Introduction to Chemical Processes

Principles, Analysis, Synthesis

Second Edition

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INTRODUCTION TO CHEMICAL PROCESSES: PRINCIPLES, ANALYSIS, SYNTHESIS, SECOND EDITION

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Dedication

To my wonderful family

Contents

CHAPTER 5 Why Reactors Aren't Perfect: Reaction Equilibrium and Reaction Kinetics 321

CHAPTER 6 Selection of Separation Technologies and Synthesis of Separation Flow Sheets 375

Preface

Introduction to Chemical Processes: Principles, Analysis, Synthesis is intended for use in an introductory one-semester or two-quarter course for students in chemical engineering and related disciplines. The text assumes that the students have had one semester of college-level general chemistry and one or two semesters of college-level calculus. Although student understanding of the material will be deeper with greater background in linear algebra or organic chemistry, the text is organized so that this background is not required for successful completion.

Course Trends

Introductory chemical engineering courses traditionally focus on chemical process calculations. Material and energy balances are taught, a few concepts in thermodynamics are introduced and miscellaneous information on units, dimensions, and curve fitting are included. By the end of the semester most students, given a well-defined problem, can set up and solve material and energy balance equations, but they do not have a good understanding of how these calculations are related to actually designing chemical processes to make products.

Several years ago the chemical engineering faculty at UW—Madison decided to redesign our introductory course. Our goals were twofold: (1) to give the students a better flavor of how chemical processes convert raw materials to useful products and (2) to provide the students with an appreciation for the ways in which chemical engineers make decisions and balance constraints to come up with new processes and products. At the end of the semester, we wanted students to be able, with a minimum amount of information, to synthesize a chemical process flowsheet that would approximate real industrial processes. This includes selection of appropriate separation technology, determination of reasonable operating conditions, optimization of key process variables, integration of energy needs, and calculation of material and energy flows. This becomes possible at the introductory level through use of limiting cases, idealizations, approximations, and heuristics. We also wished to integrate concepts in sustainable resource utilization, process safety, environmental protection, and economics at the earliest levels of engineering education, so that these principles become naturally embedded in a student's problem-solving practices.

The modern approach equips students with the tools necessary for thinking about the creative strategies of chemical process synthesis and greatly enhances students' understanding of the connection between the *chemistry* and the *process*.

It provides the students a framework for much of the rest of the curriculum: Students are more motivated to struggle through the rigor and abstraction of engineering science courses in thermodynamics, transport, and kinetics, because the connection between fundamental concepts and practical engineering problem solving has been made. Senior process design courses revisit the same terrain but at a more sophisticated level. Students learn that the principles of chemical processes, and the strategies of process synthesis and analysis, can be advantageously applied to an enormous diversity of problems, from intracellular trafficking of a drug to accumulation of pollutants in the ecosystem. The ready availability of easy-to-use computational tools means that students in an introductory course can tackle challenging and complex problems.

Organization

Many times, students decide to major in chemical engineering because they like chemistry and math, and are interested in practical applications. In designing this text, we have tried to keep this motivation in mind. We start right off the bat, in Chapter 1, providing a link to freshman chemistry courses. We show how simple stoichiometric concepts are used to make informed choices about raw materials and reaction pathways. Students should understand that engineering is not simply about doing calculations, but about using calculations wisely to make good choices. The idea of combining calculations, data and heuristics to make choices is a central theme throughout the text.

Chapter 2 introduces the simple but powerful idea of process flow sheeting as the chemical engineer's means to communicate ideas about raw materials, reaction chemistry, processing steps, and products. Here students learn the 10 Easy Steps for process flow calculations, and are introduced, in a very conceptual manner, to system variables, system and stream specifications, and material balances. Many example problems, drawn from a wide diversity of applications, are worked out in detail.

In Chapter 3 we revisit material balance equations, reaction stoichiometry, and process flow sheeting, but with a more rigorous and mathematical approach. Throughout, the text retains this spiral organization, in which we first reinforce concepts introduced in earlier chapters, and then expand and deepen student understanding of these concepts. In this chapter, material balance equations are derived from conservation-of-mass principles, using a notation that students will see in more advanced classes, and we do not shy away from transient processes. Students learn degree-of-freedom analysis as an essential tool for organizing information, identifying constraints, and developing logical problem-solving strategies.

Chapters 4 and 5 delve in greater depth into chemical reactions and reactors. In Chapter 4, students receive additional practice in applying material balance equations to reacting systems. Quantitative measures of reactor performance are introduced, and students learn how performance specifications influence reactor material balance calculations. Descriptive information on the major kinds of industrially important reactions is provided, and heuristics for synthesizing reactor flow sheets are discussed. Chapter 5 introduces key concepts in chemical reaction thermodynamics and chemical kinetics, and students learn how to integrate reaction thermodynamic or kinetic constraints with material balances to select reactor operating conditions for better performance.

Chapters 6 and 7 focus on separators. In Chapter 6, the major separation technologies are described, and heuristics for selecting an appropriate separation method and for sequencing multiple separation steps are provided. Quantitative measures of separator performance are introduced, and students learn how these performance specifications are used in separator material balance calculations. Chapter 7 delves more deeply into equilibrium-based separations. Students gain considerable experience in using physical property data, graphs and equations to obtain phase equilibrium information. They learn how phase equilibrium constraints are coupled with material balance equations to design and analyze common separation units, and learn how to select process operating conditions to improve separator performance.

