leaks. Detection systems provide warning of releases before concentrations reach hazardous levels. Personal protective equipment including respirators serves as the last line of defense but should not be considered primary protection because it depends on workers correctly donning equipment in emergency situations, often with limited warning.

11.4.2 Flammability and Combustion Hazards

Flammability hazards in reactor systems arise whenever organic chemicals or other combustible materials form vapor-air mixtures within flammable limits. Understanding flammability requires knowledge of several key parameters that characterize combustion behavior. The flash point defines the lowest temperature at which a liquid produces sufficient vapor to form an ignitable mixture with air near its surface. Below the flash point, vapor pressure is too low for ignition; above it, vapors can ignite if an ignition source is present. Flash point serves as a primary classification criterion: liquids with flash points below 37.8°C (100°F) are considered Class I flammable liquids requiring stringent handling precautions, while those with flash points between 37.8°C and 93.3°C (200°F) are Class II or III combustible liquids with somewhat relaxed requirements.

The Lower Explosive Limit (LEL) or Lower Flammable Limit (LFL) represents the minimum concentration of fuel vapor in air that will support flame propagation. Below the LEL, the mixture is too lean to burn. The Upper Explosive Limit (UEL) or Upper Flammable Limit (UFL) represents the maximum concentration above which the mixture is too rich to burn. These limits typically are expressed as volume percent or mole percent. The flammable range between LEL and UEL defines the concentrations where fire or explosion is possible if an ignition source is present.

Different materials show vastly different flammable ranges, reflecting their fundamental combustion chemistry. Methanol has an LEL of 6.7% and UEL of 36%, giving a relatively wide flammable range of nearly 30 percentage points. This broad range means many vapor-air mixtures involving methanol are flammable. In contrast, diesel fuel has an LEL of 0.6% and UEL of 7.5%, a much narrower range that makes ignition less likely under many conditions. Hydrogen presents an extreme case with LEL of 4.0% and UEL of 75%, an exceptionally wide flammable range that makes hydrogen particularly hazardous. At any concentration between 4% and 75%, hydrogen-air mixtures will burn if ignited.

Autoignition temperature (AIT) defines the temperature at which a fuel-air mixture will spontaneously ignite without any external ignition source such as spark or flame. This parameter determines the maximum safe surface temperature for equipment that might contact flammable atmospheres. Methanol's AIT of 464°C means that hot surfaces must be kept below this temperature, or preferably well below to maintain a safety margin. Some

materials have surprisingly low autoignition temperatures; carbon disulfide autoignites at only 90°C, close to the boiling point of water, making steam piping and even hot water lines potential ignition sources.

Vapor density relative to air determines how flammable vapors behave after release. Materials with vapor density greater than air tend to sink, accumulating in low spots, drains, pits, and confined spaces. This creates particular hazards as vapors can travel along the ground for considerable distances before encountering an ignition source, then flash back to the release point. Hexane with vapor relative density to air of about 3.0 behaves this way. Conversely, vapors lighter than air rise and disperse more readily. Methane with relative vapor density of 0.55 tends to rise and dissipate, though it can still accumulate in overhead spaces or against ceilings.



Figure 11-1 The fire triangle

The classic fire triangle teaches that combustion requires three elements: fuel, oxidizer (typically air), and an ignition source. Removing any one element prevents fire. Reactor safety systems exploit this principle through multiple approaches. Inerting eliminates the oxidizer by maintaining an inert atmosphere, typically nitrogen or carbon dioxide, in vapor spaces and process equipment. For inerting to be effective, oxygen concentration must be reduced below the Minimum Oxygen Concentration (MOC)—typically around 10-12% for hydrocarbons in nitrogen—at which combustion cannot propagate regardless of fuel concentration.

Implementing effective inerting requires continuous monitoring to ensure oxygen remains below the MOC, automatic makeup systems to replace inert gas lost through process vents or leaks, and procedures to verify inerting before introducing flammable materials. The required inert gas flow can be substantial, especially for processes that vent significant quantities of vapor. Economic considerations often favor inerting for batch or semi-batch processes where vapor space composition changes during reaction, while continuous

processes might use alternative protection. However, the inherent reliability of inerting—removing one leg of the fire triangle entirely—makes it attractive despite costs for highly hazardous materials.

Ignition source elimination addresses the third leg of the fire triangle. Common ignition sources in industrial facilities include electrical equipment that can spark during normal operation or fault conditions, static electricity accumulated on non-conductive surfaces or liquids and discharged as sparks, mechanical sparks from metal-to-metal impact especially involving aluminum or titanium, hot surfaces including process equipment, steam lines, and heated vessels, open flames from pilots, furnaces, or maintenance activities, and cutting and welding operations during maintenance. Systematic identification and control of all potential ignition sources requires careful attention during both design and operations.

Electrical equipment classification follows a rigorous system defined by the National Electrical Code in the United States and similar codes elsewhere. Class I locations contain flammable gases or vapors. Division 1 locations have flammable materials present continuously, periodically, or occasionally during normal operations, requiring explosionproof electrical equipment enclosed in housings that can contain an internal explosion and prevent flame propagation to the surrounding flammable atmosphere. Division 2 locations have flammable materials only under abnormal conditions such as vessel rupture, allowing somewhat less stringent purged and pressurized equipment. Within Class I, Groups A through D further subdivide materials by their ignitability characteristics, with Group D (including propane, gasoline, and hexane) being the least hazardous and Group A (acetylene) the most hazardous.

Static electricity control prevents spark discharge through several mechanisms. Bonding electrically connects all metallic components to ensure they reach the same electrical potential, eliminating potential difference that could drive a spark. Grounding connects the bonded system to earth, allowing accumulated charge to dissipate harmlessly. For non-conductive materials like plastics, static elimination may require conductive additives in the material, use of conductive rather than insulating materials in critical applications, or use of ionizing devices that neutralize static charge in the air. Liquid transfer operations deserve special attention because flowing liquid can generate substantial static charge through triboelectric effects, particularly when liquids with low conductivity flow at high velocity through piping and filters.

Fire detection and suppression systems provide protection if prevention measures fail. Heat detectors respond to fixed temperature thresholds or to rapidly rising temperatures. Smoke detectors sense combustion products using optical or ionization principles. Flame detectors respond to ultraviolet or infrared radiation characteristic of flames. Multiple

detection technologies used in combination reduce false alarm rates while improving reliability. Suppression systems might include water sprinklers for general fire protection, though water may be inappropriate for some chemical fires; foam systems for flammable liquid fires where the foam blanket excludes air and cools the fuel; gaseous suppression systems using carbon dioxide, inert gases, or clean agent halocarbons for areas where water damage must be avoided; or dry chemical systems for small equipment fires.

11.4.3 Explosivity and Pressure Hazards

Explosions represent rapid energy release creating pressure waves that can cause catastrophic damage. Understanding explosion hazards requires distinguishing between deflagrations and detonations, two fundamentally different modes of combustion. In deflagration, flame propagates through premixed fuel and oxidizer at subsonic velocity, typically 1 to 10 meters per second. The pressure wave ahead of the flame front compresses unburned material, accelerating the reaction. Deflagration pressures in confined spaces typically reach 8 to 10 times initial pressure—sufficient to destroy most process equipment not specifically designed to withstand explosion loads. In detonation, a shock wave propagates at supersonic velocity, typically 1000 to 3000 meters per second, with near-instantaneous combustion of material immediately behind the shock front. Detonation pressures can exceed 20 times initial pressure and create much more localized and severe damage than deflagration.

Most industrial explosions are deflagrations, but the distinction can blur. Deflagrations in long pipes or congested process areas may undergo transition to detonation as turbulence and flame acceleration create conditions for shock wave formation. Once detonation begins, it propagates at constant velocity until fuel is exhausted or the geometry changes to suppress the shock. Certain materials including acetylene, ethylene oxide, and some peroxides are prone to direct initiation of detonation, while most common flammable materials require substantial energy input or specific geometric configurations to detonate.

Vapor cloud explosions (VCE) have caused some of the most destructive industrial accidents. These events begin with release of large quantities of flammable vapor or liquid that vaporizes, forming a cloud that mixes with air and drifts with wind. If the cloud encounters an ignition source—which might be hundreds of meters from the release point—deflagration propagates through the cloud. The pressure wave damages structures and equipment, and thermal radiation from the fireball can cause burns and ignite secondary fires. The Flixborough disaster exemplified VCE consequences: approximately 40 tons of cyclohexane released at 155°C and near-atmospheric pressure, instantly flashing to vapor. The vapor cloud, estimated at 20 meters high and 60 meters in diameter, drifted across the

site before finding an ignition source. The resulting explosion completely destroyed the plant and caused damage in surrounding communities.

Preventing vapor cloud explosions requires preventing releases. This seemingly obvious statement drives much of process safety engineering. Primary containment through robust vessel and piping design, proper material selection to resist corrosion, and rigorous maintenance to prevent deterioration provides the first defense. Secondary containment such as dikes, catch pits, and drainage systems limits the spread of any releases that occur. Vapor detection systems throughout the facility provide warning of releases before clouds reach flammable size. Emergency isolation systems can limit release quantities by automatically closing valves. However, once a large release has occurred and a flammable cloud formed, few options remain beyond evacuation and ignition source elimination, with uncertain effectiveness of the latter since ignition sources may be numerous and hard to control.

Dust explosions present hazards less widely recognized than vapor explosions but equally capable of causing disaster. Many solid materials that seem innocuous in bulk form become extremely hazardous when finely divided and dispersed in air. The range of combustible dusts is remarkable: agricultural products including grain, flour, sugar, starch, wood dust, paper dust, and various food products; metals including aluminum, magnesium, titanium, zinc, and iron when in fine powder form; coal and other carbonaceous materials; plastics and resins; and pharmaceutical and organic chemical powders.

Dust explosion hazard depends on several material properties. The K_{st} value, measured in bar·meters/second, characterizes explosion severity through the rate of pressure rise during a standard test. Materials with K_{st} less than 200 are St-1 (weak explosion), 200 to 300 are St-2 (strong explosion), and above 300 are St-3 (very strong explosion). Minimum Ignition Energy (MIE) indicates sensitivity to ignition, with values below 10 millijoules indicating extreme sensitivity where even static sparks can ignite dust clouds. For comparison, the energy in a typical static spark from a person walking on carpet ranges from 10 to 100 millijoules. Minimum Explosible Concentration (MEC) defines the leanest dust concentration that will propagate flame, typically in the range of 50 to 500 g/m³.

The dust explosion pentagon adds two elements to the fire triangle: dispersion and confinement. For explosion, combustible dust must be dispersed in air at concentrations above the MEC, mixed with air containing sufficient oxygen, ignited by spark or hot surface, and confined in a vessel or building where pressure can build. Primary dust explosions often trigger far more destructive secondary explosions. When the primary explosion ruptures equipment or damages buildings, the pressure wave disperses dust that has accumulated on floors, walls, ledges, and overhead structures. This dust forms a much larger cloud in the

building, and if ignited by the primary explosion, deflagrates through the entire facility with catastrophic results. Several grain elevator explosions have followed this pattern, with initial dust explosions in elevator legs creating building-wide secondary explosions that destroyed entire facilities.

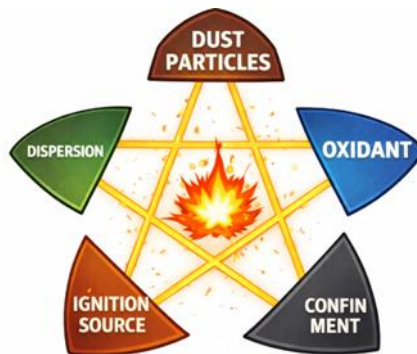


Figure 11-2 Dust explosion pentagram

The dust explosion pentagon adds two elements to the fire triangle: dispersion and confinement. For explosion, combustible dust must be dispersed in air at concentrations above the MEC, mixed with air containing sufficient oxygen, ignited by spark or hot surface, and confined in a vessel or building where pressure can build. Primary dust explosions often trigger far more destructive secondary explosions. When the primary explosion ruptures equipment or damages buildings, the pressure wave disperses dust that has accumulated on floors, walls, ledges, and overhead structures. This dust forms a much larger cloud in the building, and if ignited by the primary explosion, deflagrates through the entire facility with catastrophic results. Several grain elevator explosions have followed this pattern, with initial dust explosions in elevator legs creating building-wide secondary explosions that destroyed entire facilities.

Controlling dust explosion hazards begins with housekeeping. Regular cleaning to prevent dust accumulation removes the fuel for secondary explosions. Vacuum cleaning systems designed to safely handle combustible dusts are essential; conventional vacuum cleaners with electric motors create ignition sources. Process design seeks to minimize dust generation and maintain dust concentrations below the MEC through ventilation and exhaust. Inerting is effective but expensive, though required for some extremely hazardous materials like fine metal powders. Explosion venting provides protection by allowing pressure to discharge through a frangible panel or door before vessel rupture occurs. Explosion suppression systems detect the initial pressure rise of an incipient explosion and discharge chemical suppressant to quench the flame before pressure reaches destructive levels.

Runaway reactions create pressure through multiple mechanisms. Gas generation reactions produce non-condensable products that cannot be reduced to liquid even by cooling. Vapor generation occurs when heat from runaway reaction boils solvents or reactants. Thermal expansion of liquids can generate pressure in blocked-in vessels without any chemical reaction occurring. Decomposition reactions may generate gases from materials that seemed stable at normal operating temperatures but decompose exothermically when overheated. The 2008 Bayer CropScience incident involved methomyl oxime undergoing aldimine condensation in a residue treater, generating heat faster than cooling could remove it. Temperature rise accelerated the condensation and also triggered exothermic decomposition of residues, producing gases and heat in a runaway that the emergency relief system could not handle.

11.5 Mathematical Analysis of Reactor Stability

11.5.1 Developing Dynamic Reactor Models

Understanding reactor stability requires mathematical models that capture essential dynamic behavior. Consider an exothermic first-order reaction $A \rightarrow B$ carried out in a continuous stirred tank reactor (CSTR) with volume V , feed flow rate q_0 , and jacket cooling. The material balance on component A accounts for accumulation, input with feed, output with product stream, and consumption by reaction:

$$V \cdot \frac{dC_A}{dt} = q_0 C_{A,0} - q_0 C_A - V k(T) C_A \quad (11.1)$$

where C_A is concentration of A in the reactor (and also in the exit stream due to perfect mixing), $C_{A,0}$ is feed concentration, and $k(T)$ is the temperature-dependent rate constant following Arrhenius form $k = A \cdot \exp(-E_a/RT)$.

The energy balance considers sensible heat in feed and exit streams, heat generated by reaction, and heat removed through the jacket:

$$\rho C_p V \frac{dT}{dt} = \rho C_p q_0 T_0 - \rho C_p q_0 T + (-\Delta H_{rxn}) V k(T) C_A - UA(T - T_c) \quad (11.2)$$

where ρ is mixture density, C_p is heat capacity, T is reactor temperature, T_0 is feed temperature, $(-\Delta H_{rxn})$ is heat of reaction (positive for exothermic), U is overall heat transfer coefficient, A is heat transfer area, and T_c is coolant temperature.

These coupled nonlinear differential equations completely describe the reactor's dynamic behavior. Their solution gives $C_A(t)$ and $T(t)$ for any initial conditions and any time-varying inputs. However, analytical solution proves impossible for all but the simplest cases.

Instead, we seek to understand key features: steady states where the system can rest indefinitely, stability of these steady states, and transient behavior when moving between states or responding to disturbances.

Dividing Equation 11.1 by V and introducing residence time $\tau = V/q_0$ gives:

$$\frac{dC_A}{dt} = \frac{C_{A,0} - C_A}{\tau} - k(T) \cdot C_A \quad (11.3)$$

Similarly for the energy balance:

$$\frac{dT}{dt} = \frac{T_0 - T}{\tau} + \left[\frac{-\Delta H_{rxn}}{\rho \cdot C_p} \right] \cdot k(T) \cdot C_A - \left[\frac{UA}{\rho \cdot C_p \cdot V} \right] \cdot (T - T_c) \quad (11.4)$$

These forms more clearly show the competing processes. In the material balance, the first term $(C_{A,0} - C_A)/\tau$ represents net input of fresh reactant, tending to increase concentration when C_A is below feed concentration. The second term $k(T) \cdot C_A$ represents consumption by reaction, always decreasing concentration. At steady state these balance exactly.

In the energy balance, $(T_0 - T)/\tau$ is net sensible heat input, positive when feed is hotter than reactor and negative when reactor is hotter than feed. The second term $[(-\Delta H_{rxn})/(\rho \cdot C_p)] \cdot k(T) \cdot C_A$ represents heat generation by reaction, always positive for exothermic reactions. The third term $[UA/(\rho \cdot C_p \cdot V)] \cdot (T - T_c)$ represents heat removal through jacket, positive (removing heat) when reactor temperature exceeds coolant temperature. At steady state, sensible heat terms plus heat generation exactly balance heat removal.

Consider Equation 5.14 with heat transfer $\dot{Q} = UA_{HT}(T_c - T)$. Define:

Heat generation curve: $Q_{gen} = (-\Delta H_{rxn})rV(T)$

Heat removal curve: $Q_{rem} = F_{A,0}\bar{C}_p(T - T_0) + UA_{HT}(T - T_c)$

There may be multiple solutions for steady state for $Q_{gen}=Q_{rem}$ as seen in **Fel! Hittar inte referenskälla..**

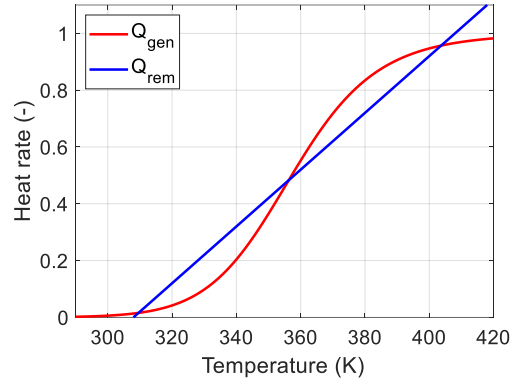


Figure 11-3 Heat generation and heat removal in a CSTR

11.5.2 Dimensionless Formulation and Parameter Groups

Physical insight improves through dimensionless formulation that reveals controlling parameter groups. Define dimensionless concentration $\omega = \mathbf{C}_A/\mathbf{C}_{A,0}$, dimensionless temperature relative to coolant $\psi = (\mathbf{T} - \mathbf{T}_c)/\mathbf{T}_c$, and dimensionless time $\theta = \mathbf{t}/\tau$. Additionally, define the dimensionless heat generation parameter $\gamma = (-\Delta H_{rxn}) \cdot \mathbf{C}_{A,0}/(\rho \cdot \mathbf{C}_p \cdot \mathbf{T}_c)$, which represents the adiabatic temperature rise (with no cooling) relative to coolant temperature if all entering reactant converts. Define the dimensionless activation energy $\beta = \mathbf{E}_a/(\mathbf{R} \cdot \mathbf{T}_c)$, which measures temperature sensitivity. Define the dimensionless heat transfer parameter $\mathbf{B} = \mathbf{UA}/(\rho \cdot \mathbf{C}_p \cdot \mathbf{q}_0)$, representing the ratio of heat removal capacity to the heat capacity flow rate of the process stream. Finally, define the Damköhler number $\mathbf{Da} = \mathbf{k}(\mathbf{T}_c) \cdot \tau$, the ratio of reaction time scale to residence time scale, evaluated at coolant temperature.