In Chapter 8, the energy balance equation is derived, and students learn the 12 Easy Steps for solving process energy calculations. Concepts such as work and heat are introduced. Students learn how to calculate changes in kinetic or potential energy, and how to find internal energy or enthalpy from equations, charts, and graphs. Plenty of worked-out example problems illustrate how to apply thermodynamic information and the energy balance equation to solve important problems. Chapter 9 is a “sampler” of more complex applications of the basic concepts taught in Chapter 8.

Chapters 1–4 and Chapter 6 provide an excellent introduction to material balances and chemical processes for instruction in a one-quarter course or for those wishing a more leisurely approach. Instructors who do not want to introduce reaction thermodynamics or phase equilibria can omit Chapters 5 and 7. Chapters 8 and 9 can be omitted if energy balances are taught in thermodynamic classes. For students with less mathematical background, all linear algebra sections as well as the unsteady-state problems can be skipped.

Changes from the first edition. The author kept the general flavor and approach of the first edition. The major changes include:

1. Simple matrix manipulations (for example, for balancing chemical reactions) were integrated into the text when the topic was introduced, rather than relegated to a separate section. Students have greater access and familiarity with programs such as MatLab or Python, or calculators that can easily solve matrix equations.
2. The Degree-of-Freedom analysis was moved from Chapter 2 to Chapter 3. This provides students with more practice with solving problems and builds their intuition before the introduction of a systematic means to count equations and variables. This also allows for the introduction of the extent of reaction concept before DOF analysis, which then makes the method of counting reaction variables clearer.

3. The development of the differential material balance equation in Chapter 3 was substantially reorganized. Notation for the integral material balance equation was simplified. The more advanced material on linear models of flowsheets was deleted, as the author found she never taught that material.
4. The old Chapter 4 was split into two chapters, with one focused on reactor performance and practice with the material balance equations in reacting systems, and the second covering more advanced materials on reaction thermodynamics and kinetics. Whereas the old Chapter 4 was rather hefty, the new Chapters 4 and 5 are more similar in scope and size to Chapters 1–3.
5. Similarly, the old Chapter 5 was split into two, with the new Chapter 6 focused on descriptive information on separators and practice on applying the material balance equations to separation flowsheets, and the new Chapter 7 covering more advanced material on phase equilibria and equilibrium-based separations. The later material was also reorganized so that the introduction of a specific type of phase equilibrium was followed immediately by application of that equilibrium data to a separation problem.
6. Additionally, the old Chapter 6 was split into two, for the same reason of making more equal-sized "bites." The new Chapter 8 provides an introduction to energy balances. The development of the energy balance equation was reorganized and the order of some material was rearranged. Now students learn how to find changes in enthalpy as temperature, pressure, and phase change, and then immediately apply this new knowledge to energy balance problems, before moving on to study enthalpy changes due to reaction or mixing. Chapter 9 includes several more advanced topics that illustrate applications of energy balances.
7. Some end-of-chapter problems were omitted, and many new problems were added. For the "Warm-up" and "Drills and Skills" problems, the problems were linked explicitly to the corresponding section in the text.

Features of the Text

The text is written to encourage students to:

- **Link to chemistry.** The text provides a clear link to freshman chemistry courses. Students will remain more interested in the processes and get a better flavor of what chemical processes do if they understand how chemistry relates to processing.
- **Synthesize chemical processes.** The text treats process calculations as a means to an end: the design of safe, reliable, environmentally sound, and economical chemical processes. The author's approach gives students a good understanding of how these calculations inform choices that must be made in designing chemical processes to make desired products.
- **Develop solid problem-solving strategies.** Developing good problem-solving strategies is an important outcome of this introductory course. Readers will find a systematic approach to deriving equations and accounting

for specifications. A novel feature of this text is the use of heuristics, introducing beginning students to the notion that practicing engineers rely not just on calculations but also on collected experiences.

- **Invent and analyze.** The text integrates the best of the "process synthesis" philosophy with modern approaches, problems, and techniques. Students learn that principles of process synthesis are gainfully applied to problems in biotechnology, medicine, materials science, and environmental protection.
- **Let pedagogy lead.** The text is heavily laden with pedagogy, tools to guide the reader and enhance the subject matter. A few of the pedagogical elements in this text include *Helpful Hints* !, *Quick Quiz, ChemiStory,* and *Case Study* sections. For a complete overview of the pedagogical elements see the Guided Tour section.
- **Explore software.** This text is not directly tied to one software program, allowing students to use software as a common tool to solve problems. An appendix illustrates the use of Excel to find fit data to equations or to find roots of equations, and the use of MATLAB to solve matrix equations.

About the Author

Regina Murphy received her S.B. in Chemical Engineering in 1978 from MIT, then took a job at Chevron's Richmond Refinery to learn about real engineering. During her 5 years at Chevron she wore several hats, all of them hard. She returned to MIT in 1983 where she obtained her Ph.D. under the guidance of Clark Colton and Martin Yarmush. In 1989 she joined the faculty in the Department of Chemical Engineering at the University of Wisconsin—Madison, where she has happily stayed for her entire academic career. Her research interests are in protein misfolding and aggregation, especially related to neurodegenerative disease. She has taught several courses throughout the undergraduate curriculum, from an introductory course for freshmen to senior design. She is the recipient of multiple teaching awards including the Chancellor's Distinguished Teaching Award, the highest campus-level recognition for contributions to education. She served as department chair from 2018–2021, where she hired several new faculty and initiated a major project to renovate instructional and research laboratory space. She lives in an old Victorian house on Lake Monona in Madison with her husband Mark Etzel, also a professor at UW. Their twin sons are both proud graduates of UW Madison.

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Guided Tour

Tools That Reinforce Concepts

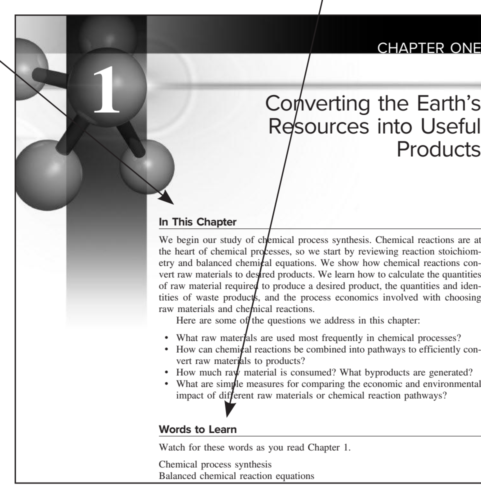
Quick Quiz 7.4

From the Antoine equation, what's the saturation pressure for H_2O at 100°C?

In This Chapter

Words to Learn

An ***In This Chapter*** section provides a brief introduction of the subject matter and a bulleted list of questions that are addressed in each chapter. A list of ***Words to Learn*** is also outlined at the beginning of each chapter. These elements help the reader to focus on the fundamental points as they read each chapter.


CHAPTER ONE

1

Converting the Earth's Resources into Useful Products

In This Chapter

We begin our study of chemical process synthesis. Chemical reactions are at the heart of chemical processes, so we start by reviewing reaction stoichiometry and balanced chemical equations. We show how chemical reactions convert raw materials to desired products. We learn how to calculate the quantities of raw material required to produce a desired product, the quantities and identities of waste products, and the process economics involved with choosing raw materials and chemical reactions.

Here are some of the questions we address in this chapter:

- What raw materials are used most frequently in chemical processes?
- How can chemical reactions be combined into pathways to efficiently convert raw materials to products?
- How much raw material is consumed? What byproducts are generated?
- What are simple measures for comparing the economic and environmental impact of different raw materials or chemical reaction pathways?

Words to Learn

Watch for these words as you read Chapter 1.

Chemical process synthesis
Balanced chemical reaction equations

Quick Quizzes

The ***Quick Quizzes*** are sprinkled within the chapters and are intended to test student understanding of the topics covered in each chapter. Answers to the quizzes are provided at the end of each chapter.

! Helpful Hint
Balance the element that appears in the fewest compounds first.

Helpful Hints

Helpful Hints **!** sections can be found in the margins sprinkled throughout the text. *Helpful Hints* are designed to help students with difficult points.

Example 2.5 **Separation with Accumulation: Air Drying**

Air is used throughout a process plant to move control valves (special valves that regulate flow). If the air is humid, it needs to be dried before being used. To produce dry air for instrument use, filtered and compressed humid room air at 83°F and 1.1 atm pressure, containing 1.5 mol% H_2O (as vapor), is pumped through a tank at a flow rate of 100 ft^3/min. The tank is filled with 60 lbs of alumina (Al_2O_3) pellets. The water vapor in the air adsorbs (sticks) onto the pellets. Dry instrument air, containing just 0.06 mol% H_2O, exits from the tank. The maximum amount of water that can adsorb to the alumina pellets is 0.22 lb H_2O per lb alumina. How long can the tank be operated before the alumina pellets need to be replaced?

Examples

Over 100 worked examples indicate the conceptual idea the problem is designed to illustrate as well as the specific application chosen. Classical and modern topics are used in the example problems.

CASE STUDY Six-Carbon Chemistry

In this case study, we illustrate how the concepts introduced in Chap. 1 are used to make decisions about raw materials, products, and reaction pathways, by looking in some depth at specific processes of importance in the organic chemicals business. These processes are linked by their connection to 6-carbon compounds. We'll look at two questions:

1. Benzene is a 6-carbon compound purified from petroleum. Suppose we have available 15,000 kg/day benzene. What are some useful 6-carbon products we might make from benzene?

Case Studies

Case Studies are provided at the end of most chapters. These in-depth examples illustrate the application of key concepts from that chapter to modern problems. Case studies integrate analysis and synthesis, and boost student confidence in their ability to tackle complex problems and issues.

End-of-Chapter Summaries

The ***Summary*** sections appear at the end of each chapter and provide an overview of the key definitions and equations from that chapter.

Summary

- Chemical processes convert raw materials into useful products. In the initial stages of **chemical process synthesis,** we choose raw materials to make a specific product, or products to make from a specific raw material. We choose a chemical reaction pathway for converting the chosen raw materials into desired products. These choices all have profound consequences on the technical and economic feasibility of the process.