With these transformations, the Arrhenius expression becomes $k(\mathbf{T}) = k(\mathbf{T}_c) \cdot \exp[\beta \cdot \psi/(1+\psi)]$ where the approximation $\mathbf{T}/(\mathbf{T}_c + (\mathbf{T} - \mathbf{T}_c)) = 1/(1+\psi)$ is used. The dimensionless material balance is:

$$\frac{d\omega}{d\theta} = 1 - \omega - \mathbf{Da} \cdot \omega \cdot \exp\left[\beta \cdot \frac{\psi}{1 + \psi}\right] \quad (11.5)$$

The dimensionless energy balance, accounting for feed temperature $\psi_0 = (\mathbf{T}_0 - \mathbf{T}_c)/\mathbf{T}_c$, becomes:

$$\frac{d\psi}{d\theta} = \psi_0 - \psi + \gamma \cdot \mathbf{Da} \cdot \omega \cdot \exp\left[\beta \cdot \frac{\psi}{1 + \psi}\right] - \mathbf{B} \cdot \psi \quad (11.6)$$

These compact equations reveal several insights. The term $\mathbf{Da} \cdot \exp[\beta \cdot \psi/(1+\psi)]$ appearing in both equations represents the effective reaction rate constant at the actual reactor temperature relative to the rate at coolant temperature. When $\psi = 0$ (reactor at coolant temperature), this term equals \mathbf{Da} . As temperature increases, the exponential factor grows rapidly due to the β in the exponent. For $\beta = 20$ and $\psi = 0.1$ (reactor 10% hotter than coolant

in absolute temperature), $\exp[20 \times 0.1 / (1 + 0.1)] \approx \exp(1.818) \approx 6.16$, so the effective Da increases more than sixfold. This exponential temperature sensitivity drives instability in exothermic systems with high activation energy.

The parameter γ appears only in the energy balance, multiplying the reaction rate term. Large γ means substantial heat generation per unit reaction, making temperature more sensitive to changes in reaction rate. The heat transfer parameter B appears in the cooling term $-B \cdot \psi$, showing that large B (good cooling) tends to stabilize by strongly resisting temperature deviations. The balance between γ (promoting temperature rise) and B (promoting temperature decrease) fundamentally determines stability characteristics.

11.5.3 Steady States and Multiplicity

Steady states exist where both time derivatives vanish: $d\omega/d\theta = 0$ and $d\psi/d\theta = 0$. From Equation 11.5 at steady state:

$$0 = 1 - \omega_s - Da \cdot \omega_s \cdot \exp[\beta \cdot \psi_s / (1 + \psi_s)]$$

Solving for ω_s :

$$\omega_s = \frac{1}{1 + Da \cdot \exp\left[\beta \cdot \frac{\psi_s}{1 + \psi_s}\right]} \quad (11.7)$$

This shows concentration as a function of temperature at steady state. As temperature increases, the exponential term grows, making the denominator larger and ω_s smaller. Physically, higher temperature means faster reaction and therefore lower steady-state reactant concentration (higher conversion).

From Equation 11.6 at steady state:

$$0 = \psi_0 - \psi_s + \gamma \cdot Da \cdot \omega_s \cdot \exp[\beta \cdot \psi_s / (1 + \psi_s)] - B \cdot \psi_s$$

Solving for ψ_s :

$$\psi_s = \frac{\psi_0 + \gamma \cdot Da \cdot \omega_s \cdot \exp\left[\beta \cdot \frac{\psi_s}{1 + \psi_s}\right]}{1 + B} \quad (11.8)$$

Equations 11.7 and 11.8 must be satisfied simultaneously. Substituting Equation 11.7 into Equation 11.8 gives:

$$\psi_s = \frac{\left[\psi_0 + \gamma \cdot Da \cdot \frac{\exp\left[\beta \cdot \frac{\psi_s}{1 + \psi_s}\right]}{\left\{1 + Da \cdot \exp\left[\beta \cdot \frac{\psi_s}{1 + \psi_s}\right]\right\}} \right]}{1 + B} \quad (11.9)$$

This implicit equation for ψ_s may have one, three, or even five solutions depending on parameter values. Multiple solutions arise from the S-shaped nature of the heat generation curve plotted against temperature (**Fel! Hittar inte referenskälla.**). At low temperatures, heat generation is low due to slow reaction rate. As temperature increases, heat generation rises exponentially. Eventually, as conversion approaches completion, further temperature increase produces less additional heat generation because reactant concentration becomes limiting. This creates an S-curve that may intersect the linear heat removal line multiple times.

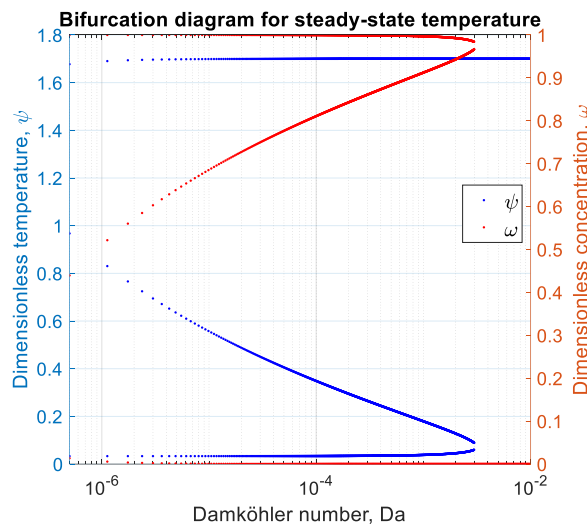


Figure 11-4 Range of multiple steady states

Understanding which parameter combinations lead to multiplicity guides design. For given values of γ , β , B , and ψ_0 , there exists a critical Damköhler number above which three steady states exist. Below this critical Da , only one steady state exists—at low temperature with low conversion if Da is very small, or at high temperature with high conversion if Da is moderate. There are two bifurcation points in the figure above. A lower point at $Da=10^{-6}$ and a higher at $Da=3 \cdot 10^{-3}$. Above the critical Da , 10^{-6} , three steady states appear: a low-temperature state with low conversion, an intermediate-temperature unstable state, and a high-temperature state with high conversion. The middle state invariably proves unstable upon stability analysis, serving as a separatrix between the basins of attraction of the stable states. A Da above $3 \cdot 10^{-3}$ only one steady state exist at high temperature and high conversion.

Increasing γ (more heat release per conversion) or β (stronger temperature sensitivity) promotes multiplicity by making the heat generation curve more nonlinear. Decreasing B (poorer cooling) has similar effect because it steepens the required heat removal line, making multiple intersections more likely. Feed temperature ψ_0 can shift the system between regimes; preheating feed may eliminate the low-temperature steady state, ensuring the reactor must operate at high temperature and conversion.

11.6 Lyapunov Stability Theory and Eigenvalue Analysis

11.6.1 Linearization Around Steady States

While phase plane visualization provides qualitative understanding, rigorous stability determination requires mathematical analysis. Lyapunov's linearization method examines system behavior near steady states by approximating the nonlinear dynamics with linear equations valid for small perturbations. Consider the general form of our reactor equations:

$$\frac{d\omega}{d\theta} = f_{\omega}(\omega, \psi) \quad (11.10)$$

$$\frac{d\psi}{d\theta} = f_{\psi}(\omega, \psi) \quad (11.11)$$

where f_{ω} and f_{ψ} represent the right-hand sides of Equations 11.5 and 11.6. At a steady state (ω_s, ψ_s) , both functions vanish: $f_{\omega}(\omega_s, \psi_s) = 0$ and $f_{\psi}(\omega_s, \psi_s) = 0$.

Define perturbations from steady state: $\delta\omega = \omega - \omega_s$ and $\delta\psi = \psi - \psi_s$. For small perturbations, Taylor series expansion gives:

$$\frac{d(\delta\omega)}{d\theta} = \left(\frac{\partial f_{\omega}}{\partial \omega}\right)_{|_s} \cdot \delta\omega + \left(\frac{\partial f_{\omega}}{\partial \psi}\right)_{|_s} \cdot \delta\psi + \text{higher order terms} \quad (11.12)$$

$$\frac{d(\delta\psi)}{d\theta} = \left(\frac{\partial f_{\psi}}{\partial \omega}\right)_{|_s} \cdot \delta\omega + \left(\frac{\partial f_{\psi}}{\partial \psi}\right)_{|_s} \cdot \delta\psi + \text{higher order terms} \quad (11.13)$$

where subscript s indicates evaluation at steady state. Neglecting higher order terms (valid for sufficiently small perturbations), we obtain the linearized system:

$$\frac{d}{d\theta} [\delta\omega] = \begin{bmatrix} \frac{\partial f_{\omega}}{\partial \omega} & \frac{\partial f_{\omega}}{\partial \psi} \end{bmatrix}_s \begin{bmatrix} \delta\omega \\ \delta\psi \end{bmatrix} \quad (11.14)$$

$$\frac{d}{d\theta} [\delta\psi] = \begin{bmatrix} \frac{\partial f_{\psi}}{\partial \omega} & \frac{\partial f_{\psi}}{\partial \psi} \end{bmatrix}_s \begin{bmatrix} \delta\omega \\ \delta\psi \end{bmatrix} \quad (11.15)$$

The matrix of partial derivatives is the Jacobian matrix J , evaluated at the steady state:

$$J = \begin{bmatrix} J_{11} & J_{12} \\ J_{21} & J_{22} \end{bmatrix} \quad (11.16)$$

where

$$J_{11} = \frac{\partial f_\omega}{\partial \omega} = -1 - Da \cdot \exp \left[\beta \cdot \frac{\psi_s}{1 + \psi_s} \right] \quad (11.17)$$

$$J_{12} = \frac{\partial f_\omega}{\partial \psi} = -Da \cdot \omega_s \cdot \beta \cdot \frac{\exp \left[\beta \cdot \frac{\psi_s}{1 + \psi_s} \right]}{(1 + \psi_s)^2} \quad (11.18)$$

$$J_{21} = \frac{\partial f_\psi}{\partial \omega} = \gamma \cdot Da \cdot \exp \left[\beta \cdot \frac{\psi_s}{1 + \psi_s} \right] \quad (11.19)$$

$$J_{22} = \frac{\partial f_\psi}{\partial \psi} = -(1 + B) + \gamma \cdot Da \cdot \omega_s \cdot \beta \cdot \frac{\exp \left[\beta \cdot \frac{\psi_s}{1 + \psi_s} \right]}{(1 + \psi_s)^2} \quad (11.20)$$

These derivatives capture how changes in ω and ψ affect the rates of change $d\omega/d\theta$ and $d\psi/d\theta$. Element J_{11} shows how concentration rate of change responds to concentration perturbations. The negative sign indicates that higher concentration leads to more rapid decrease (through increased reaction consumption), a stabilizing effect. Element J_{12} shows how concentration rate responds to temperature perturbations. Negative sign indicates that higher temperature increases reaction rate, consuming more reactant and decreasing concentration.

Element J_{21} shows how temperature rate responds to concentration perturbations. Positive sign reflects that more reactant produces more heat generation (for exothermic reactions with $\gamma > 0$), increasing temperature—a destabilizing effect. Element J_{22} shows how temperature rate responds to temperature perturbations. The term $-(1+B)$ is stabilizing (higher temperature increases heat removal), while the term $+\gamma \cdot Da \cdot \omega_s \cdot \beta \cdot \exp[\dots]/(\dots)$ is destabilizing (higher temperature increases reaction rate and heat generation). Their relative magnitudes determine whether the net effect stabilizes or destabilizes.

11.6.2 Eigenvalue Calculation and Stability Criteria

The linearized system $d(\delta x)/d\theta = J \cdot \delta x$, where $\delta x = [\delta \omega, \delta \psi]^T$, has solutions of the form $\delta x(\theta) = v \cdot \exp(\lambda \theta)$, where λ is an eigenvalue and v is the corresponding eigenvector. Substituting into the differential equation:

$$\lambda \cdot v \cdot \exp(\lambda \theta) = J \cdot v \cdot \exp(\lambda \theta)$$

Simplifying:

$$J \cdot v = \lambda \cdot v$$

This is the eigenvalue problem. Nontrivial solutions ($v \neq 0$) exist only when:

$$\det(J - \lambda I) = 0 \quad (11.21)$$

where I is the identity matrix. For our 2×2 system:

$$\det \begin{bmatrix} J_{11} - \lambda & J_{12} \\ J_{21} & J_{22} - \lambda \end{bmatrix} = 0 \quad (11.22)$$

Expanding the determinant:

$$\begin{aligned} (J_{11} - \lambda)(J_{22} - \lambda) - J_{12} \cdot J_{21} &= 0 \\ \lambda^2 - (J_{11} + J_{22}) \cdot \lambda + (J_{11} \cdot J_{22} - J_{12} \cdot J_{21}) &= 0 \end{aligned}$$

results in

$$\lambda^2 - \text{tr}(J) \cdot \lambda + \det(J) = 0 \quad (11.23)$$

where $\text{tr}(J) = J_{11} + J_{22}$ is the trace and $\det(J) = J_{11} \cdot J_{22} - J_{12} \cdot J_{21}$ is the determinant. The quadratic formula gives:

$$\lambda_{1,2} = [\text{tr}(J) \pm \sqrt{(\text{tr}(J))^2 - 4 \cdot \det(J)}] / 2 \quad (11.24)$$

The eigenvalues completely determine linear stability. If both eigenvalues have negative real parts, all perturbations decay exponentially: $\delta\omega(\theta)$ and $\delta\psi(\theta) \rightarrow 0$ as $\theta \rightarrow \infty$. The steady state is asymptotically stable. If at least one eigenvalue has positive real part, some perturbations grow exponentially and the steady state is unstable. If eigenvalues have zero real part (purely imaginary eigenvalues), the linearization is marginally stable with oscillatory response, though neglected nonlinear terms might cause growth or decay.

For 2×2 matrices, algebraic conditions on trace and determinant directly determine stability:

Lyapunov stability criteria

Stable if and only if:

$$\text{tr}(J) < 0 \text{ AND } \det(J) > 0 \quad (11.25)$$

Unstable if:

$$\text{tr}(J) > 0 \text{ OR } \det(J) < 0 \quad (11.26)$$

The trace condition $\text{tr}(J) < 0$ requires that the sum of diagonal elements be negative. Since J_{11} is always negative (from the -1 term), this condition primarily demands that J_{22} not be too positive. Recalling $J_{22} = -(1+B) + \gamma \cdot Da \cdot \omega_s \cdot \beta \cdot \exp[\dots]/(\dots)$, the condition requires that heat

removal term $-(1+B)$ dominate the heat generation term. Strong cooling (large B) promotes stability by making J_{22} more negative. Weak cooling allows J_{22} to become positive, leading to instability.

The determinant condition $\det(J) > 0$ requires $J_{11} \cdot J_{22} > J_{12} \cdot J_{21}$. Since J_{11} and J_{12} are both negative while J_{21} is positive, the product $J_{12} \cdot J_{21}$ is negative. The product $J_{11} \cdot J_{22}$ can be positive or negative depending on the sign of J_{22} . When J_{22} is negative (good cooling dominates heat generation temperature sensitivity), $J_{11} \cdot J_{22}$ is positive and $\det(J) > 0$ is satisfied. When J_{22} becomes positive, $J_{11} \cdot J_{22}$ becomes negative, and $\det(J)$ may become negative, indicating a saddle point instability.

Complex eigenvalues occur when $(\text{tr}(J))^2 < 4 \cdot \det(J)$, giving:

$$\lambda_{1,2} = [\text{tr}(J) \pm i \cdot \sqrt{4 \cdot \det(J) - (\text{tr}(J))^2}] / 2 \quad (11.27)$$

The real part $\text{tr}(J)/2$ determines stability while the imaginary part $\omega_{\text{osc}} = \sqrt{4 \cdot \det(J) - (\text{tr}(J))^2}/2$ determines oscillation frequency. Negative real part with nonzero imaginary part produces damped oscillations spiraling toward steady state. Positive real part produces growing oscillations spiraling away from steady state. Zero real part (requiring $\text{tr}(J) = 0$ exactly) produces sustained oscillations of constant amplitude, though this is not robust to parameter variations.

The eigenvalue analysis provides not just stability determination but quantitative information about dynamic response. The eigenvalue with largest (least negative) real part dominates long-time behavior, determining the time constant for return to steady state after disturbances. If this dominant eigenvalue is -0.5 , perturbations decay with time constant $2/\tau$ (since $\theta = t/\tau$). If both eigenvalues are -3 and -10 , the system responds quickly with time constant approximately $\tau/3$ for the fast mode and $\tau/10$ for the faster mode.

11.7 Parametric Sensitivity and Safe Operating Regions

11.7.1 Defining and Quantifying Sensitivity

Parametric sensitivity describes disproportionate response of steady-state values to small changes in operating parameters. A reactor with high sensitivity might see outlet temperature change by 50 K when feed temperature changes by 2 K, or conversion drop from 95% to 70% when coolant temperature rises by 5 K. Such extreme sensitivity makes the process difficult to control and creates safety concerns because normal parameter variations can trigger major upsets.

Sensitivity can be quantified through dimensionless sensitivity coefficients:

$$S_p = \left(\frac{\partial x_s}{\partial p} \right) \cdot \left(\frac{p}{x_s} \right) \quad (11.28)$$

where x_s is a steady-state variable of interest (temperature or concentration), p is a parameter (feed temperature, coolant temperature, residence time), and $\partial x_s / \partial p$ is the partial derivative evaluated at the nominal operating point. This dimensionless coefficient represents the fractional change in x_s per fractional change in p . Values near unity indicate proportional response: 1% change in parameter causes roughly 1% change in state variable. Values much greater than unity indicate high sensitivity.

Computing sensitivity requires differentiating the steady-state equations (11.7 and 11.8) with respect to the parameter of interest. For example, sensitivity to coolant temperature T_c affects the reactor through the dimensionless parameters $\beta = Ea/(R \cdot T_c)$, $\psi = (T - T_c)/T_c$, and $B = UA/(\rho \cdot C_p \cdot q_0)$. Each contains T_c , so changing T_c affects the entire dimensionless formulation. This analysis becomes algebraically complex but can be performed numerically by solving for steady state at several nearby values of T_c and computing finite difference approximations to $\partial T_s / \partial T_c$.

High sensitivity occurs near bifurcation points where the system behavior changes qualitatively. At a saddle-node bifurcation, two steady states (one stable, one unstable) collide and annihilate as a parameter varies. Near this bifurcation point, small parameter changes cause large state changes because the system is transitioning between regimes with different numbers of steady states. Physically, the heat generation and removal curves are nearly tangent at such points, so slight parameter shifts dramatically change their intersection.

Operating near high sensitivity regions, while sometimes unavoidable for achieving desired conversion, requires robust control systems and conservative operating margins. If coolant temperature must be maintained within ± 2 K to keep reactor temperature within acceptable range, the cooling system must have sufficient capacity and reliability to achieve this tight control even during upsets. Process design that minimizes sensitivity—through inherent safety measures or operating point selection—proves more reliable than depending on control to manage sensitive operation.

11.7.2 Thermal Runaway Criteria and Warning Signs

Thermal runaway occurs when heat generation capability exceeds heat removal capacity with no stable steady state existing. The system possesses no equilibrium point to approach; instead, temperature and reaction rate accelerate without bound until reactants are exhausted, pressure relief occurs, or catastrophic failure intervenes. Preventing thermal runaway requires understanding conditions under which it becomes possible.

A classical runaway criterion for the CSTR system emerges from analyzing when the heat generation curve becomes everywhere steeper than the heat removal line. This occurs when:

$$\frac{\gamma \cdot \beta \cdot Da}{1 + B} > 4 \quad (11.29)$$

This criterion combines the four key dimensionless parameters. Large γ (high exothermicity), large β (strong temperature sensitivity), large Da (fast reaction relative to residence time), and small B (poor cooling) all promote runaway potential. The threshold value of 4 is approximate, derived from simplified analysis, but provides useful guidance.