ChemiStory: Of Toothbrushes and Hosiery

The Roaring 20s was a wild, exciting time in U.S. history—a time of bootleg booze and speakeasies, rising skirts and rising fortunes. The DuPont family was one of several fabulously wealthy families of the time. The DuPont Company started as a gunpowder manufacturer, and had grown to become the major supplier of explosives to the Allied forces in World War I. With the end of WWI and the beginning of the peacetime economic expansion, the company wisely moved from explosives to consumer goods. DuPont illustrated its new consumer focus through their famous motto: "Better Things for Better Living through Chemistry." Using their expertise

ChemiStories

ChemiStories describe historical events in the lives of the people who contributed to the chemical industry and its products. The stories bring to life the chemical products we take for granted, illustrate the humanity of the heroes of chemical technology, demonstrate that social and political forces drive scientific and engineering progress, and caution readers that technological breakthroughs sometimes have unwanted adverse effects.

Chapter 2 Problems

Warm-Ups

Section 2.2

P2.1 You put a 100-mL volumetric flask on a balance and then tare the balance so it reads 0.00 g. Then you add anhydrous fructose ($C_6H_{12}O_6$—the major sugar in fruit) into the flask until the balance reads 15.90 g. You fill the flask with water up to the 100 mL line. The balance reads 105.97 g. Calculate the wt% fructose and the mol% fructose of the solution.

P2.2 Soybean meal is a product made from soybeans after the oil has been extracted. The meal contains about 48 wt% protein along with carbohydrates and indigestible fiber. In a typical processing plant, about 70% of that protein can be recovered as "soy protein isolate," which can then be spun, mixed, and shaped into soy "bacon," "burgers," or other meat substitutes. For 100 lb of soybean meal, about how many lb of soy protein isolate can be made? If soybean meal sells for $375/metric ton, what is an estimate of the cost per lb of soy protein isolate?

Drills and Skills

Section 2.2

P2.37 11.2 lb N_2 and 2.4 lb H_2 are added to a rigid vessel with a volume of 170,000 cm^3. The vessel is at 298 K. (a) Calculate the pressure in the vessel using the ideal gas law. Report your answer in units of psia, psig, bar, kPa, and atm. (b) The nitrogen reacts completely with the hydrogen to make ammonia (NH_3). If the temperature is still 298 K and the ammonia is a gas, what is the *change* in pressure in the vessel (in bar)?

P2.38 Your company needs on-site storage for 45,000 lb ammonia (NH_3). What is the diameter (in ft) of a spherical vessel needed to store the

Homework Problems

Homework Problems are broken into four categories:

-Warm-Ups: Short-answer questions that cover basic definitions and straightforward calculations. Minimal proficiency.

-Drills and Skills: Drills and Skills problems cover the fundamental skills and concepts learned in that chapter. Average proficiency.

-Scrimmage: Scrimmage problems require application of more than one skill or concept and may involve material from multiple (previous) chapters. Creativity is needed and some problems require students to make judicious decisions in the absence of complete information.

-Game Day: Game Day problems are best suited for use as group projects and can be used to promote teamwork and improve communication skills.

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- Jordan Cunningham,
Eastern Washington University

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List of Nomenclature (Typical Units)

a_i	activity of compound i (dimensionless)
C_p	heat capacity at constant pressure, (J/gmol °C or J/g K)
C_v	heat capacity at constant volume, (J/gmol °C or J/g K)
E_k	kinetic energy (kJ)
E_p	potential energy (kJ)
f_{Ci}	fractional conversion of reactant i (dimensionless)
f_{Rij}	fractional recovery of component i in stream j (dimensionless)
f_{Sj}	fractional split to stream j (dimensionless)
g	acceleration due to gravity (m/s^2)
$\Delta\hat{G}_f^\circ$	standard molar Gibbs energy of formation (kJ/gmol)
$\Delta\hat{G}_r$	molar Gibbs energy of reaction (kJ/gmol)
$\Delta\hat{G}_r^\circ$	standard molar Gibbs energy of reaction (kJ/gmol)
h	height above a reference plane (m)
H_i	Henry's law constant (atm)
H	enthalpy (kJ)
$\dot{H}$	enthalpy flow (kJ/s)
$\hat{H}$	molar or specific enthalpy (kJ/gmol or kJ/g)
$\Delta\hat{H}_c^\circ$	standard enthalpy of combustion (kJ/gmol)
$\Delta\hat{H}_f^\circ$	standard molar enthalpy of formation (kJ/gmol)
$\Delta\hat{H}_m$	molar or specific enthalpy of melting (kJ/gmol or kJ/g)
$\Delta\hat{H}_{mix}$	molar or specific enthalpy of mixing (kJ/gmol or kJ/g)
$\Delta\hat{H}_r$	molar enthalpy of reaction (kJ/gmol)
$\Delta\hat{H}_r^\circ$	standard molar enthalpy (kJ/gmol)
$\Delta\hat{H}_{\mathrm{soln}}$	molar or specific enthalpy of solution (kJ/gmol or kJ/g)

$\Delta\hat{H}_v$	molar or specific enthalpy of vaporization (kJ/gmol or kJ/g)
K_a	chemical reaction equilibrium constant
M	molar mass (g/gmol)
m_{sys}	mass in system (g)
$\dot{m}$	mass flow rate (g/s)
n_{sys}	moles in system (gmol)
$\dot{n}$	molar flow rate (gmol/s)
P	pressure (atm, N/m^2, bar)
p_i	partial pressure of compound i (atm, N/m^2, bar)
P_i^{sat}	saturation pressure of compound i (atm, N/m^2, bar)
Q	heat (kJ)
$\dot{Q}$	rate of heat transfer (kJ/s)
R	ideal gas constant (J/gmol-K, bar cm^3/gmol K)
$\dot{R}_{ik}$	mass rate of reaction of compound i in reaction k (g/s)
$\dot{r}_{ik}$	molar rate of reaction of compound i in reaction k (gmol/s)
$s_{A\rightarrow P}$	selectivity for conversion of reactant A to product P (dimensionless)
t	time (s)
T	temperature (°C, K)
T_b	normal boiling point temperature (°C, K)
T_m	normal melting point temperature (°C, K)
U	internal energy (kJ)
$\hat{U}$	molar or specific internal energy (kJ/gmol or kJ/g)
v	velocity (m/s)
V	volume (m^3)
$\hat{V}$	molar or specific volume (m^3/gmol, m^3/kg)
w_i	weight fraction of i (dimensionless)
W	work (kJ)
W_s	shaft work (kJ)
$\dot{W}$	rate of work transfer (kJ/s, kW, hp)

$\dot{W}_s$	rate of shaft work transfer (kJ/s, kW, hp)
x_i	mole fraction of *i,* typically in the liquid phase (dimensionless)
x_{is}	mole fraction of *i* in the solid phase (dimensionless)
y_i	mole fraction of *i* in the vapor phase (dimensionless)
$y_{A \to P}$	fractional yield for conversion of reactant A to product P (dimensionless)
z_i	mole fraction of *i,* typically when phase is undefined (dimensionless)

Subscripts

f	final
h	element
i	compound or component
j	stream
k	reaction
sys	system
0	initial

Greek Letters

α_{AB}	separation factor for components A and B (dimensionless)
ε_{hi}	number of atoms of element *h* in compound *i*
ν_{ik}	stoichiometric coefficient of compound *i* in reaction *k*
ρ	density (kg/m^3 or gmol/m^3)
ξ	extent of reaction (gmol)
$\dot{\xi}$	extent of reaction (gmol/s)
χ_k	multiplying factor for reaction *k*
η	efficiency (dimensionless)

List of Important Equations

Material Balance Equations

Differential form:

Total mass:

$$\frac{dm_{\text{sys}}}{dt} = \sum_{\text{all } j_{\text{in}}} \dot{m}_j - \sum_{\text{all } j_{\text{out}}} \dot{m}_j$$

Mass of i:

$$\frac{dm_{i,\text{sys}}}{dt} = \sum_{\text{all } j_{\text{in}}} \dot{m}_{ij} - \sum_{\text{all } j_{\text{out}}} \dot{m}_{ij} + \sum_{\text{all } k} \nu_{ik} M_i \dot{\xi}_k$$

Total moles:

$$\frac{dn_{\text{sys}}}{dt} = \sum_{\text{all } j_{\text{in}}} \dot{n}_j - \sum_{\text{all } j_{\text{out}}} \dot{n}_j + \sum_{\text{all } k} \sum_{\text{all } i} \nu_{ik} \dot{\xi}_k$$

Moles of i:

$$\frac{dn_{i,\text{sys}}}{dt} = \sum_{\text{all } j_{\text{in}}} \dot{n}_{ij} - \sum_{\text{all } j_{\text{out}}} \dot{n}_{ij} + \sum_{\text{all } k} \nu_{ik} \dot{\xi}_k$$

Integral form

Total mass:

$$m_{\text{sys},f} - m_{\text{sys},0} = \sum_{\text{all } j_{\text{in}}} m_j - \sum_{\text{all } j_{\text{out}}} m_j$$

Mass of i:

$$m_{i,\text{sys},f} - m_{i,\text{sys},0} = \sum_{\text{all } j_{\text{in}}} m_{ij} - \sum_{\text{all } j_{\text{out}}} m_{ij} + \sum_{\text{all } k} M_i \nu_{ik} \xi_k$$

Total moles:

$$n_{\text{sys},f} - n_{\text{sys},0} = \sum_{\text{all } j_{\text{in}}} n_j - \sum_{\text{all } j_{\text{out}}} n_j + \sum_{\text{all } k} \sum_{\text{all } i} \nu_{ik} \xi_k$$

Moles of i:

$$n_{i,\text{sys},f} - n_{i,\text{sys},0} = \sum_{\text{all } j_{\text{in}}} n_{ij} - \sum_{\text{all } j_{\text{out}}} n_{ij} + \sum_{\text{all } k} \nu_{ik}\xi_k$$

System Performance Specifications

Splitter

Fractional split:

$$f_{Sj} = \frac{\text{moles leaving in stream } j}{\text{moles fed to splitter}} = \frac{\dot{n}_j}{\dot{n}_{\text{in}}}$$

Reactor

Fractional conversion:

$$f_{Ci} = \frac{\text{moles of } i \text{ consumed by reaction}}{\text{moles of } i \text{ fed to reactor}} = \frac{-\sum_{\text{all } k} \nu_{ik}\dot{\xi}_k}{\dot{n}_{i,\text{in}}}$$