Interpreting this criterion physically: γ represents adiabatic temperature rise potential if all feed converts with no cooling. β represents how strongly reaction rate responds to this temperature rise. The product $\gamma \cdot \beta$ thus captures the inherent thermal sensitivity of the chemistry. Da represents how fast the reaction proceeds, determining how quickly heat generates. The ratio $(1+B)$ represents cooling effectiveness; small B means poor cooling. When the ratio of thermal generation potential to cooling capacity exceeds the critical threshold, runaway becomes possible.

Practical warning signs of approaching thermal runaway include:

Temperature rising steadily despite cooling system operating at maximum capacity. In normal stable operation, the control system maintains temperature by modulating cooling. If temperature rises while cooling valve is wide open and additional cooling capacity is unavailable, the system may be entering runaway.

Positive feedback in temperature response: small increases in temperature produce disproportionately large increases in the rate of temperature rise (d^2T/dt^2). This indicates that the exponential Arrhenius term is dominating the dynamics.

Loss of control authority: the cooling system no longer effectively regulates temperature. Moving the coolant valve produces little effect on reactor temperature because heat generation is overwhelming removal.

Accelerating approach to relief valve set point: if temperature or pressure is approaching safety relief conditions and the rate of approach is increasing, runaway may be imminent and emergency action is required immediately.

These observational criteria supplement theoretical analysis and enable operating personnel to recognize and respond to developing runaways before relief system activation or vessel failure.

11.7.3 Safe Operating Windows and Bifurcation Diagrams

The safe operating region defines parameter ranges where only stable steady states exist, with adequate margins against instability, runaway, or other hazardous conditions. Mapping this region requires examining how steady-state behavior changes as parameters vary—an analysis captured in bifurcation diagrams that plot steady-state values versus a parameter.

Consider a bifurcation diagram with Damköhler number Da on the horizontal axis and dimensionless steady-state temperature ψ_s on the vertical axis, with other parameters (γ, β, B, ψ_0) fixed if **Fel! Hittar inte referenskälla..** At very low Da (slow reaction), only one steady state exists at low temperature, near $\psi_s \approx \psi_0$, with low conversion because insufficient time exists for reaction. As Da increases, this low-temperature steady state moves upward in temperature as faster reaction produces more heat. At a critical Da value, two additional steady states appear suddenly through a saddle-node bifurcation. The bifurcation diagram shows three branches: the low-temperature branch continuing upward, a middle branch of unstable saddle points, and an upper branch of high-temperature high-conversion stable states.

A safe operating window can be analyzed for all the operating variables. **Fel! Hittar inte referenskälla.** shows the attainable steady states as function of cooling.

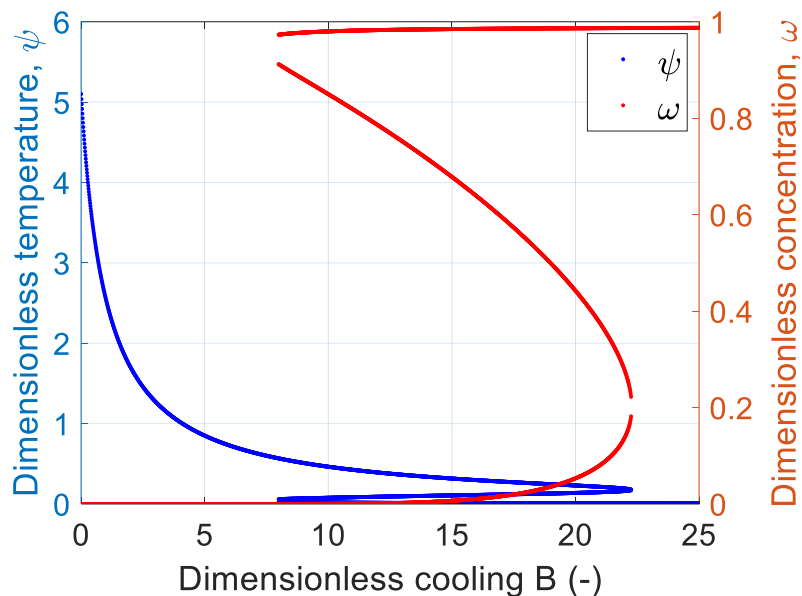


Figure 11-5 Bifurcation diagram vs cooling

At low cooling with $B < 8$ only one steady state at high conversion is possible. In the range $8 < B < 22$ there are three possible steady states, but the intermediate steady state is probably unstable. With high cooling rate ($B > 22$) only one steady state exist with very low conversion.

This S-shaped bifurcation diagram creates hysteresis: the system behavior depends on history, not just current parameters. If we gradually increase cooling starting from low values at (1), the reactor follows the high-temperature branch until reaching the upper saddle-node point (2), where this branch disappears. The system then jumps discontinuously to the lower temperature branch (3). If we subsequently decrease cooling, the reactor follows the low-temperature branch and only returns to high temperature when cooling decreases below the lower saddle-node point (4). The reactor can operate at different steady states depending on whether cooling is being increased or decreased.

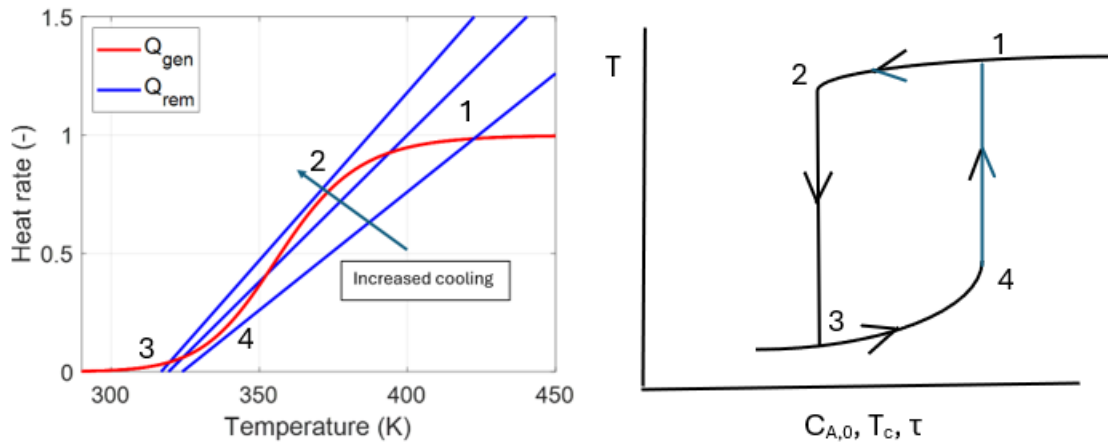


Figure 11-6 Possible steady-states depending on cooling rate (left) and corresponding hysteresis loop (right)

Understanding this hysteresis proves crucial for startup. Simply setting parameters to their intended operating values may place the reactor in the basin of attraction of the undesired low-temperature state rather than the desired high-temperature state. Startup procedures must temporarily use parameter values that eliminate the low-temperature steady state, ensuring the reactor ignites and reaches high conversion, then adjust parameters to final values where high-temperature operation remains stable.

The safe operating window excludes regions where unstable operation occurs, where runaway is possible, where steady-state conversion is unacceptably low, where temperature or pressure approach equipment limits, or where small parameter variations cause transitions to undesired states. Conservative design operates well within the safe window, providing margins against process variability, equipment degradation, and operational errors. Operating near boundaries risks upset from inevitable disturbances.

Constructing safe operating maps requires solving the steady-state equations and performing stability analysis across ranges of relevant parameters. Modern computational tools enable this analysis, producing contour plots showing regions of stable operation,

curves of bifurcation points, and iso-lines of constant conversion or temperature. Such maps guide process design by revealing the interplay between parameters and by identifying which parameter adjustments most effectively improve stability.

11.8 Process-Related Risks in Reactor Operation

11.8.1 Thermal Runaway Mechanisms and Consequences

Beyond the theoretical stability analysis, understanding how thermal runaways actually develop in industrial reactors requires examining the specific mechanisms through which control is lost and the cascading consequences that follow. Reaction rate runaway represents the most straightforward mechanism, arising directly from the Arrhenius temperature dependence combined with inadequate heat removal. When a disturbance causes temperature to rise slightly—perhaps from a feed composition upset, partial loss of cooling, or momentary agitation failure—the reaction rate increases exponentially. This faster reaction generates additional heat at a rate that exceeds the cooling system's ability to respond. The temperature rises further, accelerating the reaction even more rapidly, establishing a vicious cycle that feeds on itself.

The mathematics of this acceleration reveal why thermal runaways can develop so suddenly. Consider a system with dimensionless activation energy $\beta = 25$, not unusual for industrially important reactions. A temperature increase of just 5% above the coolant temperature (ψ increasing from 0 to 0.05) causes the rate constant to increase by a factor of $\exp[25 \times 0.05/(1.05)] = \exp(1.19) = 3.3$. The reaction proceeds more than three times faster, generating heat three times faster, from just a 5% temperature increase. If this heat cannot be removed quickly enough, temperature continues rising. A further increase to $\psi = 0.10$ gives rate enhancement of $\exp[25 \times 0.10/1.10] = \exp(2.27) = 9.7$ times the initial rate. By the time temperature has risen 20% ($\psi = 0.20$), the reaction proceeds 46 times faster than at coolant temperature. This exponential acceleration explains why runaways that seem manageable in their early stages can suddenly become uncontrollable.

Accumulation runaway presents a particularly insidious hazard in semi-batch reactors where one reactant is added gradually to another. This operating mode is often chosen specifically to control exothermic reactions by limiting the quantity of reactant present at any time. However, if cooling fails or becomes insufficient during the addition period, temperature rises but may remain subcritical because the reaction rate, though elevated, consumes reactant as fast as it enters. The key danger is that unreacted material accumulates. If the operator stops feed to address the temperature upset but then resumes feed after cooling is restored, the accumulated material suddenly reacts with the freshly added reactant. The heat release from this accumulated inventory can overwhelm the

cooling system that was adequate for normal feed rates, triggering runaway despite cooling now functioning properly.

The Seveso disaster of 1976 illustrated accumulation runaway with tragic consequences. During production of 2,4,5-trichlorophenol, an exothermic reaction was underway when the batch had to be interrupted over a weekend. Heating was shut off but agitation also stopped, allowing material to settle. When the reactor was reheated on Monday for the next reaction step, the accumulated material suddenly reacted, temperature rose uncontrollably, and pressure ruptured a safety disc. The release vented dioxin-contaminated material across the town of Seveso, Italy, contaminating an area that required decades to remediate.

Decomposition runaway occurs when temperature rises beyond the normal operating range trigger exothermic decomposition of products, intermediates, or even intended reactants. Many organic compounds decompose exothermically at elevated temperatures, and some of these decompositions autocatalyze or produce gases that further increase pressure. Nitro compounds, peroxides, azo compounds, and various organic intermediates in pharmaceutical synthesis can exhibit such behavior. The primary reaction may be well-controlled, but if temperature rises significantly due to cooling loss or other upset, decomposition initiates and provides an additional heat source independent of the intended reaction chemistry. This secondary heat source can sustain runaway even if the primary reaction is stopped by terminating feed.

The consequences of thermal runaway depend on the specific chemistry, containment strength, and relief system capacity. Pressure rise invariably accompanies temperature increase. For reactions generating gaseous products or occurring in systems where boiling occurs, pressure can increase faster than temperature. The ideal gas relationship $P/T = \text{constant}$ (at fixed volume and moles) suggests that doubling absolute temperature doubles pressure, but in reality gas generation reactions increase both temperature and number of moles, producing pressure increases far exceeding what thermal expansion alone would predict. A runaway that reaches 100 K temperature rise might easily produce 5-10 bar pressure increase, potentially exceeding vessel design pressure if the initial operating pressure was significant.

If pressure exceeds the relief valve set point, the relief system activates, venting vapor and potentially liquid to a disposal system. Properly sized relief provides protection by preventing pressure from exceeding vessel rupture pressure. However, relief system activation itself creates hazards. The relieved material may be toxic, requiring scrubbing or other treatment before atmospheric release. If flammable vapors are relieved to atmosphere, vapor clouds may form and subsequently ignite. For runaway reactions, the relief rate may be quite large,

and the duration may extend for many minutes or even hours as all reactive material must decompose or convert. Disposal systems must handle these worst-case scenarios.

Two-phase flow complicates relief system design substantially. When liquid boils vigorously or when chemical reactions generate gas bubbles rapidly within liquid, the two-phase mixture occupies far greater volume than liquid alone, reducing the effective cross-sectional area available for vapor flow. Relief devices sized for vapor-only service using conventional methods may have capacity reduced by factors of two to five when relieving two-phase mixtures. The DIERS (Design Institute for Emergency Relief Systems) methodology, developed specifically to address runaway reaction venting, provides correlations for two-phase relief sizing based on experimental measurements of reaction violence and vapor generation characteristics.

If pressure rises faster than the relief system can handle, or if the relief system fails to operate, vessel rupture becomes possible. Ductile rupture typically occurs through tearing along seams or at nozzles, releasing contents through the opening but leaving most of the vessel structure intact. Brittle fracture shatters the vessel into fragments that become projectiles, and the rapid release of stored energy propels these fragments considerable distances. Blast waves from rapid pressure release can damage nearby structures and injure personnel. If flammable or toxic materials are released, secondary consequences follow.

11.8.2 Equipment Failure Modes and Reliability

Reactor safety depends critically on proper functioning of numerous equipment items, each with its own failure modes and characteristic failure rates. Understanding these failure mechanisms enables better design, maintenance, and protection system specification. Pumps, essential for circulating cooling water, transferring feed, and removing product, fail through several mechanisms. Mechanical seal failures represent the most common problem, occurring when the seal faces separate due to misalignment, vibration, wear, or loss of seal flush. Modern reactor installations increasingly use double mechanical seals with barrier fluid in the space between seals. Failure of the inner seal contaminates the barrier fluid but maintains containment, triggering an alarm that allows controlled shutdown before outer seal failure would release process fluid. For especially hazardous services, magnetic drive pumps eliminate shaft seals entirely by using magnetic coupling to transmit torque through a containment shell.

Pump bearing failures result from lubrication loss, contamination, misalignment, or fatigue. Vibration monitoring can detect deteriorating bearings before catastrophic failure, enabling preventive maintenance. Cavitation, caused by insufficient net positive suction head (NPSH), creates vapor bubbles at the impeller inlet that subsequently collapse violently, eroding impeller surfaces and generating high-frequency vibration and noise. Proper suction

system design ensuring adequate NPSH available exceeds NPSH required by safe margin prevents cavitation damage.

Agitators in reactors provide mixing essential for heat transfer, mass transfer, and reaction uniformity. Agitator failure can cause local hot spots, settling of solids, phase separation in immiscible systems, or loss of heat transfer effectiveness. Mechanical seal failures occur similarly to pumps. Shaft failures, though rare, can occur from fatigue at stress concentrations, particularly if the shaft experiences alternating stresses from unbalanced loads or vibration. If an agitator shaft breaks, the impeller may remain in the vessel or may fall to the bottom, either case potentially damaging the vessel bottom or internal coils. More significantly, loss of agitation immediately compromises heat transfer and mixing, potentially initiating thermal runaway in exothermic systems.

Heat exchangers can fail through fouling, corrosion, erosion, or mechanical failure. Fouling deposits accumulate on heat transfer surfaces from precipitation of dissolved materials, polymerization, coking, or biological growth. Fouling acts as insulation, reducing the overall heat transfer coefficient U and diminishing cooling capacity. Reactors must be designed accounting for anticipated fouling rates, and fouling must be monitored so that cleaning occurs before heat transfer degradation becomes critical. Corrosion can attack either process-side or utility-side surfaces depending on fluid chemistry. Cooling water containing chlorides can cause stress corrosion cracking of stainless steel. Acidic process streams can corrode carbon steel shells. Tube-side corrosion may cause tube wall thinning leading to leaks that allow intermixing of process fluid and cooling water, potentially causing contamination, loss of cooling, or hazardous reactions if the two streams are incompatible.

Instrumentation failures create hazards by providing incorrect information for control decisions or failing to detect abnormal conditions. Sensor drift, where measured values gradually deviate from true values, results from aging, exposure to harsh environments, coating or fouling of sensing elements, or changes in calibration. Regular calibration compensates for drift, but the required frequency depends on service conditions. Some applications require continuous self-diagnostics with automatic alarms if sensor output becomes suspect. Complete sensor failure, where output freezes or becomes clearly erroneous, is often more easily detected than subtle drift, but fail-safe design requires planning for how the system should respond. Temperature sensors typically fail to low readings (open circuit in thermocouples, infinite resistance in RTDs), so a failed sensor would indicate impossibly cold conditions. This "fail-low" characteristic means that safety systems using high-temperature trips must be configured to trip on sensor failure as well as high reading, preventing the scenario where actual high temperature cannot trip the system because the sensor has failed low.

Control valve failures can strand the valve in position (freeze), cause slow or erratic movement, or allow internal leakage past the seat when closed. Valve freeze occurs from loss of actuation air, mechanical binding, freezing of process fluid, or packing that has been overtightened. Control systems must specify whether each valve should fail open or fail closed on loss of actuation pressure, with the choice made based on safety considerations. For a cooling water valve supplying a reactor jacket, fail-open provides maximum cooling if actuation fails, generally the safer choice. For a reactant feed valve, fail-closed prevents continued feed if control is lost, again usually safer. Some processes require fail-in-place valves that lock in their last position on actuation loss, though this provides no failure protection and is only appropriate when any valve position can be tolerated safely.

The reliability engineering discipline quantifies failure probabilities using failure rate data from industry databases, manufacturer information, and plant-specific experience. Failure rates are typically expressed as failures per year or failures per million hours of operation. A centrifugal pump might have failure rate of 0.5 per year (mean time between failures of 2 years), while a manual valve might have failure rate 0.01 per year (mean time between failures of 100 years). These base failure rates apply to well-maintained equipment in moderate service. Aggressive environments, poor maintenance, or operation beyond design conditions significantly increase failure rates.

When multiple components must function together, overall system reliability depends on component configuration. Series systems, where failure of any single component causes system failure, have reliability less than the least reliable component. If two components with individual reliabilities $R_1 = 0.99$ and $R_2 = 0.98$ are in series, system reliability is $R_{sys} = R_1 \times R_2 = 0.97$. Parallel (redundant) systems, where all components must fail simultaneously for system failure, achieve higher reliability. If two components each with reliability 0.99 are in parallel, system reliability is $1 - (1-R_1)(1-R_2) = 1 - (0.01)(0.01) = 0.9999$. This dramatic improvement explains why critical safety systems employ redundancy.

11.8.3 Human Factors and Organizational Influences

Statistical analysis of major industrial accidents consistently reveals that human error contributes to 60-80% of incidents, but this figure requires careful interpretation. The term "human error" encompasses a wide range of behaviors from simple slips and lapses through mistakes in judgment to intentional violations of procedures. More importantly, most "human errors" are symptoms of deeper organizational problems including inadequate procedures, insufficient training, poor equipment design, production pressure that undermines safety, and management systems that fail to identify and correct unsafe conditions before accidents occur.

Errors of omission occur when operators forget steps in procedures, overlook required checks, or fail to notice abnormal conditions. A classic example involves maintenance work where equipment has been isolated, depressurized, and drained for repairs. Upon completion, all steps must be reversed to restore the equipment to service. If an operator forgets to open a block valve after maintenance, the equipment cannot function and may be damaged when startup is attempted. Checklists provide robust protection against omission errors, but only if rigorously used and independently verified. The tendency to skip checklist use for "routine" tasks, or to check off items from memory rather than actually verifying them, undermines this protection.

Errors of commission involve performing the wrong action, such as opening the wrong valve, entering incorrect setpoints, or mixing incompatible materials. Clear labeling, good human-machine interface design, and forcing functions that prevent incorrect actions all reduce commission error rates. Computer control systems can implement interlocks that prevent physically impossible or unsafe combinations of actions, such as opening a drain valve while pressure remains in the vessel. However, interlocks must be carefully designed to prevent both unsafe actions without also preventing safe recovery actions during abnormal situations.

Sequence errors occur when correct actions are performed in the wrong order. Written procedures specifying required sequences, along with interlocks that enforce the sequence where critical, provide protection. Timing errors, where actions occur too early or too late, can be prevented by time-delay interlocks for time-critical steps and clear indication in procedures of required waiting periods or deadlines for action.

Rule violations differ from errors in that the operator consciously chooses to deviate from procedures or bypass interlocks. Understanding why violations occur is essential for reducing them. Routine violations happen when prescribed methods are perceived as inefficient, cumbersome, or unnecessary, and alternative methods have been used successfully in the past without adverse consequences. The operator intends no harm but sees the prescribed procedure as poorly designed. Addressing routine violations requires procedure review to eliminate unnecessary steps while maintaining safety, combined with explanation to operators of why each step matters. Situational violations occur when operators face conflicting demands, such as production deadlines versus safety procedures, and choose to compromise safety. This typically reflects organizational failure to prioritize safety consistently. Exceptional violations happen in unusual circumstances not covered by procedures, where operators must improvise. Clear guidance on when to stop operations and seek technical support, rather than improvising, prevents inappropriate exceptional violations.

Fatigue significantly impairs human performance, increasing error rates, slowing response times, and degrading decision-making ability. Chemical plants often operate continuously, requiring shift work that disrupts normal sleep patterns. Shift schedules should minimize consecutive night shifts, avoid rapid rotation, and ensure adequate rest between shifts. Automation reduces operator workload during routine operations but must maintain operator engagement to prevent vigilance failure where operators cannot respond quickly to abnormal situations because attention has drifted.

The concept of safety culture captures organizational attitudes, beliefs, perceptions, and values that determine commitment to safety management. Organizations with strong safety cultures demonstrate that safety is a core value, not merely a priority that competes with production and costs. Leadership actively promotes safety through visible commitment, adequate resource allocation, and response to safety concerns. Workers feel empowered to raise safety issues without fear of retribution. Reporting systems encourage disclosure of errors and near-misses so that learning occurs before major accidents. Investigation of incidents focuses on system improvements rather than individual blame. Safety culture cannot be imposed through policies alone but develops through consistent demonstration that safety concerns are heard, investigated, and addressed.

11.9 Safety Instrumented Systems and Layer of Protection Analysis

11.9.1 Safety Instrumented System Architecture and Performance

Safety Instrumented Systems (SIS) provide automated protective actions when process conditions deviate beyond safe limits. Unlike Basic Process Control Systems (BPCS) that optimize normal operations, SIS is specifically designed to prevent or mitigate hazardous events. This functional separation ensures that SIS remains available even when BPCS fails or when the failure that initiated the hazardous sequence affects process control. A well-designed SIS follows the principle of independence: the sensors, logic solver, and final elements that comprise the SIS are separate from those used for normal control and are unaffected by the initiating event.

Safety Integrity Level (SIL) quantifies the reliability of Safety Instrumented Functions (SIF). Four SIL levels exist, with SIL 1 providing lowest reliability and SIL 4 highest. Each SIL corresponds to a range of Probability of Failure on Demand (PFD), representing the likelihood that the SIF will fail to operate when needed. SIL 1 corresponds to PFD between 0.1 and 0.01 (10% to 1% failure probability), providing 10-fold to 100-fold risk reduction. SIL 2 corresponds to PFD between 0.01 and 0.001 (1% to 0.1%), providing 100-fold to 1000-fold risk reduction. SIL 3 corresponds to PFD between 0.001 and 0.0001, providing 1000-fold to

10,000-fold risk reduction. SIL 4, rarely used in process industries, corresponds to PFD between 0.0001 and 0.00001.

Achieving a specified SIL requires careful attention to sensor selection and voting logic, logic solver design and diagnostics, final element configuration and testing, and systematic proof testing to detect dangerous undetected failures. Sensors in SIS must be independent of those used for process control. For critical applications, redundant sensors with voting logic provide protection against sensor failures. A 1oo2 configuration (1 out of 2) trips if either sensor indicates a hazardous condition, providing high availability but with greater risk of spurious trips. A 2oo3 configuration (2 out of 3) requires two sensors to indicate hazardous conditions before tripping, reducing spurious trips while maintaining high reliability through redundancy. The third sensor provides continued operation if one sensor fails, and maintenance can repair the failed sensor without shutting down.

Logic solvers range from relay-based systems (used historically but now obsolete for new installations) through programmable logic controllers (PLCs) to specialized safety PLCs designed specifically for SIS applications. Safety PLCs incorporate extensive self-diagnostics, dual processors with comparison, and communication protocols that detect corruption. Programming is simplified and constrained to reduce the possibility of introducing errors. The IEC 61508 and IEC 61511 standards provide requirements for safety PLC design, programming, testing, and maintenance.

Final elements execute protective actions, typically closing or opening valves but sometimes including motor stops, damper positioning, or activation of quench or suppression systems. Final elements must be capable of moving to the safe position under all foreseeable conditions, including loss of utilities, adverse process conditions, and partial mechanical failure. Valve actuators are therefore selected to fail in the safe direction (fail-closed for most feed valves, fail-open for most cooling valves) using stored energy in springs. Regular stroke testing verifies that valves move through their full range without binding or excessive friction. Partial stroke testing, performed more frequently, moves valves part way to detect incipient problems without disrupting operation.

Proof testing represents systematic testing at defined intervals to detect dangerous failures that are not revealed by continuous diagnostics. During proof testing, the entire SIF is taken through simulated dangerous conditions to verify proper response. For example, a high-temperature trip might be tested by simulating high-temperature sensor readings (by removing sensors from process and applying heat or electrical signals) and verifying that the logic solver receives the signal, processes it correctly, and commands final elements to move, with actual valve movement confirmed. Proof test intervals range from monthly to annually depending on target SIL, with higher SIL requiring more frequent testing.

11.9.2 Emergency Shutdown System Design and Philosophy

Emergency Shutdown (ESD) systems provide a coordinated response to major upsets, securing the plant in a safe state when continued operation would risk catastrophic failure. Unlike individual SIFs that address specific hazards, ESD systems take multiple simultaneous actions affecting large portions of the plant. Designing effective ESD systems requires clear definition of the safe state to be achieved, identification of initiating conditions that demand emergency shutdown, specification of all actions required to reach the safe state, determination of appropriate action sequencing and timing, and verification that the safe state can be maintained indefinitely without additional operator action.

For a reactor system, the safe state typically requires stopping all reaction by eliminating at least one leg of the fire triangle for combustion hazards or breaking the feedback loop for thermal runaway. This might involve stopping reactant feed immediately to prevent additional reactive material from entering, stopping or reversing heating and maximizing cooling if available, adding inhibitor or quench material if applicable for the specific chemistry, isolating the reactor from other process equipment to prevent propagation of the upset, and inerting vapor spaces if flammable materials are present. The reaction must cease or at least be controlled before pressure or temperature reach critical levels where the relief system would activate or vessel integrity would be threatened.

The sequence and timing of ESD actions require careful analysis. Immediate actions, typically executed within two seconds of ESD initiation, include closing all feed valves to stop reactant addition and opening emergency vent valves if provided for pressure relief. Slightly delayed actions, perhaps 5 to 10 seconds after initiation, might include stopping agitators after ensuring that feed has stopped (to allow mixing of any quench material that was added before agitation stops) and maximizing cooling water flow or starting emergency cooling systems. Actions within 30 to 60 seconds might include verifying that all intended actions have completed and alarming if any have not, and placing the plant in a safe hold state where it can remain indefinitely. Follow-up actions over minutes to hours might include cooling to ambient temperature, depressurizing if safe to do so, and initiating restart procedures only after investigation confirms the cause of the ESD and verifies that conditions support safe operation.

ESD systems must be fail-safe, meaning that loss of power, loss of pneumatic or hydraulic supply, or failure of control equipment causes the system to move toward the safe state rather than remaining in the operating state. This typically means that ESD logic is de-energized to shutdown: normal operation requires continuous power or air pressure to keep ESD from activating, and loss of utilities causes automatic shutdown. While this creates potential for spurious ESD activations from utility failures or equipment problems, the safety

priority justifies this conservative approach. The economic cost of spurious ESD activations, including production loss, restart effort, and equipment stress from thermal and pressure cycling, creates pressure to minimize false trips, but this must never compromise the reliability of ESD to activate when truly needed.

Testing ESD systems presents challenges because full functional testing requires actually shutting down the process. Partial testing can verify some aspects: sensor inputs can be simulated, logic solver operation can be verified using test signals, and valve movement can be tested during planned shutdowns. However, only occasional full functional tests during turnarounds can verify complete ESD performance including all initiating conditions, all logic paths, all final element responses, and achievement of the defined safe state. Between full tests, continuous monitoring of ESD system health, periodic partial tests of individual components, and analysis of any inadvertent ESD activations to confirm proper system response all contribute to confidence in ESD reliability.

11.10 Summary

This chapter has integrated classical chemical reactor stability theory with comprehensive process safety and risk management. The fundamental insight is that reactor instability arises from nonlinear coupling between highly temperature-dependent reaction rates and exothermic heat generation, creating positive feedback loops that can lead to thermal runaway, multiple steady states, parametric sensitivity, and oscillatory behavior. Mathematical analysis through dynamic modeling, phase plane analysis, and Lyapunov stability criteria provides rigorous tools for predicting stability, but this theoretical foundation must be augmented with broader consideration of process risks, chemical hazards, and protective systems.

Process hazards extend beyond thermal stability to encompass equipment failures, human errors, organizational factors, and external events. Systematic hazard identification through HAZOP and FMEA, semi-quantitative analysis through LOPA, and full quantitative risk assessment through event trees and fault trees provide structured approaches to identifying what can go wrong and determining appropriate protection. Chemical hazards including toxicity, flammability, explosivity, and chemical reactivity demand detailed characterization through exposure limits, flammability parameters, explosion indices, and reactivity testing.

Safety systems provide defense-in-depth through multiple independent protective layers: basic process control maintains normal operation, alarms and operator intervention respond to abnormal conditions, safety instrumented systems provide automatic protective actions, pressure relief prevents overpressure catastrophe, and passive features limit consequences if all active systems fail. Each layer must be independent, reliable, and

properly designed for the specific hazards present. However, inherent safety principles—elimination, substitution, intensification, and attenuation—represent the highest level of protection by reducing hazards at the source rather than managing them through added protective systems.

The responsible chemical engineer designs reactors that achieve production objectives while maintaining acceptable risk to personnel, the public, property, and environment. This requires equal attention to thermodynamics and kinetics, transport phenomena and control systems, stability analysis and hazard assessment, protective systems and safety culture. Modern reactor engineering is truly an integrated discipline where technical excellence in all these areas combines to produce processes that are not only efficient and economical but also inherently safer and operationally reliable. The accidents of history teach that overlooking any aspect of this integration invites catastrophe; comprehensive attention to stability, safety, and risk management from the earliest design stages provides the foundation for sustainable chemical processing.

Problem 11.1 (Exothermic stirred-tank reactor stability)

A perfectly mixed CSTR of volume $V = 1.0 \text{ m}^3$ treats a liquid feed containing species A. The irreversible reaction

$A \rightarrow \text{products}$

is first order in A and exothermic. The reactor has a cooling jacket.

Given data

Rate:

$$r_A = k(T) C_A, k(T) = k_0 e^{-E/RT}$$

Reactor & feed

- $V = 1.0 \text{ m}^3$
- $F = 1.0 \text{ m}^3/\text{min} \Rightarrow \tau = V/F = 1.0 \text{ min}$
- $C_{A0} = 2.0 \text{ kmol/m}^3$
- $T_0 = 300 \text{ K}$

Thermal / kinetic

- $\rho C_p = 2.0 \times 10^6 \text{ J/(m}^3 \cdot \text{K)}$
- $\Delta H = -2.0 \times 10^5 \text{ J/mol}$ (exothermic)
- $UA = 4.0 \times 10^5 \text{ J/(min} \cdot \text{K)}$
- $T_c = 290 \text{ K}$
- $k_0 = 7.2 \times 10^{10} \text{ min}^{-1}$
- $E = 8.0 \times 10^4 \text{ J/mol}$
- $R = 8.314 \text{ J/(mol} \cdot \text{K)}$

Tasks

1. Write the dynamic mass and energy balances.
2. Compute the steady state (C_A^*, T^*) .

3. Linearize the system around the steady state and determine stability from eigenvalues.
4. Display the x vs T trajectories for the initial temperatures [300 350 450] C
5. Display x vs time

Chapter 11 Summary: What You Should Have Learned

After completing this chapter, you should be able to:

1. Analyze steady-state multiplicity and stability in CSTRs
2. Understand parametric sensitivity and runaway reactions
3. Apply stability criteria to reactor design
4. Identify potential safety hazards
5. Apply inherently safer design principles

Chapter 12: Transport Resistance in Heterogeneous Catalysis

Learning Objectives

After completing this chapter, you should be able to:

- Recognize that heterogeneous catalytic reactions involve multiple sequential transport steps including external mass transfer from bulk fluid to catalyst surface, pore diffusion within catalyst pellets, and surface reaction, understanding that the slowest step controls the overall rate.
- Analyze external mass transfer limitations using film theory, calculating the mass transfer coefficient from correlations, and determining when bulk concentration differs significantly from surface concentration through dimensionless analysis.
- Derive and apply the effectiveness factor η for catalyst pellets, recognizing that internal diffusion limitations reduce the observable reaction rate below the intrinsic kinetic rate, with η ranging from near unity for reaction-controlled regimes to much less than one for diffusion-controlled regimes.
- Calculate the Thiele modulus ϕ for different pellet geometries and reaction orders, understanding that ϕ represents the ratio of reaction rate to diffusion rate and determines the extent of concentration gradients within the catalyst.
- Utilize the generalized Thiele modulus and effectiveness factor relationships for first-order, second-order, and nth-order reactions, applying appropriate correlations to predict catalyst performance under diffusion-limited conditions.
- Apply the Weisz-Prater criterion to determine whether pore diffusion limitations are significant, calculating the Weisz modulus Φ from observable quantities and using the criterion $\Phi \ll 1$ to confirm reaction-controlled kinetics without needing intrinsic rate constants.
- Design catalyst pellets considering the trade-off between activity (small pellets, high effectiveness factor) and pressure drop (large pellets), selecting optimal particle size, shape, and porosity for different reaction systems.

Nomenclature

The following symbols are introduced in this chapter and supplement the comprehensive nomenclature in previous chapters:

Roman Letters

a_v	External surface area per unit volume (m^2/m^3 or cm^2/cm^3)
C_B	Bulk fluid concentration (mol/L or mol/m^3)
C_S	Surface concentration (mol/L or mol/m^3)
D_{eff}	Effective diffusivity in porous catalyst (m^2/s or cm^2/s)

d_p	Particle diameter (m or mm)
k_c	Mass transfer coefficient (m/s or cm/s)
k_s	Surface reaction rate constant (units vary with order)
L	Characteristic length of catalyst pellet (m or cm)
R, r	Pellet radius for spherical particles (m or cm)
r_{obs}	Observed reaction rate ($\text{mol}/(\text{s}\cdot\text{m}^3_{cat})$ or $\text{mol}/(\text{s}\cdot\text{g}_{cat})$)
S_g	Internal surface area per unit mass (m^2/g)
V_p	Pellet volume (m^3 or cm^3)

Greek Letters

ϵ_p	Pellet porosity (void fraction), dimensionless
η	Effectiveness factor, dimensionless
ϕ	Thiele modulus, dimensionless
Φ	Weisz-Prater modulus, dimensionless
ρ_p	Pellet density (kg/m^3 or g/cm^3)
τ_p	Tortuosity factor, dimensionless

12.1 Introduction to Heterogeneous Catalysis

Heterogeneous catalysis involves reactions occurring at the interface between different phases, most commonly gas-solid or liquid-solid systems. Unlike homogeneous reactions where reactants and catalyst occupy the same phase, heterogeneous catalytic reactions require reactants to be transported to the catalyst surface, undergo chemical transformation, and have products transported away.

The vast majority of industrial chemical processes employ heterogeneous catalysts:

- *Petroleum refining: Fluid catalytic cracking (FCC), hydrocracking, reforming on zeolite or metal catalysts*
- *Chemical synthesis: Ammonia synthesis (Fe catalyst), methanol synthesis (Cu/ZnO), Fischer-Tropsch synthesis (Co/Fe)*
- *Environmental: Automotive catalytic converters (Pt/Pd/Rh), selective catalytic reduction (SCR) of NO_x*
- *Polymer production: Ethylene polymerization (Ziegler-Natta, metallocene catalysts)*

The advantages of heterogeneous catalysts include easy separation from products, thermal stability, and the ability to operate continuously in fixed-bed reactors. However, their

performance is significantly affected by transport limitations that do not occur in homogeneous systems.

Understanding and quantifying transport resistance is essential for:

- Accurate kinetic studies: Ensuring measured rates reflect intrinsic kinetics rather than transport artifacts
- Reactor design: Predicting actual conversion accounting for mass transfer limitations and effectiveness factor $\eta < 1$
- Catalyst design: Optimizing pellet size, shape, and pore structure
- Scale-up: Avoiding transport limitations that may appear on a commercial scale but not in laboratory studies

12.2 Mass Transfer Steps in Heterogeneous Catalysis

12.2.1 The Seven-Step Mechanism

A complete heterogeneous catalytic reaction involves the following sequential steps:

1. Mass transfer of reactants from bulk fluid to external catalyst surface (external diffusion)
2. Diffusion of reactants through catalyst pores to internal active sites (internal diffusion)
3. Adsorption of reactants onto catalyst surface
4. Surface reaction (chemical transformation)
5. Desorption of products from catalyst surface
6. Diffusion of products through pores to external surface (internal diffusion)
7. Mass transfer of products from external surface to bulk fluid (external diffusion)

These steps occur in series, so the overall rate is controlled by the slowest step. Steps 3-5 (adsorption, surface reaction, desorption) are often grouped together as the intrinsic surface reaction kinetics.

12.2.2 Resistances in Series

The overall process can be viewed as resistances in series:

$$\frac{1}{r_{overall}} = \frac{1}{r_{external}} + \frac{1}{r_{internal}} + \frac{1}{r_{reaction}} \quad (12.1)$$

where each term represents a resistance. The smallest rate (largest resistance) dominates. This leads to three limiting regimes:

A: Reaction-controlled regime: Surface reaction is slowest. Transport is fast, so concentrations are uniform throughout catalyst and equal to bulk concentration. Observable kinetics reflect intrinsic surface kinetics.

D: External diffusion-controlled regime: Mass transfer from bulk to surface is slowest. Surface concentration $C_S \ll C_B$, and reaction rate is proportional to mass transfer coefficient k_C rather than kinetic constants.

B, C: Internal diffusion-controlled regime: Concentration gradients exist within catalyst, with concentration decreasing from surface toward center. In region C only outer shell of catalyst is utilized effectively.