Selectivity:

$$s_{A\to P} = \frac{\text{moles of reactant A converted to product P}}{\text{moles of reactant A consumed}} = \frac{\nu_{A1}}{\nu_{P1}} \frac{\sum_{\text{all } k} \nu_{Pk}\dot{\xi}_k}{\sum_{\text{all } k} \nu_{Ak}\dot{\xi}_k}$$

Yield:

$$y_{A\to P} = \frac{\text{moles of reactant A converted to desired product P}}{\text{moles of reactant A fed}}$$

$$= -\frac{\nu_{A1}}{\nu_{P1}} \frac{\sum_{\text{all } k} \nu_{Pk}\dot{\xi}_k}{\dot{n}_{A,\text{in}}}$$

Separator

Fractional recovery:

$$f_{Rij} = \frac{\text{moles of } i \text{ leaving in stream } j}{\text{moles of } i \text{ fed to separator}} = \frac{\dot{n}_{ij}}{\dot{n}_{i,\text{in}}}$$

Separation factor:

$$\alpha_{AB} = \frac{z_{A1}}{z_{A2}} \frac{z_{B2}}{z_{B1}} = \frac{\dot{n}_{A1}}{\dot{n}_{A2}} \frac{\dot{n}_{B2}}{\dot{n}_{B1}}$$

Chemical Reaction Equilibrium

$$K_a = \prod_{\text{all } i} a_i^{\nu_i}$$

where, to a first approximation,

$$a_i = \frac{y_i P}{1 \text{ atm}} \qquad \text{for a gas}$$

$$a_i = x_i \qquad \text{for a liquid}$$

$$a_i = 1 \qquad \text{for a solid}$$

$$\ln K_{a,T} = \frac{-\Delta \hat{G}_r^\circ}{298R} + \frac{\Delta \hat{H}_r^\circ}{R}\left[\frac{1}{298} - \frac{1}{T}\right]$$

where $\Delta \hat{G}_r^\circ = \sum \nu_i \Delta \hat{G}_{i,f}^\circ$ and $\Delta \hat{H}_r^\circ = \sum \nu_i \Delta \hat{H}_{i,f}^\circ$.

Phase Equilibrium

Raoult's law:

$$y_i = \frac{P_i^{\text{sat}}}{P} x_i$$

Henry's law:

$$y_i = \frac{H_i}{P} x_i$$

Energy Balance Equations

Differential form:

$$\frac{d(E_{k,\text{sys}} + E_{p,\text{sys}} + U_{\text{sys}})}{dt} = \sum_{\text{all } j_{\text{in}}} \dot{m}_j(\hat{E}_{kj} + \hat{E}_{pj} + \hat{H}_j) - \sum_{\text{all } j_{\text{out}}} \dot{m}_j(\hat{E}_{kj} + \hat{E}_{pj} + \hat{H}_j) + \sum_j \dot{Q}_j + \sum_j \dot{W}_{sj}$$

Integral form:

$$(E_{k,\text{sys}} + E_{p,\text{sys}} + U_{\text{sys}})_f - (E_{k,\text{sys}} + E_{p,\text{sys}} + U_{\text{sys}})_0 = \sum_{\text{all } j_{\text{in}}} m_j(\hat{E}_{kj} + \hat{E}_{pj} + \hat{H}_j) - \sum_{\text{all } j_{\text{out}}} m_j(\hat{E}_{kj} + \hat{E}_{pj} + \hat{H}_j) + \sum_j Q_j + \sum_j W_{sj}$$

CHAPTER ONE

1

Converting the Earth's Resources into Useful Products

In This Chapter

We begin our study of chemical process synthesis. Chemical reactions are at the heart of chemical processes, so we start by reviewing reaction stoichiometry and balanced chemical equations. We show how chemical reactions convert raw materials to desired products. We learn how to calculate the quantities of raw material required to produce a desired product, the quantities and identities of waste products, and the process economics involved with choosing raw materials and chemical reactions.

Here are some of the questions we address in this chapter:

- What raw materials are used most frequently in chemical processes?
- How can chemical reactions be combined into pathways to efficiently convert raw materials to products?
- How much raw material is consumed? What byproducts are generated?
- What are simple measures for comparing the economic and environmental impact of different raw materials or chemical reaction pathways?

Words to Learn

Watch for these words as you read Chapter 1.

Chemical process synthesis
Balanced chemical reaction equations
Stoichiometric coefficients
Generation-consumption analysis
Atom economy
Basis
Scale factor
Process economy

1.1 Introduction

Chemical processes convert raw materials into needed products by changing the chemical and/or physical properties of the materials (Fig. 1.1). Why do humans synthesize, design, build, and operate chemical processes?

To make a product that has a specific desired function. Many children bring lunch to school every day. Wouldn't it be great to have a lightweight, safe, easy-open packaging material for carrying juice or milk? Aseptically packaged drink boxes fulfill these product requirements and have replaced heavy, bulky thermoses in the nation's lunch bags. But, although throwaway products are convenient, they carry with them waste disposal concerns.

To convert waste materials into useful products. It takes about 10 pounds of milk to make 1 pound of cheese. The other 9 pounds end up as whey. Whey used to be simply a waste product, dumped in nearby waterways or sprayed on farmers' fields. Now processes have been developed that recover the useful components of whey. For example, the protein lactoferrin is purified from whey and used in infant formula to improve iron uptake. Whey sugars serve as a feedstock for production of biodegradable polymers.