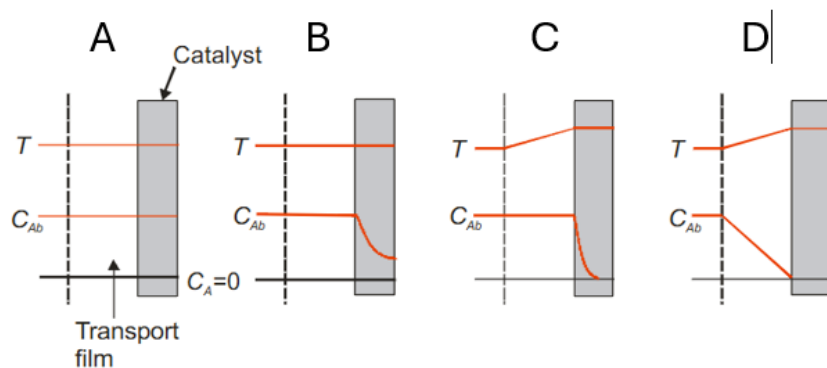


Figure 12-1 Transport and reaction restrictions in heterogeneous catalysis

12.3 External Mass Transfer - Film Theory

12.3.1 Film Model for External Transport

Film theory postulates a stagnant film of thickness δ surrounding the catalyst particle through which reactants diffuse. The mass transfer rate is:

$$N_A = k_C \cdot (C_B - C_S) \quad (12.2)$$

where k_C is the mass transfer coefficient (m/s). At steady state, this flux equals the surface reaction rate:

$$k_C \cdot (C_B - C_S) = k_S \cdot f(C_S) \quad (12.3)$$

where $f(C_S)$ is the kinetic expression (e.g., C_S for first-order, C_S^2 for second-order).

12.3.2 Mass Transfer Coefficients

The mass transfer coefficient depends on flow conditions and is correlated using dimensionless numbers:

$$Sh = k_C \cdot \frac{d_P}{D_{AB}} \quad (12.4)$$

where Sh is the Sherwood number, d_P is particle diameter, and D_{AB} is molecular diffusivity.

For packed beds, common correlations include:

$$Sh = 2.0 + 1.1 \cdot Re^{0.6} \cdot Sc^{1/3} \quad (\text{for } 3 < Re < 10,000) \quad (12.5)$$

where $Re = \rho \cdot u \cdot d_P / \mu$ (Reynolds number) and $Sc = \mu / (\rho \cdot D_{AB})$ (Schmidt number).

For fluidized beds:

$$Sh = 2.0 + 0.6 \cdot Re^{0.5} \cdot Sc^{1/3} \quad (12.6)$$

12.3.3 Criterion for External Diffusion Limitations

External mass transfer is affecting when:

$$\frac{C_B - C_S}{C_B} > 0.05 \quad (12.7)$$

A useful criterion derived from Equation 12.3 for first-order kinetics:

$$\frac{k_S \cdot \rho_P \cdot R}{k_C \cdot C_B} < 0.05 \quad (12.8)$$

If this ratio is much less than 0.05, external diffusion is negligible. If it approaches or exceeds 0.05, external transport limits the observed rate.

12.4 Internal Diffusion and the Effectiveness Factor

12.4.1 Concentration Profiles in Catalyst Pellets

For a porous catalyst pellet, reactants must diffuse through the pore network to reach internal sites. The concentration decreases from the external surface (C_S) toward the pellet center, creating a concentration gradient.

A material balance on a differential element within the pellet gives:

$$D_{eff} \cdot \nabla^2 C_A = r(C_A) \quad (12.9)$$

where D_{eff} is the effective diffusivity accounting for porosity and tortuosity:

$$D_{eff} = \varepsilon_P \cdot \frac{D_{AB}}{\tau_P} \quad (12.10)$$

where ε_P is the fraction of the surface that is open for diffusion and τ_P is a measure of the increased transport pathway due to the porous structure of the catalyst. In the gas phase, when pores are narrow and their size is much smaller than the mean free path of gas

molecules, the molecules will collide more often with the pore walls than with each other. Under these conditions, the diffusivity can be estimated using Knudsen diffusion.

$$D_{AB} \approx D_{K,A} = \frac{1}{3} d_p \sqrt{\frac{8RT}{\pi M_A}}$$

where d_p is the average pore diameter and M_A the molecular weight of the molecule A.

For a spherical pellet with first-order reaction ($r_A = k_S \cdot C$), Equation 12.9 as function of radius, r , becomes:

$$D_{eff} \cdot \left(\frac{1}{r^2}\right) \cdot \frac{d}{dr} \left(r^2 \cdot \frac{dC}{dr}\right) = k_S \cdot C \quad (12.11)$$

Boundary conditions: $C = C_S$ at $r = R$ (surface), $dC/dr = 0$ at $r = 0$ (symmetry).

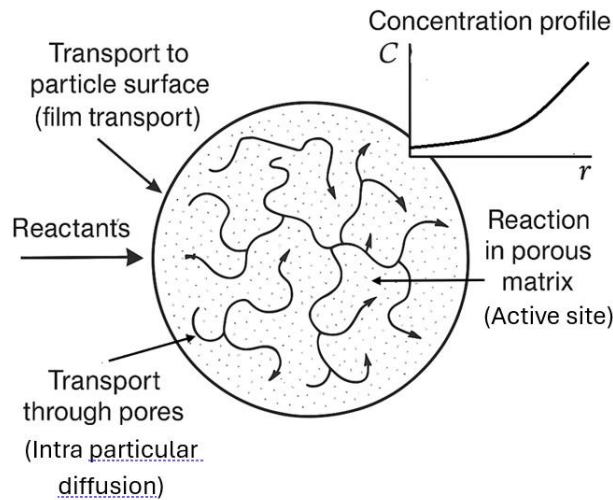


Figure 12-2 Transport and reaction into and in a porous catalyst

12.4.2 Derivation of Effectiveness Factor

The effectiveness factor η is defined as:

$$\eta = \frac{\text{actual rate with diffusion}}{\text{rate if entire pellet at } C_S} \quad (12.12)$$

Mathematically:

$$\eta = \frac{\int_0^V r(C(r)) dV}{V \cdot r(C_S)} \quad (12.13)$$

For a spherical pellet with first-order kinetics, solving Equation 12.11 gives:

$$C(r) = C_S \cdot \left(\frac{R}{r}\right) \cdot \frac{\sinh\left(\frac{\phi r}{R}\right)}{\sinh(\phi)} \quad (12.14)$$

where ϕ is the Thiele modulus (defined in the next section).

Integrating to find the effectiveness factor:

$$\eta = \left(\frac{3}{\phi}\right) \cdot \left(\frac{1}{\tanh(\phi)} - \frac{1}{\phi}\right) \text{ for spheres} \quad (12.15)$$

This can be simplified to:

$$\eta = \left(\frac{3}{\phi^2}\right) \cdot (\phi \cdot \coth(\phi) - 1) \quad (12.16)$$

For other geometries, the effectiveness factor takes different forms but maintains the same qualitative behavior.

12.5 The Thiele Modulus

12.5.1 Definition and Physical Meaning

The Thiele modulus ϕ is a dimensionless parameter that characterizes the relative importance of reaction rate to diffusion rate:

$$\phi = L \cdot \sqrt{\frac{k_S}{D_{eff}}} \quad (12.17)$$

where L is the characteristic length of the pellet often defined as volume to surface $L=V_p/S_p$.

For different geometries:

$$\text{Sphere: } L = \frac{R}{3}, \text{ so } \phi^* = \left(\frac{R}{3}\right) \cdot \sqrt{\frac{k_S}{D_{eff}}}$$

$$\text{Infinite cylinder: } L = \frac{R}{2}, \phi^* = \left(\frac{R}{2}\right) \cdot \sqrt{\frac{k_S}{D_{eff}}}$$

Infinite slab: $L = \text{half-thickness} = \delta/2$

More commonly, for a sphere:

$$\phi = R \cdot \sqrt{\frac{k_S}{D_{eff}}} \text{ (sphere)} \quad (12.18)$$

The Thiele modulus represents:

$$\phi \propto \sqrt{\frac{\text{reaction rate}}{\text{diffusion rate}}} \quad (12.19)$$

Physical interpretation:

$\phi \ll 1$: Diffusion is very fast compared to reaction. Concentration is nearly uniform throughout pellet. $\eta \approx 1$ (no diffusion limitation).

$\phi \gg 1$: Reaction is very fast compared to diffusion. Reactant is consumed near the external surface. Only a thin outer shell is utilized. $\eta \ll 1$ (severe diffusion limitation).

$\phi \approx 1$: Reaction and diffusion rates are comparable. Intermediate effectiveness factor.

12.5.2 Effectiveness Factor as Function of Thiele Modulus

The relationship between η and ϕ depends on geometry and reaction order. For first-order reactions:

Sphere: $\eta = \left(\frac{3}{\phi^2}\right) \cdot (\phi \cdot \coth(\phi) - 1)$ (Equation 12.16)

Infinite cylinder: $\eta = \left(\frac{2}{\phi}\right) \cdot \frac{I_1(\phi)}{I_0(\phi)}$ where I_0, I_1 are modified Bessel functions

Infinite slab: $\eta = \frac{\tanh(\phi)}{\phi}$

12.5.3 Generalized Thiele Modulus for nth-Order Reactions

For nth-order reactions ($r = k_S \cdot C^n$), a generalized Thiele modulus is defined:

$$\phi_n^* = L \cdot \sqrt{\frac{k_S \cdot C_S^{n-1}}{D_{eff}}} \quad (12.20)$$

For a sphere:

$$\phi_n = R \cdot \sqrt{\frac{k_S \cdot C_S^{n-1}}{D_{eff}}} \quad (12.21)$$

The effectiveness factor can be approximated for large ϕ_n :

$$\eta \approx \frac{n+1}{3} \frac{1}{\phi_n^{2/(n+1)}} \text{ for } \phi_n > 4 \text{ (sphere)} \quad (12.22)$$

12.6 The Weisz-Prater Criterion

12.6.1 The Weisz Modulus

A practical challenge is that calculating the Thiele modulus requires knowing the intrinsic rate constant k_S , which may not be available if diffusion limitations are present. The Weisz-Prater criterion overcomes this by using only observable quantities.

The Weisz modulus Φ is defined as:

$$\Phi = \frac{r_{obs} \cdot \rho_P R^2}{D_{eff} \cdot C_S} \quad (12.23)$$

where r_{obs} is the observed reaction rate per unit mass of catalyst.

The Weisz modulus is related to the Thiele modulus and effectiveness factor:

$$\Phi = \phi^2 \cdot \eta \quad (12.24)$$

For first-order reactions in the diffusion-limited regime where $\eta \approx 3/\phi$:

$$\Phi \approx 3\phi \quad (12.25)$$

12.6.2 Criterion for Absence of Diffusion Limitations

The Weisz-Prater criterion states:

If $\Phi \ll 1$, then internal diffusion is negligible

More specifically:

$\Phi < 0.15$: No significant diffusion limitations ($\eta > 0.95$)

$0.15 < \Phi < 4$: Intermediate regime, some diffusion effects

$\Phi > 4$: Severe diffusion limitations ($\eta \ll 1$)

The beauty of this criterion is that it can be evaluated experimentally without knowing intrinsic kinetics:

1. Measure r_{obs} at known C_S (or C_B if external resistance is negligible)
2. Determine or estimate D_e from porosity measurements or correlations
3. Calculate Φ from Equation 12.25
4. If $\Phi \ll 1$, the measured kinetics are intrinsic

This criterion is invaluable for kinetic studies to ensure measured rates reflect true chemical kinetics rather than transport artifacts.

12.6.3 Extension to nth-Order Reactions

For nth-order reactions, the generalized Weisz modulus is:

$$\Phi_n = \frac{r_{obs} \cdot \rho_P R^2}{D_{eff} \cdot C_S^n} \quad (12.26)$$

The criterion $\Phi_n < 0.15$ indicates negligible diffusion effects for nth-order kinetics.

12.7 Effect of Mass Transfer on Apparent Kinetics

When mass transfer resistance is significant, the observed or apparent kinetic parameters differ from the intrinsic parameters of the chemical reaction. This has profound implications for reactor design, scale-up, and kinetic studies. Understanding these effects is essential for distinguishing between transport artifacts and true chemical kinetics.

12.7.1 Apparent Activation Energy

The activation energy is a fundamental kinetic parameter that characterizes the temperature dependence of the reaction rate. For an intrinsic chemical reaction following Arrhenius behavior:

$$k_{intrinsic} = A \exp\left(-\frac{E_{true}}{RT}\right) \quad (12.27)$$

However, when mass transfer resistance is present, the observed rate depends on both the intrinsic kinetics and the transport rate.

Case 1: External Mass Transfer Control

When external mass transfer completely dominates (film diffusion control), the observed rate is:

$$r_{obs} = k_c(C_b - C_s) \quad (12.28)$$

where k_c is the mass transfer coefficient. If the reaction is very fast such that $C_s \approx 0$:

$$r_{obs} = k_c C_b \quad (12.29)$$

The mass transfer coefficient depends weakly on temperature. For gases, typical dependence is:

$$k_c \propto T^{0.5 \text{ to } 0.75} \quad (12.30)$$

This gives an apparent activation energy of:

$$E_{app} \approx 4 \text{ to } 8 \text{ kJ/mol}$$

This is **much lower** than typical activation energies for chemical reactions (40-200 kJ/mol). This dramatic difference is a key diagnostic: if measured $E_{app} < 15$ kJ/mol, external mass transfer is likely controlling the observed rate.

Case 2: Internal Diffusion Control

For strong internal diffusion limitations ($\phi \gg 1, \eta \approx 1/\phi$), the observed rate becomes:

$$r_{obs} = \eta k_s C_s \approx \left(\frac{1}{\phi}\right) k_s C_s \quad (12.31)$$

For a first-order reaction, $\phi = \frac{L}{2} \left(\frac{k_s}{D_{eff}}\right)$, so:

$$r_{obs} \propto (k_s D_{eff})^{1/2} C_s \quad (12.32)$$

The temperature dependence now involves both k_s (strong temperature dependence with E_{true}) and D_{eff} (weak temperature dependence, $D_{eff} \propto T^{1.5 \text{ to } 2}$):

$$E_{app} = \frac{E_{true} + E_D}{2} \quad (12.33)$$

where E_D is the activation energy for diffusion (typically 4 - 8 kJ/mol). Therefore:

$$E_{app} \approx \frac{E_{true}}{2} \quad (12.34)$$

For severe internal diffusion limitations, the apparent activation energy is approximately **half** the true activation energy. If measured E_{app} is 40-70 kJ/mol when chemical reactions typically have $E = 80-150$ kJ/mol, internal diffusion limitations are likely present.

12.7.2 Apparent Reaction Order

Mass transfer also alters the apparent reaction order. Consider an n :th order intrinsic reaction:

$$r_{intrinsic} = k_s C^n \quad (12.35)$$

For External Mass Transfer Control:

If external mass transfer dominates with $C_s \approx 0$:

$$r_{obs} = k_c C_b \quad (12.36)$$

The apparent reaction order is **always first order**, regardless of the true reaction order. This is a powerful diagnostic: if a reaction that should be second-order (e.g., bimolecular gas-phase reaction) appears first-order experimentally, external mass transfer may be limiting.

For Internal Diffusion Control:

For strong internal diffusion limitations ($\phi \gg 1$), the generalized Thiele modulus for n -th order reactions gives $\eta \propto \phi^{-1}$, where $\phi_n \propto C_s^{(n-1)/2}$. Therefore:

$$r_{obs} = \eta k_s C_s^n \propto C_s^{\frac{n+1}{2}} \quad (12.37)$$

The apparent reaction order becomes:

$$n_{app} = \frac{n + 1}{2} \quad (12.38)$$

This relationship has important implications:

- For a truly first-order reaction ($n = 1$): $n_{app} = 1.0$ (no change)
- For a truly second-order reaction ($n = 2$): $n_{app} = 1.5$
- For a truly zero-order reaction ($n = 0$): $n_{app} = 0.5$

12.7.3 Diagnostic Summary

The following table summarizes how to diagnose mass transfer limitations from observed kinetic parameters:

Regime	Apparent E_{act}	Apparent Order
Intrinsic Kinetics (No limitations)	E_{true} (40-200 kJ/mol)	n_{true}
External Mass Transfer Control	4-8 kJ/mol (very low)	1 (first-order)

Regime	Apparent E_{act}	Apparent Order
Internal Diffusion Control	$\frac{E_{true}}{2}$ (half of true)	$\frac{n + 1}{2}$

Key Diagnostic Guidelines:

- **Very low activation energy** (< 15 kJ/mol): External mass transfer control is likely.
- **Activation energy about half expected** (e.g., 40 kJ/mol when 80-100 kJ/mol expected): Internal diffusion control is likely.
- **First-order behavior for all reactions**: Suggests external mass transfer limitation.
- **Fractional reaction order** (e.g., 1.5 for nominally second-order): Suggests internal diffusion limitation.
- **Particle size dependence**: If rate per unit mass decreases with increasing particle size, internal diffusion is limiting.
- **Flow rate dependence**: If rate increases with gas velocity or stirring speed, external mass transfer is limiting.

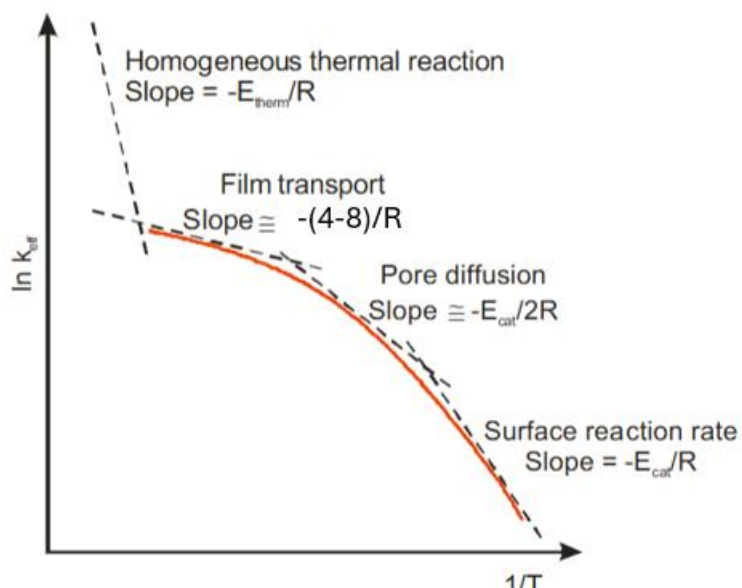


Figure 12-3 The apparent activation energies due to transport limitations

Implications for Reactor Design:

Understanding apparent kinetics is critical because:

- **Scale-up errors:** Using apparent kinetics measured in mass transfer-limited lab conditions will lead to serious design errors when scaling up.
- **Temperature sensitivity:** A reactor designed based on mass transfer-limited kinetics will show much stronger temperature dependence than expected.
- **Operating regime changes:** Conditions that eliminate mass transfer limitations (smaller particles, higher velocities) may shift the reactor into a different kinetic regime.
- **Catalyst utilization:** Apparent low activation energy may mask poor catalyst utilization due to internal diffusion, leading to oversized reactors.

The key to proper reactor design is ensuring that kinetic measurements are made under conditions where mass transfer limitations are minimized, as verified by the diagnostic criteria above. The Weisz-Prater criterion (Section 12.6) provides a quantitative test for the absence of internal diffusion effects.

12.8 Design Considerations for Catalyst Pellets

12.8.1 Particle Size Selection

The choice of catalyst particle size involves trade-offs:

Small particles:

Advantages: Small ϕ , high η (better catalyst utilization), faster response

Disadvantages: High pressure drop in fixed beds, difficult handling, potential fluidization issues

Large particles:

Advantages: Low pressure drop, easy handling, good mechanical strength

Disadvantages: Large ϕ , low η (poor catalyst utilization), potential hot spots

Since $\phi \propto R$, the effectiveness factor decreases with increasing particle size. For highly active catalysts, diffusion limitations may require using smaller particles than mechanically desirable, or accepting lower effectiveness factors.

12.8.2 Optimal Pellet Shape

For a given volume, different shapes have different characteristic lengths and surface areas:

- Slab: Largest characteristic length for given volume, lowest η
- Sphere: Intermediate, commonly used for good mechanical strength
- Cylinder: Can be optimized by varying length/diameter ratio
- Ring or hollow cylinder: Reduces diffusion path length, higher η than solid cylinder
- Trilobe, quadrulobe: Commercial shapes offering low pressure drop and good effectiveness

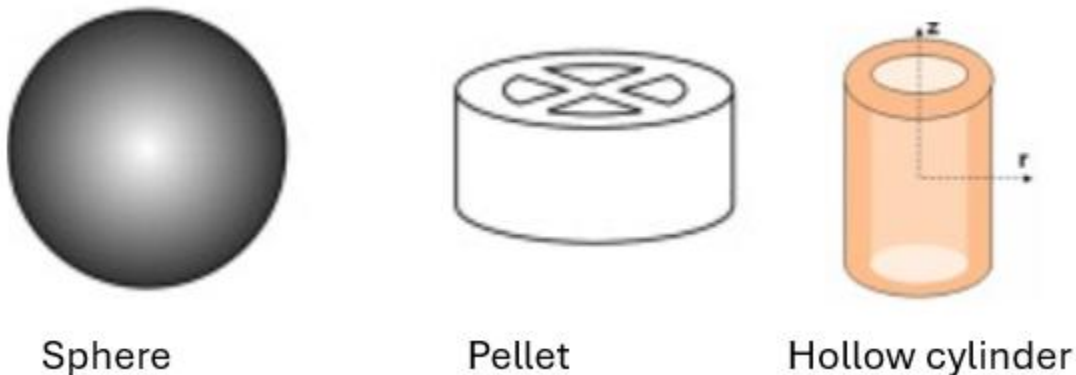


Figure 12-4 Catalyst particles with different external surface area

The optimal shape maximizes the ratio (external surface area)/(characteristic length) while maintaining mechanical integrity.

12.8.3 Bi-Modal Pore Structures

Modern catalysts often employ bi-modal pore structures:

Macropores (>50 nm): Provide low-resistance transport pathways to interior

Micropores (<2 nm): Provide high surface area for catalytic sites

This design combines the benefits of small diffusion distances (via macropores) with high active site density (via micropores). The effective diffusivity in bi-modal structures is higher than in mono-modal microporous materials.

12.9 Worked Examples

Example 12.1: Calculation of Effectiveness Factor for Spherical Pellet

Problem Statement:

A first-order catalytic reaction $A \rightarrow B$ occurs in spherical catalyst pellets with radius $R = 3$ mm. The intrinsic rate constant is $k_s = 0.08 \text{ s}^{-1}$, and the effective diffusivity is $D_e = 1.2 \times 10^{-7} \text{ m}^2/\text{s}$. Calculate: (a) the Thiele modulus, (b) the effectiveness factor, (c) the fraction of catalyst volume that is effectively utilized, (d) the percentage increase in overall rate if the pellet radius is reduced to 1.5 mm.

Solution:

Part (a): Thiele modulus

Convert radius to meters: $R = 3 \text{ mm} = 0.003 \text{ m}$

Using Equation 12.18:

$$\phi = R \cdot \sqrt{(k_s/D_e)} = 0.003 \times \sqrt{(0.08/(1.2 \times 10^{-7}))}$$

$$\phi = 0.003 \times \sqrt{(6.667 \times 10^5)} = 0.003 \times 816.5$$

$$\phi = 2.45$$

Part (b): Effectiveness factor

Using Equation 12.16 for a sphere:

$$\eta = (3/\phi^2) \cdot (\phi \cdot \coth(\phi) - 1)$$

First calculate $\coth(\phi) = \coth(2.45)$:

$$\coth(2.45) = \cosh(2.45)/\sinh(2.45) = 5.835/5.753 = 1.014$$

$$\eta = (3/(2.45)^2) \cdot (2.45 \times 1.014 - 1)$$

$$\eta = (3/6.00) \cdot (2.484 - 1) = 0.500 \times 1.484$$

$$\eta = 0.742 \text{ or } 74.2\%$$

Part (c): Effective catalyst volume fraction

The effectiveness factor of 0.742 means that 74.2% of the catalyst is effectively utilized. For high Thiele modulus, most reaction occurs in an outer shell.

The effective utilization depth can be estimated from where concentration drops significantly. For $\phi = 2.45$, roughly the outer 60-70% of radius is effectively used.

Approximately 74% of the catalyst volume is effectively utilized.

Part (d): Effect of reducing pellet size

New radius: $R_{new} = 1.5 \text{ mm} = 0.0015 \text{ m}$

New Thiele modulus: $\phi_{new} = 0.0015 \times 816.5 = 1.225$

$$\eta = (3/\phi^2) \cdot (\phi \cdot \coth(\phi) - 1) = 0.912$$

Actually, I'll use the alternative formula: $\eta = 3(\phi \cdot \coth(\phi) - 1)/\phi^2$

Percentage increase: $(0.912 - 0.742)/0.742 \times 100\% = 23\%$

Reducing the pellet radius by 50% increases the overall rate by approximately 23%.

Note: The rate per unit mass increases because η increases, even though the total catalyst mass may be the same.

Example 12.2: Application of Weisz-Prater Criterion

Problem Statement:

In a kinetic study, the following data were obtained for the catalytic decomposition of compound A on spherical catalyst pellets ($R = 2.5 \text{ mm}$, $\rho_P = 1200 \text{ kg/m}^3$):

Observed rate: $r_{obs} = 3.5 \times 10^{-4} \text{ mol}/(\text{kg}_{Cat} \cdot \text{s})$

Bulk concentration: $C_B = 0.50 \text{ mol/L}$

Estimated $D_e = 8 \times 10^{-8} \text{ m}^2/\text{s}$

Porosity $\varepsilon_P = 0.45$, tortuosity $\tau_P = 3.5$

Determine: (a) whether internal diffusion limitations are significant using the Weisz-Prater criterion, (b) if external mass transfer resistance is negligible given $k_c = 0.01 \text{ m/s}$, (c) whether the measured kinetics represent intrinsic behavior.

Solution:

Part (a): Weisz-Prater criterion

Calculate the Weisz modulus using Equation 12.25:

$$\Phi = r_{obs} \cdot \rho_P \cdot R^2 / (D_e \cdot C_S)$$

Assuming $C_S \approx C_B$ (to be verified):

Convert units: $R = 2.5 \text{ mm} = 0.0025 \text{ m}$, $C_B = 0.50 \text{ mol/L} = 500 \text{ mol/m}^3$

$$\Phi = (3.5 \times 10^{-4}) \times 1200 \times (0.0025)^2 / (8 \times 10^{-8} \times 500)$$

$$\Phi = (3.5 \times 10^{-4}) \times 1200 \times 6.25 \times 10^{-6} / (4 \times 10^{-5})$$

$$\Phi = 2.625 \times 10^{-6} / (4 \times 10^{-5}) = 0.0656$$

$$\Phi = 0.066$$

Since $\Phi = 0.066 < 0.15$, internal diffusion limitations are NOT significant.

Part (b): External mass transfer resistance

Check using the criterion from Equation 12.8. First, estimate k_s :

If diffusion is negligible, $\eta \approx 1$, so:

$$r_{\text{obs}} = k_s \cdot C_s \text{ (for first-order)}$$

$$r_{\text{obs}} \text{ (per volume)} = r_{\text{obs}} \cdot \rho_P = 3.5 \times 10^{-4} \times 1200 = 0.42 \text{ mol}/(\text{m}_{\text{cat}}^3 \cdot \text{s})$$

$$\text{For first-order: } k_{s,\text{vol}} = r_{\text{obs,vol}}/C_s = 0.42/500 = 8.4 \times 10^{-4} \text{ s}^{-1}$$

Now check external resistance:

$$k_s \cdot R / (k_c \cdot C_B) = (0.42/500) \times 0.0025 / (0.01 \times 500) = 4.2 \times 10^{-7}$$

This is $\ll 0.05$, so external mass transfer resistance is NEGLIGIBLE.

Part (c): Intrinsic kinetics

Since both $\Phi < 0.15$ (no internal diffusion limitation) and the external resistance criterion is satisfied, the measured kinetics represent intrinsic behavior.

Conclusion: The measured rate data can be used directly for kinetic parameter estimation without transport corrections. The effectiveness factor is essentially unity ($\eta \approx 1$).

Example 12.3: Design of Catalyst Pellet Size

Problem Statement:

A second-order gas-phase reaction $2A \rightarrow B$ is to be carried out in a packed bed reactor using spherical catalyst pellets. Laboratory studies with small particles ($R = 0.5 \text{ mm}$) showed no diffusion limitations with intrinsic kinetics: $r = k_s \cdot C_A^2$ where $k_s = 15 \text{ L}/(\text{mol} \cdot \text{s})$. For the commercial reactor:

Operating concentration: $C_{A,s} = 2.0 \text{ mol/L}$

Temperature: 450 K

$$D_e = 5 \times 10^{-7} \text{ m}^2/\text{s}$$

To minimize pressure drop, pellets with $R = 4 \text{ mm}$ are desired. Determine: (a) the Thiele modulus for the large pellets, (b) the effectiveness factor, (c) the required catalyst mass compared to the ideal case with no diffusion limitations, (d) whether smaller pellets should be used if $\eta < 0.3$ is unacceptable.

Solution:

Part (a): Thiele modulus for second-order reaction

$$k_s = 15 \text{ L}/(\text{mol} \cdot \text{s}) = 15 \cdot 10^{-3} \text{ m}^3/(\text{mol} \cdot \text{s})$$

For second-order reaction ($n = 2$), use the generalized Thiele modulus from Equation 12.23:

$$\phi_2 = R \cdot \sqrt{(k_s \cdot C_{A,s})^{(n-1)} / D_e} = R \cdot \sqrt{(k_s \cdot C_{A,s}) / D_e}$$

Convert: $R = 4 \text{ mm} = 0.004 \text{ m}$, $C_{A,s} = 2.0 \text{ mol/L} = 2000 \text{ mol/m}^3$

$$\phi_2 = 0.004 \times \sqrt{(15 \times 10^{-3} \times 2000 / (5 \times 10^{-7}))} = 31$$

$$\phi_2 \approx 31$$

This is a large Thiele modulus, indicating diffusion limitations.

Part (b): Effectiveness factor

For large ϕ_2 ($\phi_2 \gg 4$), use the asymptotic approximation from Equation 12.24:

$$\eta \approx (3/\phi_2) \cdot \sqrt{(n+1)/2} = (3/31) \cdot \sqrt{3/2} = 0.118$$

$$\eta \approx 0.118 \text{ or } 12\%$$

Only about 12% of the catalyst is effectively utilized!

Part (c): Required catalyst mass

With no diffusion limitations, the required catalyst mass is M_0 .

With $\eta = 0.118$, the actual rate is only 11.8% of the intrinsic rate, so:

$$\text{Required mass} = M_0 / \eta = M_0 / 0.118 = 8.47 \cdot M_0$$

The reactor would need 8 times more catalyst than the ideal case!

Part (d): Evaluation of smaller pellet size

If $\eta < 0.3$ is unacceptable, we need $\eta \geq 0.3$.

$$\text{From the asymptotic formula: } \eta = (3/\phi_2) \cdot \sqrt{3/2}$$

$$0.3 = (3.67) / \phi_2$$

$$\phi_{2,\text{max}} = 3.67 / 0.3 = 12.2$$

Since $\phi_2 \propto R$:

$$R_{\text{max}} = R \times (\phi_{2,\text{max}} / \phi_2) = 4 \text{ mm} \times (12.2 / 98) = 0.498 \text{ mm} \approx 0.5 \text{ mm}$$

To achieve $\eta \geq 0.3$, the pellet radius must be reduced to approximately 0.5 mm, which defeats the purpose of using large pellets for low pressure drop.

Recommendation: Consider alternative designs such as: (1) hollow cylindrical pellets to reduce diffusion path, (2) monolith catalysts with straight channels, (3) accepting lower per-pass conversion and using recycle, or (4) using a different catalyst formulation with higher D_{eff} .

12.10 Guided Learning Examples

The following examples use a guided problem-solving approach. Do not solve the problems directly. Instead, I will ask you questions to help you understand the fundamental assumptions and guide you toward the solution.

Guided Example 12.1: Combined External and Internal Resistances

Problem Statement:

A first-order reaction $A \rightarrow B$ occurs on spherical catalyst pellets ($R = 3 \text{ mm}$, $\rho_P = 1500 \text{ kg/m}^3$, $D_e = 1 \times 10^{-7} \text{ m}^2/\text{s}$) in a packed bed. The bulk fluid concentration is $C_B = 1.5 \text{ mol/L}$, the mass transfer coefficient is $k_C = 0.008 \text{ m/s}$, and the intrinsic rate constant is $k_S = 0.12 \text{ s}^{-1}$. Both external and internal resistances may be significant. Determine the overall observed reaction rate accounting for both resistances. Calculate the surface concentration C_S and the concentration at the pellet center C_{center} .

My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the fundamental assumptions in the modelling by asking me questions and wait for my answer to each question.

Guided Example 12.2: Temperature Effects on Effectiveness Factor

Problem Statement:

A catalyst operates at $T = 400 \text{ K}$ with $\phi = 2.0$ and $\eta = 0.71$. The activation energy for the intrinsic reaction is $E_A = 80 \text{ kJ/mol}$, while the effective diffusivity has activation energy $E_D = 15 \text{ kJ/mol}$. If temperature is increased to 450 K , analyze: (a) how the Thiele modulus changes, (b) whether the effectiveness factor increases or decreases, (c) whether the overall observed rate increases or decreases, (d) the implications for optimal temperature selection in diffusion-limited regimes.

My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the fundamental assumptions in the modelling by asking me questions and wait for my answer to each question.

Guided Example 12.3: Catalyst Pellet Shape Optimization

Problem Statement:

A manufacturer must choose between three pellet shapes for a new catalyst, all with the same volume $V = 0.5 \text{ cm}^3$: (1) sphere with $R = 4.92 \text{ mm}$, (2) infinite cylinder with $R = 3.99 \text{ mm}$ and length $L = 10 \text{ mm}$, (3) hollow cylinder with outer radius $R_o = 4.5 \text{ mm}$, inner radius R_i

= 2.0 mm, and length $L = 10$ mm. The reaction is first-order with $k_s = 0.2 \text{ s}^{-1}$ and $D_e = 2 \times 10^{-7} \text{ m}^2/\text{s}$. Compare the effectiveness factors and recommend the optimal shape considering both catalyst utilization and mechanical strength (hollow cylinders are more fragile).

My objective is to learn and understand chemical reaction engineering. Do not solve the problem immediately. Instead, help me understand the fundamental assumptions in the modelling by asking me questions and wait for my answer to each question.

12.11 Practice Problems

Advanced Exercises

Exercise 12.1: Derive the effectiveness factor expression for a catalyst slab of half-thickness L with n th-order reaction kinetics $r = k_s \cdot C^n$. Start from the diffusion-reaction equation $D_e \cdot d^2C/dx^2 = k_s \cdot C^n$ with boundary conditions $C = C_s$ at $x = 0$ and $dC/dx = 0$ at $x = L$ (center). Transform to dimensionless variables $\omega = C/C_s$ and $\xi = x/L$. Show that the generalized Thiele modulus is $\varphi_n = L \cdot \sqrt{(k_s \cdot C_s^{n-1}/D_e)}$. Derive the exact solution for $n = 1$ and show that $\eta = \tanh(\phi)/\phi$. For $n \neq 1$, show that numerical integration is required and develop an asymptotic approximation for large φ_n .

Exercise 12.2: A complex reaction network occurs in a catalyst pellet: $A \rightarrow B$ (first-order, k_1), $B \rightarrow C$ (first-order, k_2), where $k_2 = 0.5 \cdot k_1$. Develop the coupled diffusion-reaction equations for A and B in a spherical pellet. Show that the selectivity to B depends on both the intrinsic kinetics (k_1/k_2 ratio) and the Thiele modulus. For $\phi_A = R \cdot \sqrt{(k_1/D_{e,A})}$ ranging from 0.1 to 10, calculate and plot: (a) the concentration profiles of A and B vs. radial position, (b) the overall selectivity to B at the pellet exit, (c) the optimal pellet size that maximizes B yield. Assume $D_{e,A} = D_{e,B}$. Discuss why smaller pellets may give lower selectivity even though they have higher effectiveness factors.

Exercise 12.3: For a non-isothermal catalyst pellet with exothermic reaction, both concentration and temperature vary with position. The coupled equations are: $D_e \cdot \nabla^2 C = k_s(T) \cdot f(C)$ and $k_{\text{eff}} \cdot \nabla^2 T = (-\Delta H_{\text{rxn}}) \cdot k_s(T) \cdot f(C)$, where k_{eff} is effective thermal conductivity. Define dimensionless parameters: $\beta = E_A/(RT_s)$ (activation energy), $\gamma = (-\Delta H_{\text{rxn}}) \cdot D_e \cdot C_s / (k_{\text{eff}} \cdot T_s)$ (heat generation parameter). Analyze the case where $\phi = 5$, $\beta = 20$, $\gamma = 0.3$ for a spherical pellet with first-order kinetics. Show that temperature increases toward the pellet center (hot spot formation). Calculate the maximum internal temperature and compare the non-isothermal effectiveness factor to the isothermal case. Discuss conditions under which thermal effects are significant.

Exercise 12.4: Design a laboratory kinetic study to measure intrinsic rate constants while avoiding transport artifacts. The reaction is $A + B \rightarrow C$ on a supported metal catalyst. You have

variable-size catalyst particles (0.1-5 mm diameter), adjustable flow rates (0.1-10 L/min), and temperature control (300-500 K). Develop an experimental protocol that includes: (a) criteria for selecting particle size and flow rate to ensure $\Phi < 0.15$ and negligible external resistance, (b) a systematic procedure to verify absence of transport limitations by varying particle size and flow rate while checking that measured rate constants remain unchanged, (c) estimation of D_e from structural properties ($\varepsilon_p = 0.55$, $\tau_p = 4$, $T = 400$ K) using the dusty-gas model, (d) uncertainty analysis showing how errors in D_e estimation affect the confidence that transport is negligible. Apply your protocol to specific conditions: $C_A = 0.5$ mol/L, $C_B = 0.3$ mol/L, expected $k_S \approx 0.05$ L/(mol·s) at 400 K, $E_A \approx 70$ kJ/mol.

Simple Hand-Calculation Exercises

Exercise 12.5: A spherical catalyst pellet has $R = 2$ mm, $k_S = 0.05$ s⁻¹, and $D_e = 8 \times 10^{-8}$ m²/s for a first-order reaction. Calculate: (a) the Thiele modulus ϕ , (b) estimate the effectiveness factor using the asymptotic formula $\eta \approx 3/\phi$ if $\phi > 4$, or $\eta \approx 1 - \phi^2/6$ if $\phi < 0.4$, or interpolate if intermediate, (c) what particle radius would give $\phi = 1$?

Exercise 12.6: Experimental data give: $r_{obs} = 2.5 \times 10^{-4}$ mol/(kg·s), $\rho_p = 1400$ kg/m³, $R = 3$ mm, $C_S = 0.8$ mol/L, $D_e = 1.5 \times 10^{-7}$ m²/s. Calculate the Weisz-Prater modulus Φ . Is internal diffusion significant? If the measured activation energy is $E_{App} = 45$ kJ/mol and the true activation energy is known to be $E_{true} = 90$ kJ/mol for this first-order reaction, is this consistent with your Weisz-Prater analysis? (Hint: under severe diffusion limitation, $E_{App} \approx E_{true}/2$)

Exercise 12.7: For a second-order reaction with $k_S = 0.20$ L/(mol·s), $C_{A,s} = 1.5$ mol/L, $D_e = 6 \times 10^{-8}$ m²/s in a spherical pellet of radius $R = 2.5$ mm, calculate: (a) the generalized Thiele modulus ϕ_2 , (b) the approximate effectiveness factor using $\eta \approx (3/\phi_2) \cdot \sqrt{3/2}$ for large ϕ_2 , (c) the intrinsic rate $r_{intrinsic} = k_S \cdot C_{A,s}^2$ per unit volume, (d) the actual rate $r_{actual} = \eta \cdot r_{intrinsic}$.