To improve the performance of a natural material. Vincristine is a vinca alkaloid present in minute quantities in the periwinkle plant. Concentrated and purified, vincristine has proved to be a powerful drug for treating leukemia and lymphomas. Its success has led to synthesis in the laboratory of structurally related compounds, any of which might serve as effective medicines to treat cancers.

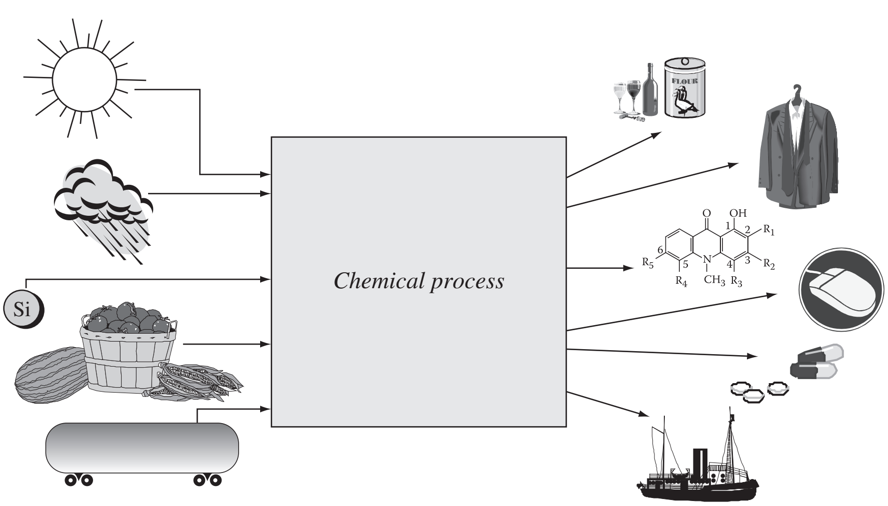

Figure 1.1 Chemical processes convert raw materials into desired products. In synthesizing chemical processes, we choose appropriate raw materials, then select chemical reactions and physical operations to change the properties of the raw materials to those of the desired products. We aim to design a chemical process that is safe to operate, that uses raw materials efficiently and economically, that reliably produces the desired products, and that has minimal environmental impact.

To convert material into energy. Huge quantities of energy are used every day to heat or cool our homes, power our motor vehicles, and cook our food. Much of this energy is derived from combustion of fossil fuels—natural gas, oil, or coal. In this process, the raw material reacts with oxygen to form carbon dioxide and water. It is the energy released by the reaction, not the reaction products, that is useful.

An enormous breadth of industries—paper, foods, plastics, fibers, glass, electronic materials, fuels, pharmaceuticals, to name a few—depend on chemical processes. The art and science of **chemical process synthesis** is in choosing appropriate raw materials and chemical reaction pathways, and in developing an *efficient, economical, reliable,* and *safe* chemical process. Articulation of product requirements must be made before process development can begin; thus, product engineering and process engineering are inextricably linked. The quality and availability of raw materials, economic forecasts, product safety and reliability, marketing concerns, patents, and proprietary technology all influence process design.

1.2 Raw Materials

Ultimately, we derive all of our raw materials from the earth. The fundamental raw materials are air, water, minerals, fossil fuels, and agricultural products.

Air. Plentiful, readily available, and cheap, air serves as the source of oxygen and nitrogen in many chemical processes. Oxygen is used widely for oxidation reactions, the most important of which is the burning of fuels to generate heat and electricity. Discovery of a method to convert atmospheric nitrogen to liquid ammonia spawned the agricultural fertilizer industry, with enormous repercussions for production of sufficient food to feed the growing world population.

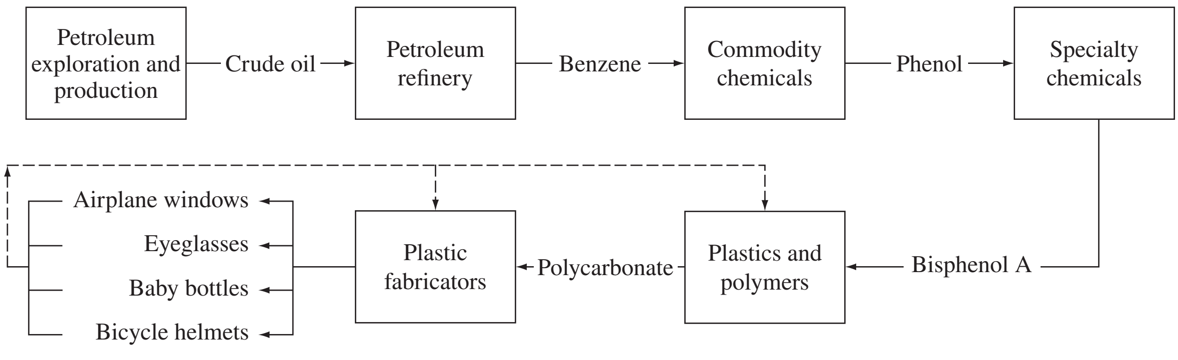

Figure 1.2 Many companies and processes are needed to convert a raw material such as crude oil to products such as bicycle helmets. Companies and municipalities are trying to close the loop, by recovering consumer products at the end of their useful life and reprocessing the materials into new products.