Exercise 12.8: A catalyst pellet has $\varepsilon_p = 0.48$ and $\tau_p = 3.2$. The molecular diffusivity of reactant A in the gas phase at reaction conditions is $D_{AB} = 2.5 \times 10^{-5}$ m²/s. Calculate the effective diffusivity D_{eff} using Equation 12.10. If the temperature is increased by 50 K and D_{AB} increases to 3.0×10^{-5} m²/s (assuming porosity and tortuosity remain constant), what is the new D_{eff} ? By what percentage does D_{eff} increase?

Chapter 12 Summary: What You Should Have Learned

After completing this chapter, you should be able to:

1. Understand mass and heat transfer limitations in heterogeneous catalysis
2. Define and calculate the Thiele modulus for catalyst pellets
3. Calculate effectiveness factors for different pellet geometries and reaction orders
4. Apply the Weisz-Prater criterion to assess internal diffusion limitations
5. Understand external mass transfer limitations and calculate mass transfer coefficients
6. Design catalyst pellets and reactors to minimize transport resistances
7. Understand the interplay between intrinsic kinetics and transport phenomena

Index

- Accumulation runaway, 244
- Adiabatic, 99
- Adiabatic Layers, 175
- Adiabatic PFR, 109, 144
- Adiabatic Reactor Design, 171
- AI, 21
- Apparent Kinetics, 265
- Arrhenius Equation, 65
- asymptotic stability, 206
- Autoignition, 225
- Axial Dispersion Model, 193
- Batch Reactor, 80, 101
- Batch Reactors, 39
- bifurcation, 235
- Bifurcation Diagrams, 242
- Bubble Column, 48
- Classification, 35
- Cold Shot Cooling, 176
- Combined Reactor Systems, 155
- Complex Reaction Networks, 152
- Consecutive Reactions, 127, 152, 154
- Consequence*, 213
- Continuous Stirred Tank Reactor, 85, 104
- Continuously Stirred Tank Reactor
CSTR, 35
- Conversion, 63
- CSTR, 35, 85, 122, 171
- Damköhler number Da , 233
- Decomposition runaway, 245
- deflagration, 228
- detonations, 228
- dimensionless activation energy β , 208, 233
- dimensionless concentration ω , 233
- dimensionless energy balance, 233
- dimensionless heat generation γ , 233
- dimensionless material balance, 233
- dimensionless sensitivity coefficients, 239
- dimensionless temperature ψ , 233
- dimensionless time θ , 233
- dust explosion pentagon, 230
- Dust explosions, 229
- effective diffusivity, 261
- Effectiveness Factor, 261, 262
- Emergency Shutdown, 252
- Energy Balance, 99
- Energy Balances, 98
- Equilibrium, 69
- Equilibrium Constant, 168
- Equilibrium Conversion Curve, 168
- Equilibrium Limitations, 170
- Equilibrium-Limited, 165
- Equipment Failure, 246
- Errors of commission, 249
- Errors of omission, 249
- ESD, 252
- Event tree analysis, 222
- Explosivity, 228
- Exposure Limits, 223
- extent of reaction*, 119
- Extent of Reaction, 62
- Extent of Reaction Approach, 119
- External Mass Transfer, 260
- Fault tree analysis, 222
- Film Theory, 260
- Fire detection, 227
- fire triangle, 226
- Fixed Bed, 45
- Flammability, 225
- Fluidized Bed, 53
- FMEA, 219, 220
- HAZOP, 216
- Heat generation, 105
- Heat generation curve, 232
- Heat of Reaction, 100
- Heat removal, 105
- Heat removal curve, 232
- Heterogeneous, 33
- Heterogeneous catalysis, 258
- Homogeneous, 32
- Human Factors, 248
- hysteresis, 243
- hysteresis loop, 243

IDLH, 223
 Ignition, 227
 Inerting, 230
 IPL, 221
 Isothermal, 99, 136
 IUPAC, 62
 Knudsen diffusion, 262
 Langmuir-Hinshelwood Kinetics, 68
 Layer of Protection Analysis, 220, 250
 LEL, 225
 LFL, 225
 Liapunov stability criteria, 238
 Liapunov Stability Theory, 236
 Limiting Reactants, 63
 LOPA, 220
 Lower Explosive Limit, 225
 Lower Flammable Limit, 225
 marginal stability, 206
 Mass Transfer Steps, 259
 MEC, 229
 Minimum Explosible Concentration, 229
 Minimum Oxygen Concentration, 226
 Mixing, 35
 MOC, 226
 Multiple Reaction, 61
 Multiple Reactions, 126, 150
 Multiple Reactor Configurations, 174
 Multiple steady states, 207
 Multiple Steady States, 105
 Multiplicity, 234
 Non-Ideal Reactors, 185
 Non-Isothermal, 139
 oscillatory behavior, 207
 Parallel Reactions, 72, 126, 153
 Parametric sensitivity, 207
 Parametric Sensitivity, 239
 Pellet Shape, 270
 PFR, 36, 89, 124, 170
 PHA, 216
 Plug Flow, 36
 Plug Flow Reactor, 89, 108, 143
 Pressure Hazards, 228
Probability, 213
 Pulse Input Experiment, 187
 Rate Laws, 67
 Reaction Rate, 62
 Reactor Stability, 203, 206, 231
 Residence Time Distribution, 185
 Resistances in Series, 259
 Reversible Endothermic Reactions, 173
 Reversible Exothermic Reactions, 173
 Reversible Reactions, 69, 166, 167
Risk, 213
 Risk Assessment, 213
 Risk Management, 203
 Risk matrices, 214
 Risk Priority Number, 219
 Risk tolerance, 215
 Risks in Reactor Operation, 244
 RPN, 219
 RTD for Ideal Reactors, 189
 Rule violations, 249
 Runaway, 231
 Runaway Criteria, 240
 Safe Operating Regions, 239
 Safe Operating Windows, 242
 Safety Instrumented Systems, 250
 Safety Integrity Level, 250
segregation model, 190
 Selectivity, 71, 149, 153
 Semi-Batch, 42
 Sherwood number, 261
 Shutdown, 145
 SIL, 250
 SIS, 250
 Stability Criteria, 237
 Startup, 137, 145
 Steady State, 234
 Steady-State Approximation, 73
 STEL, 223
 Step Input Experiment, 188
 Stoichiometric Coefficient, 61
 Tanks in Series, 38, 174
 Tanks-in-Series Model, 192
 The Weisz-Prater Criterion, 264
 Thermal Runaway, 244
 Thiele Modulus, 263
 Threshold Limit, 223

TLV, 223
Toxicity, 223
Trickle Bed, 50
TWA, 223
UEL, 225
unstable system, 206
Unsteady-State, 135, 136
Upper Explosive Limit, 225
Van't Hoff Equation, 167
Vapor cloud explosions, 228
Variable Density Systems, 118
VCE, 228
x-T Trajectory, 171
Yield, 153
Zero Parameter Model, 190

APPENDIX A: Using the Textbook with AI

A Student Guide

The course textbook has been made available for you to upload directly to Claude (claude.ai), ChatGPT or any AI. Once uploaded, the AI has full access to the book and can assist you in a range of powerful ways throughout your studies. This guide explains what you can do and how to get the most out of this capability.

1. Ask Questions About the Content in any language

You can ask the AI to explain any part of the book — a concept, a derivation, a figure, or an equation. This is particularly useful when you want to understand the reasoning behind a result, not just accept it.

- *"What are the assumptions behind equation 4.6?"*
- *"Why does the author introduce the concept of residence time at this point?"*
- *"Can you explain Figure 7.3 in simpler terms?"*

2. Get Summaries of Chapters or Sections

Ask for concise summaries to review material efficiently before lectures, tutorials, or exams. You can request summaries at different levels of detail.

- *"Give me a one-paragraph overview of Chapter 5."*
- *"Summarize the key equations and when to use them in Section 3.2."*

3. Work Through Exercises

The AI can help with any exercise in the book. You can ask for a short numerical answer to check your work, or for a step-by-step explanation of how to arrive at the solution. For deeper learning, try the Socratic mode described below.

- *"What is the answer to Exercise 6.4?"*
- *"Walk me through the solution to Exercise 9.2, explaining each step."*

4. Learn Through Guided Questions (Recommended)

Rather than receiving answers directly, you can ask the AI to guide you to the solution through questions. This approach builds genuine understanding and is much more effective for exam preparation. Start a project and use the following prompt:

"I will upload a problem from the textbook. Please do not solve it directly, as my goal is to learn. Instead, guide me through the solution by asking questions about the underlying fundamental relationships. Use high accuracy in any calculations, but do not ask questions about numerical details. Wait for my response before proceeding to the next step. Once the problem is fully solved, provide a summary of both the solution and the key concepts I should have learned."

The project will remember these instructions and use it whenever you add a task to the project.

You can use this super prompt in all your subjects

5. Use It in Any Language

You can interact with the AI in any language — Swedish, Arabic, Spanish, or any other. The book content is fully accessible regardless of the language you write in. This can be especially helpful when working through difficult material in your native language first.

Tips for Effective Use

- Always verify AI-generated solutions against your own work and the book — AI can occasionally make errors.
- Be specific in your questions. "Explain Section 4.2" is more effective than "explain the chapter."
- Use the Socratic mode for exercises before attempting the guided solution — it produces better learning outcomes.
- Upload the book once at the start of a session; it remains available for the rest of that conversation.

APPENDIX B Safe Use of AI - Project

My prompt:

"I am including AI as an engineering tool in my course in chemical reaction engineering. Suggest a project for the students using AI to design a process. The focus should be on safe use of AI and the responsibility of the engineer. Are the most appropriate models used, state of the art. Are the calculation correct?"

Here's a project that puts AI responsibility front and center while keeping the chemical engineering technically rigorous.

A Capstone Project: AI-Assisted Reactor Design with Critical Engineering Oversight

"Design of a Continuous Reactor System for [Assigned Process] — Using AI as a Tool, Not a Crutch"

Project Concept

Each student group is assigned a real industrial reaction (suggestions below). They use one or more AI tools to assist with the design, but the **central deliverable is not the reactor design itself — it is the critical audit of what AI got right, what it got wrong, and how the engineer took responsibility for the final result.**

— AI-Assisted Design

Task 1: Problem scoping and AI selection

Groups define the design problem: feed composition, desired conversion, throughput, and safety constraints. They then select which AI models to use and must justify their choices in writing — why GPT-4o vs. Claude vs. Gemini vs. a domain-specific tool, and what each model's known limitations are for technical calculation tasks. This forces students to think critically about model capabilities before they start.

Task 2: AI-generated design

Groups prompt AI tools to propose a reactor type, derive or apply the design equation, estimate required volume, suggest operating conditions, and flag safety concerns. They must use at least two different AI systems and document every prompt and response in an appendix. No editing of AI outputs — raw responses are preserved.

Task 3: Independent hand calculation

Students solve the same design problem themselves using the methods from the course — the appropriate form of the design equation (PFR, CSTR, or PBR as warranted), proper stoichiometry, energy balance if relevant, and a safety analysis based on standard hazard identification. This is the engineering baseline against which AI outputs will be compared.

— Critical Audit and Engineering Sign-Off

Task 4: Systematic AI audit

This is the intellectual core of the project. For each AI response, students evaluate:

- Is the **reactor model** appropriate for the system (flow regime, phase, heat effects)?
- Are the **design equations** correct and properly applied?
- Is the **kinetics** handled correctly — right rate law form, units consistent, Arrhenius parameters reasonable?
- Are **numerical results** within an acceptable margin of the hand calculation? If not, why?
- Did the AI identify the correct **safety hazards** — runaway potential, toxic intermediates, flammability limits?
- Did the AI **hallucinate** any kinetic data, cite nonexistent correlations, or present uncertain numbers with false confidence?

Students should score each AI response on a simple rubric and write a narrative explaining each discrepancy.

Task 5: Design refinement and engineering sign-off

Groups produce a final design that they are personally willing to sign off on as engineers. This means all numbers have been independently verified, all safety concerns have been addressed with reference to standard methods (HAZOP concepts, Damköhler number for thermal runaway screening, etc.), and any AI-generated content that could not be verified has been explicitly excluded or corrected.

Task 6: Presentations

Each group presents both their final reactor design *and* their AI audit findings. A portion of the grade depends on how rigorously they caught and explained AI errors.

Suggested Reaction Systems

The reactions below are industrially relevant, have accessible kinetics in the open literature, and present interesting safety or selectivity challenges:

- Ethylene oxide production (highly exothermic, flammable, toxic — rich safety case)
 - Methanol synthesis from CO/H₂ (equilibrium-limited, catalyst deactivation)
 - Saponification of ethyl acetate (liquid phase, simple kinetics, good for a first audit exercise)
 - Selective oxidation of o-xylene to phthalic anhydride (multiple reactions, hot spots)
 - Catalytic hydrogenation of nitrobenzene to aniline (H₂ handling, exothermicity)
-

Learning Outcomes

By the end of the project, students should be able to articulate why an engineer can never simply accept AI-generated calculations without verification, identify the specific failure modes AI models exhibit on technical problems (unit errors, inappropriate model assumptions, confident hallucination of data), and demonstrate that they understand where professional and legal responsibility lies — with the engineer, not the tool.

This framing — AI as a junior colleague whose work must always be checked before it goes out the door — is probably the most transferable professional lesson you can give them alongside the reaction engineering itself.

Common AI mistakes in Chemical Engineering

Here are the key risk areas specific to chemical engineering:

Thermodynamics & Physical Properties

- Retrieving accurate numerical data (vapor pressures, enthalpies, activity coefficients) — AI may confuse values between compounds or conditions
- Applying the right equation of state for non-ideal systems
- Phase equilibrium calculations, especially for multicomponent systems

Reaction Engineering

- Sign conventions in energy balances (exo vs. endothermic) — a frequent source of errors
- Correctly applying rate laws for complex kinetics (non-elementary, enzymatic, heterogeneous)
- Handling variable-density systems in PFR design — exactly the kind of subtlety you've addressed by eliminating the expansion factor approach
- Mixing up batch, CSTR, and PFR equations under non-isothermal conditions

Numerical & Mathematical Work

- Insufficient numerical accuracy e.g. solving integrals numerically using the Trapezoid Method with too few internal points
- Setting up ODEs correctly for coupled heat and mass balances
- Boundary and initial conditions — easily dropped or misspecified
- Stability analysis of steady states (getting eigenvalue signs wrong)
- Stiff ODE systems where naive solvers fail silently

Transport Phenomena

- Conflating film resistance, pore diffusion, and bulk diffusion effects
- Incorrect Thiele modulus or effectiveness factor application
- Dimensional consistency in correlations (Nu, Sh, Re relationships)

Process Design & Safety

- Scaling from lab to industrial scale — AI may apply correlations outside their valid range





- Runaway reaction conditions — qualitative understanding is often fine, but quantitative thresholds need verification
- HAZOP-style reasoning can be superficial without deep process context

Units & Conventions

- Mixing SI and engineering units silently (a classic dangerous error)
- Inconsistent use of molar vs. mass basis
- Pressure units (bar, atm, kPa, psia) causing off-by-a-factor mistakes

Literature & Data

- Hallucinating kinetic parameters, Arrhenius constants, or equilibrium data
- Citing papers that don't exist or misattributing results
- Confusing correlations valid for specific geometries or catalysts
- AI errors are **not random—they are systematic**:

Type of task	Risk level
Brainstorming / explanation	 Low
Structured derivation	 Medium
Multi-step calculation	 High
Safety-critical engineering decisions	 Very high

Practical advice for your project:

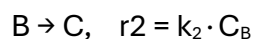
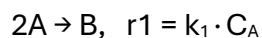
- Always verify numerical values and kinetic data against primary sources
- Have AI generate the *structure* and *reasoning* of derivations, then check the algebra yourself
- Be especially cautious when AI handles simultaneous constraints (e.g., recycle + heat integration + safety limits together)
- AI tends to do well on standard textbook problems but can struggle with your more advanced formulations, like the multi-bed adiabatic quench reactor with full recycle

APPENDIX C Old examination problems

Problem 1 (5 points)

Liquid-phase reaction in a stirred tank reactor (CSTR).

A consecutive liquid-phase reaction takes place in an isothermal continuous stirred tank reactor (CSTR). Both reactions are first order with respect to the reactant and can be considered irreversible:



with $k_1 = 2.7 \text{ min}^{-1}$ and $k_2 = 1.3 \text{ min}^{-1}$.

The reactor volume is 1.65 m^3 . The volumetric flow rate is $0.8 \text{ m}^3/\text{min}$ and the inlet concentration of A is 5 mol/dm^3 . The inlet contains no B, which is the desired product.

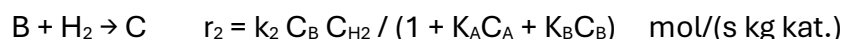
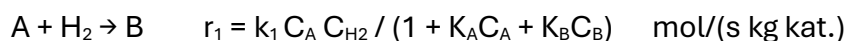
a) Calculate the outlet concentration of B, the production rate of B (mol/min), and the flow-based selectivity of B. (4 points)

b) The product B is a commercial success and production should be increased without new investments. How is the production of B and the selectivity of B affected if the inlet flow rate is doubled? Motivate. (1 point)

Problem 2 (6 points)

a) A is hydrogenated to B, which is then hydrogenated further to C. The pressure is increased from 70 bar to 120 bar.

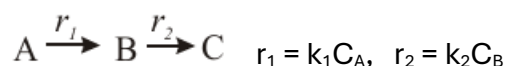
Is the selectivity to B affected by this pressure increase? Motivate. (1 point)



b) The reaction $A \rightarrow B$ occurs on a catalyst with very complex kinetics where the rate first decreases, reaches a minimum at $x = 0.4$, and then increases up to $x = 1$, where x is conversion.

Which reactor(s) should be used to optimize the process if the desired outlet conversion of A is 0.8? Clear motivation is required. (2 points)

c) The following reactions occur on a catalyst (3 points):



$C \rightarrow D$ with rate $r_3 = k_3 C_C^2$

$B \rightarrow E$ with rate $r_4 = k_4 C_B^3$

(i) How is the selectivity of B affected by external mass transfer? Motivate clearly.

(ii) The activation energies are $E_1 = 30$ kJ/mol, $E_2 = 130$ kJ/mol, $E_3 = 50$ kJ/mol, $E_4 = 60$ kJ/mol.

If the selectivity of C is to be maximized, how should the temperature be chosen?

Problem 3 (7 points)

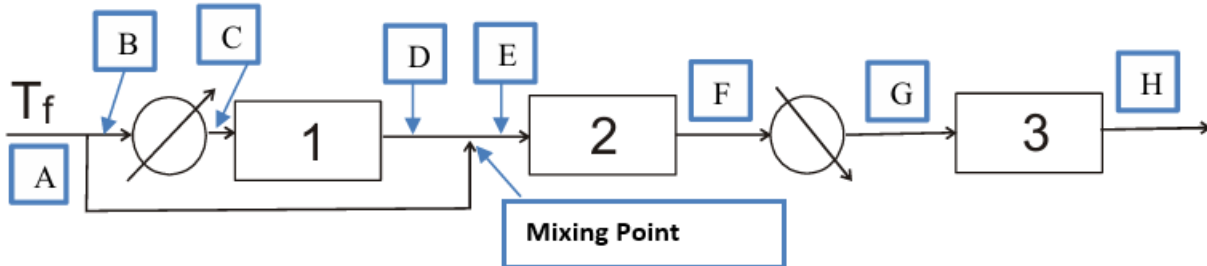
The reaction $A \rightleftharpoons B$ is an exothermic equilibrium reaction in the liquid phase.

To increase conversion, the reaction is carried out in three CSTRs in series.

Before the second reactor a cold shot is introduced, and before the third reactor intermediate cooling is applied.

The liquid feed temperature T_f is 180°C. This stream is heated to 300°C before reactor 1.

The temperature into reactor 3 is cooled to 350°C.



a) Draw an X-T diagram including the equilibrium curve and the locus of maximum rates. Sketch the process for optimal operation and mark points A-H. Motivate their placement. (4 points)

b) Set up a mass balance and an energy balance around the mixing point where the cold stream mixes with the effluent from reactor 1. (2 points)

c) Derive the operating line for reactor 3. (1 point)

Problem 4 (5 points)

A tracer experiment is performed to study non-ideality in a tubular reactor (diameter 2.2 cm, length 60 cm). A pulse is injected just before the tube and the concentration is measured directly after the tube. Experimental residence-time data are given.

Time (s)	C (mol/dm ³)
0	0
4	24
8	30
12	38
16	44
20	58
24	48
28	36
32	18
36	8
40	0

a) Determine the number of tanks in a tanks-in-series model representing the tube. (3 points)

b) Determine the dispersion coefficient in a dispersion model assuming no dispersion in the inlet and outlet. (2 points)

Problem 5 (7 points)

A first-order liquid-phase reaction $A \rightarrow B$ with rate $r = kC_A$ occurs in a vertical tubular reactor. The catalytic material consists of spherical pellets. External mass-transfer resistance is important. What catalyst mass is required to achieve 90% conversion at the reactor outlet?

Given:

$$k = 0.040 \text{ m}^3/(\text{s} \cdot \text{kg catalyst})$$

$$C_{A,\text{in}} = 350 \text{ mol/m}^3$$

$$\text{Sh} = 3$$

$$\text{Flow rate } q = 0.03 \text{ m}^3/\text{s}$$

$$\text{Diffusivity } D = 3 \times 10^{-5} \text{ m}^2/\text{s}$$

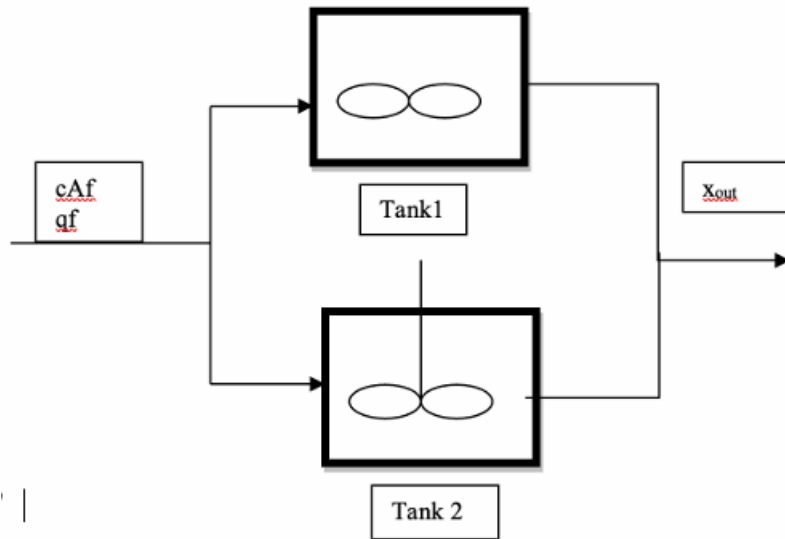
$$\text{Particle diameter } d_p = 3 \text{ mm}$$

$$\text{Particle density } \rho_p = 1000 \text{ kg/m}^3$$

Problem 1 (5 points)

The following liquid-phase reaction occurs:

$A \rightarrow P$ (first-order reaction)



In a process, there is initially one reactor, but capacity must be increased and therefore reactor 2 is built (see the figure: the feed is split between Tank 1 and Tank 2 in parallel, and the outlets are mixed).

What volume should reactor 2 have in order to achieve an overall conversion from the entire plant (x_{out}) of 85%?

Given:

Concentration of A into the whole plant $C_{A,f} = 350 \text{ mol/m}^3$

Flow into the whole plant $q_f = 0.25 \text{ m}^3/\text{s}$ ()

Fraction of the flow to reactor 1: 35%

Pre-exponential factor: $A = 2.2 \times 10^{10} \text{ s}^{-1}$

Activation energy: $E_a = 120 \text{ kJ/mol}$

Reactor temperature: $T = 300^\circ\text{C}$

Volume of reactor 1: $V_1 = 2.0 \text{ m}^3$

Gas constant: $R = 8.314$

Problem 2 (7 points)

The questions below are independent:

a) Transport limitations in catalytic reactions can affect conversion and selectivity. Are transport limitations beneficial or not in the series reaction $A \rightarrow B \rightarrow C$, where all reactions are first order and the goal is to produce B?

Motivate your answer. (1 point)

b) What does it imply if the σ^2 value (variance) of the residence time in a certain reactor is large? (1 point)

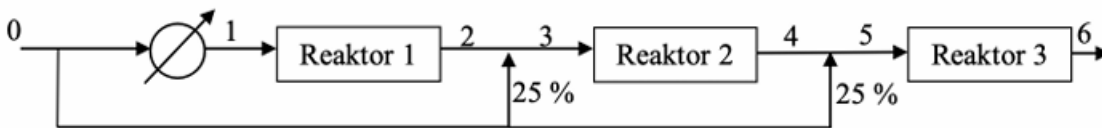
c) Sketch schematically how the residence time distribution function changes when the number of tanks is increased from 1 to 40. (1 point)

d) Describe the different steps that occur in a heterogeneous catalytic process, starting from reactant A in the gas phase until product B is in the gas phase. (2 points)

e) Describe what a semi-batch reactor is. Make a schematic sketch of a semi-batch reactor and set up the material balance. The equation does not need to be solved. The accumulation term should be expressed in terms of volume and concentration. (2 points)

Problem 3 (6 points)

A reactor system consists of three CSTRs in series, cooled by cold feed addition (“cold shot cooling”) in the liquid phase. The reaction $A + B \rightleftharpoons C + D$ is carried out.



The fresh feed to the reactor system consists of equal parts A and B at 380 K and has:

- total molar flow rate: 0.8 kmol/s
- mass flow rate: 25 kg/s

This flow is split such that:

- 50% goes to the first reactor,
- 25% is added to the flow to the second reactor,
- and the remainder is added to the flow to the third reactor.

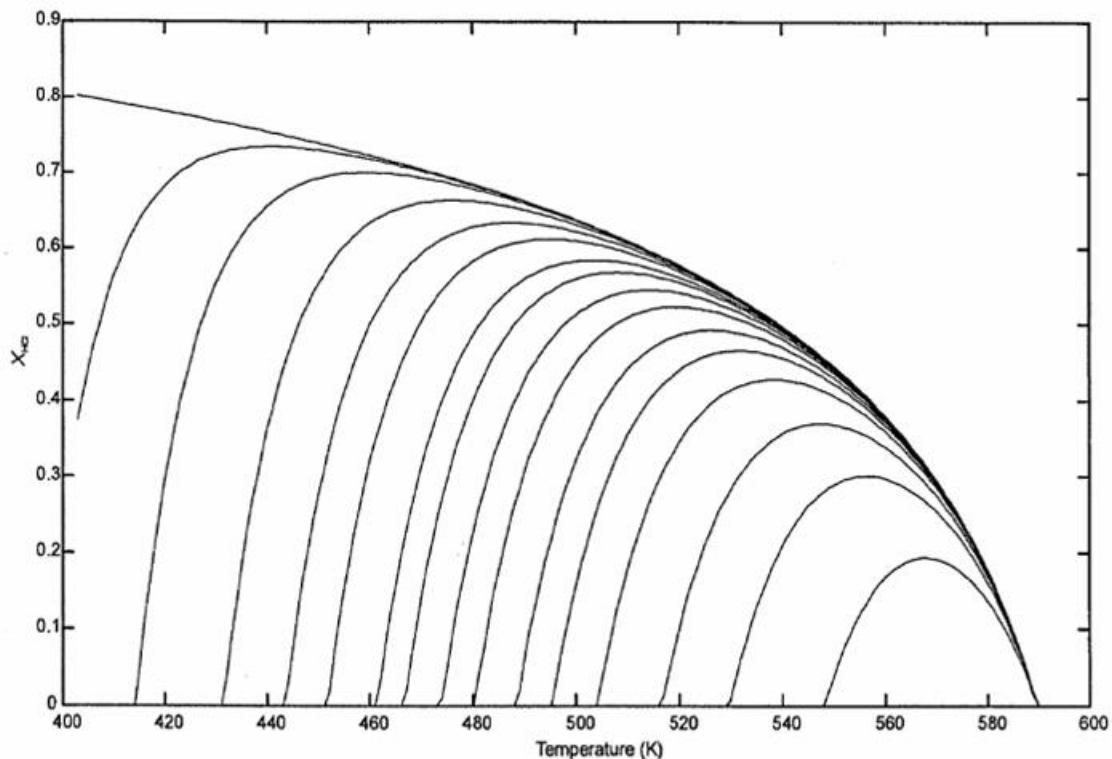
Before the first reactor, the cold feed stream is preheated to 480 K. The reactors operate under equilibrium conditions. A graph is provided showing equilibrium conversion as a function of temperature, as well as lines of constant reaction rate.

The molar heat capacity can be assumed $c_p = 6 \text{ kJ}/(\text{kg}\cdot\text{K})$ for all fluid streams.

The reaction enthalpy is $\Delta H_R = -75 \text{ kJ}/\text{mol}$ under all conditions.

Calculate the conversion of A after the third reactor.

Tip: C_p is given in $\text{kJ}/(\text{kg}\cdot\text{K})$ and is the same for all streams. The liquid can be assumed incompressible (mass flow does not change). Use dimensional analysis in the balances.



Problem 4 (6 points)

a) The reaction $A \rightarrow B$ with rate $r = kC_A^2$ occurs in a reactor combination (one or several reactors).

Which reactor combination(s) should you choose to minimize the total reactor volume if the reaction is:

(i) Endothermic

(ii) Exothermic

Motivate clearly; graphical illustrations are welcome. (3 points)

b) The reaction $A \rightarrow B$ occurs with rate $r = kC_A^2$ (second-order).

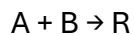
Derive an expression for how the conversion can be determined for a non-ideal reactor via the segregation model.

Available data: a pulse tracer experiment with measured concentration versus time, inlet concentration $C_{A,f}$, and rate constant k .

No integrals need to be evaluated. (3 points)

Problem 5 (6 points)

Product R is formed from A and B. The reactions occur in the liquid phase and are first order with respect to A.



The process is carried out in a batch reactor at constant temperature (80°C).

At this temperature, the rate constant is $k_1 = 0.04 \text{ min}^{-1}$.

Initial concentrations:

$$C_{A,0} = 0.85 \text{ kmol/m}^3 \text{ of A}$$

$$C_{B,0} = 15 \text{ kmol/m}^3 \text{ of B}$$

(no R initially)

The time to empty and fill the batch reactor is 30 min.

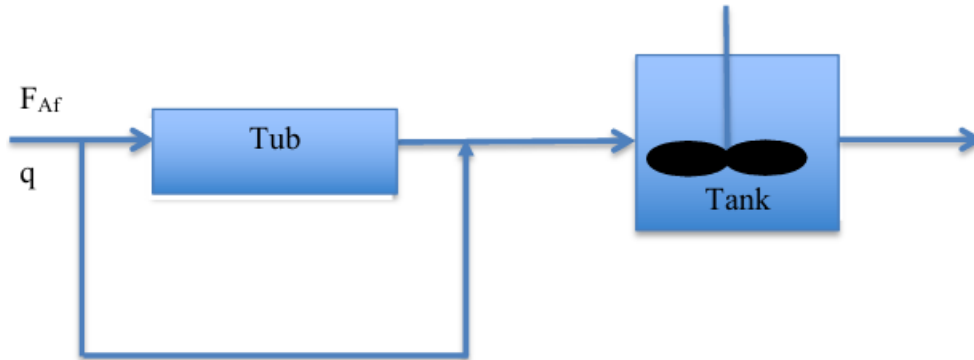
The production rate of R is 80 kg/h and the concentration of R in the product is 0.5 kmol/m^3 .

What reactor volume is required and what reaction time is required?

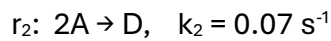
Data (molecular weights): $M_A = 80 \text{ g/mol}$, $M_B = 18 \text{ g/mol}$, $M_R = 98 \text{ g/mol}$

Problem 1 (6 points)

A reactor system is used as shown in the figure: a fraction of the feed bypasses the tubular reactor and then mixes with the tube effluent before entering a stirred tank reactor (CSTR).



The system is used for two parallel liquid-phase reactions (both first order with respect to A):



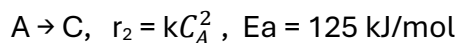
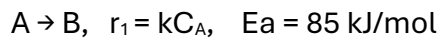
30% of the flow bypasses the tubular reactor. The tube volume is 0.6 m^3 . The volumetric flow rate is $q = 0.15 \text{ m}^3/\text{s}$ and the molar flow of A in the fresh feed is $F_{A,f} = 25 \text{ mol/s}$.

What tank volume is required to achieve an overall conversion of 75% from the entire plant?

Problem 2 (7 points)

The questions below are independent.

a) The following parallel reactions occur in the gas phase:



where B is the desired product.

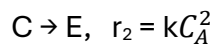
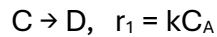
- (i) Should a CSTR, PFR, or batch reactor be chosen? A clear justification is required. (1 point)

(ii) Which process conditions should be selected? A clear justification is required. (2 points)

b) What is the difference between bulk diffusion and Knudsen diffusion? (1 point)

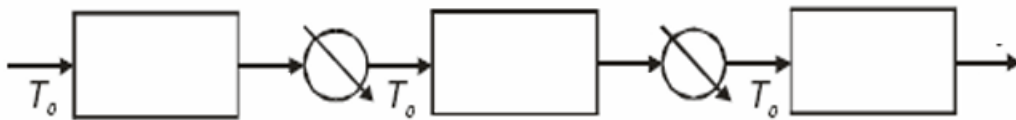
c) What does it mean that the Thiele modulus is large? (1 point)

d) The following parallel reactions occur in liquid phase:



D is the desired product. How is the selectivity to D affected by external mass-transfer limitations? (2 points)

Problem 3 (5 points)



The reaction $A \rightleftharpoons B$ is an exothermic equilibrium process. The reaction is first order with respect to A and B and occurs in liquid phase.

It is carried out in three stirred tank reactors (CSTRs) with intermediate cooling. The inlet temperature to all three reactors is 280°C ($T_0 = 280^\circ\text{C}$). A “locus of maximum rates” curve is provided in the exam.

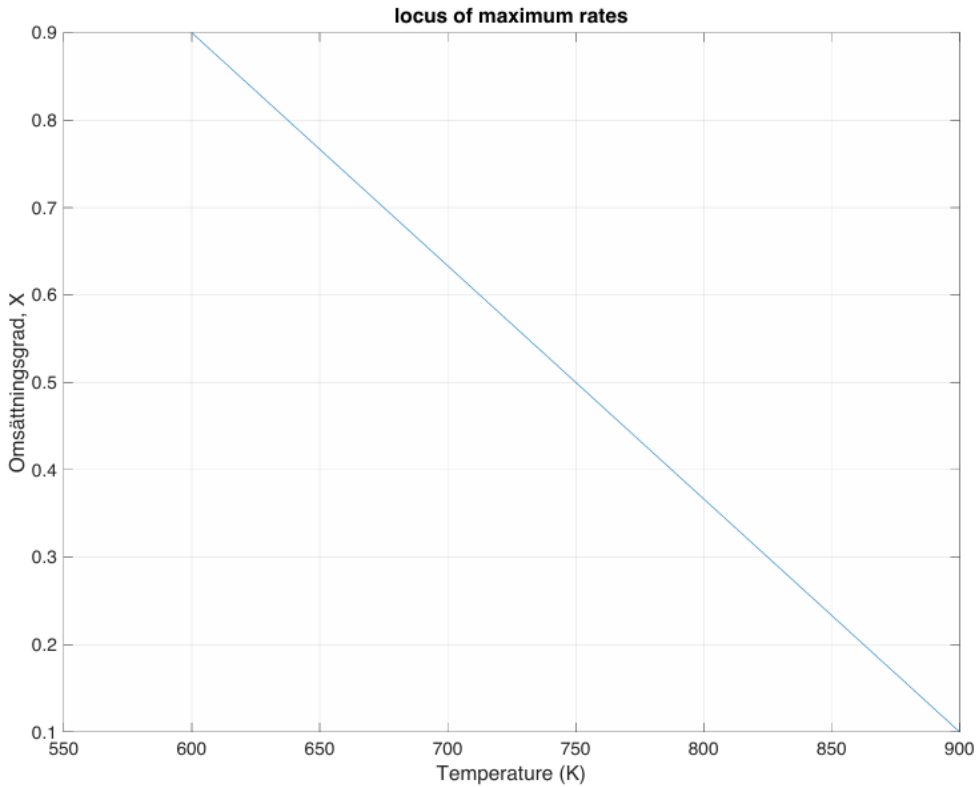
The feed consists of 0.4 mol/s of A and 0.8 mol/s of inert material I.

Heat capacities:

$$C_{P,A} = 55 \text{ J}/(\text{mol K}), \quad C_{P,B} = 62 \text{ J}/(\text{mol K}), \quad C_{P,I} = 52 \text{ J}/(\text{mol K}).$$

Heat of reaction: $\Delta H = -75 \text{ kJ/mol}$.

What is the conversion after reactor 3?



Problem 4 (7 points)

A company wants to carry out the following liquid-phase reactions:



They have an unused reactor and consider whether it is suitable. To characterize the reactor, a tracer experiment is carried out. The measured concentration at different times is:

t (s): 0, 3, 6, 9, 12, 15, 18, 21, 24, 27, 30, 33

C (mol/m³): 0, 0, 9, 30, 23, 18, 12, 9, 6, 5, 2, 0

The engineer decides to use the tanks-in-series model to calculate the expected conversion of C_A after the reactor. External mass-transfer resistance around the catalyst particles is important.

Given:

$$C_{A,in} = 4000 \text{ mol/m}^3$$

$$q = 0.005 \text{ m}^3/\text{s}$$

$$r_1 = k_1 C_A, \quad k_1 = 1.70 \text{ s}^{-1}$$

$$r_2 = k_2, \quad k_2 = 7.48 \times 10^{-4} \text{ mol/(s m}^3\text{)} \text{ (NOTE: } r_2 \text{ is constant, independent of concentration)}$$

$$V = 0.400 \text{ m}^3$$

$$k_c = 0.251 \text{ m/s}$$

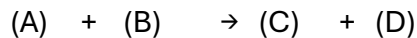
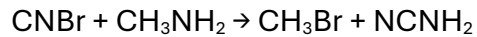
Geometric conversion factor: $S = 0.1 \text{ m}^{-1}$ (m^2 catalyst surface/ m^3 reactor)

- a) How many tanks are required to describe the process? (3 points)
- b) What is the conversion X_A after the reactor? (4 points)

Problem 5 (5 points)

The production of methyl bromide is carried out in an isothermal semi-batch reactor.

Reaction:



The reaction is first order in both the concentration of methylamine (B) and bromocyanide (A), with rate constant k .

A solution of methylamine (B) in methanol with concentration $C_{B,f}$ is fed at volumetric flow rate q .

Initially, the reactor contains a volume V_0 of a solution of bromocyanide (A) in ethanol, with initial concentration $C_{A,0}$.

Internal mass-transfer is important and the effectiveness factor is η .

Set up all relations needed to compute the reactant concentrations as functions of time during filling of the semi-batch reactor.

The differential equations do not need to be solved, but state the integration limits (the system must be solved numerically).