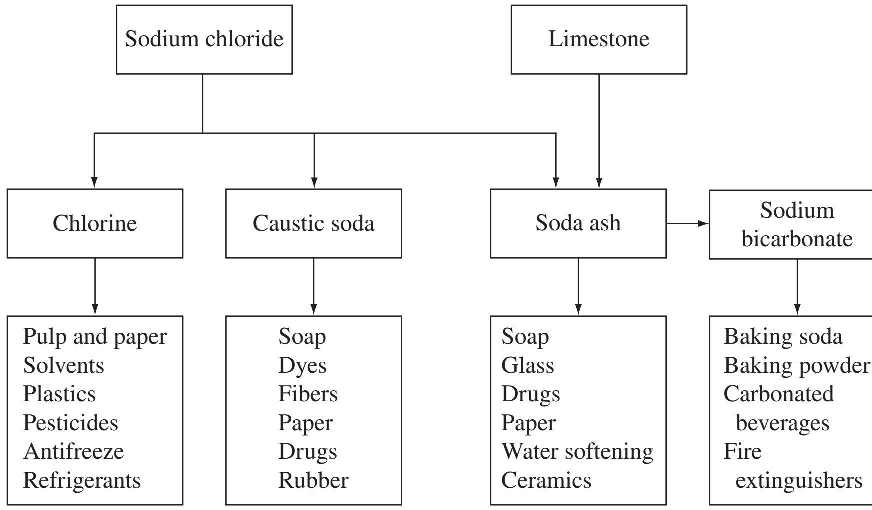

Figure 1.3 Important commodity chemicals as well as common household products are made from sodium chloride and limestone, as part of the chlor-alkali industry. Adapted from *Chemical Process Industries,* 4th ed. by R. N. Shreve and J. A. Brink, 1977.

Water. Water is used as a reactant in many chemical processes and serves an important role as a solvent. This is especially true for the biotechnology industries—old (e.g., beer making), middle-aged (antibiotic production by fermentation), or new (antibody production from genetically engineered cells). Water may eventually serve as a source of hydrogen, a clean-burning fuel.

Fossil fuels. Natural gas, crude oil, and coal are all hydrocarbon materials produced by the decay of once-living things. Besides providing us with heat, light, and electricity, fossil fuels serve as the raw material for the synthesis of carbon-based products like polymers for plastic soft drink bottles and contact lenses, fibers for clothing and furnishings, medicines, and pesticides (Fig. 1.2).

Minerals. Minerals are solid inorganic elements or compounds. One important mineral is salt (sodium chloride), which, besides its use as a preservative and a flavoring, serves as the raw material for the enormous chlor-alkali industry (Fig. 1.3). Minerals are the feedstocks for the inorganic chemicals industries, which produce silicon chips for computers and aluminum for bicycles.

Agricultural and forest products. Living plants are carbon-based, but they also contain a significant quantity of fixed oxygen and (sometimes) nitrogen. Our food, of course, is produced from these raw materials. Other products derived from agricultural raw materials include paper, natural fibers such as wool or cotton, natural rubber, and medicines. There is an increasing interest in using agricultural materials (also called biomass) as raw materials for production of carbon-containing chemicals, thus reducing our reliance on non-renewable fossil fuels. For example, DuPont and partners developed processes in which corn-derived glucose is fermented, using engineered bacteria, to make 1,3-propanediol. The 1,3-propanediol is purified and then reacted to form a polymer called 3GT, which is spun into fibers and woven into a fabric (Fig. 1.4).

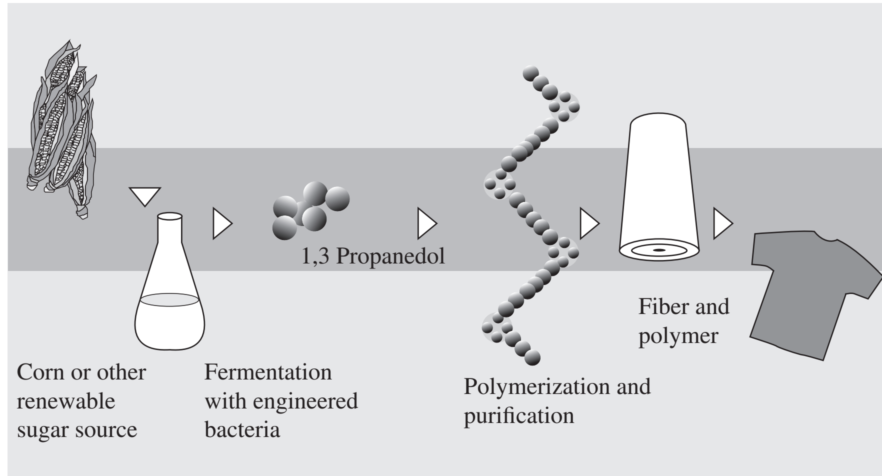

Figure 1.4 New processes to make chemical products from renewable resources are being developed, like this process to synthesize fiber from corn.

Some chemical processors start with raw materials and make intermediates that are sold to industrial partners, which then will further process those intermediates into consumer products. For example (Fig. 1.2):

- An oil company extracts crude oil from underground reservoirs.
- A petroleum refining company processes the oil to recover benzene.
- A commodity chemicals company reacts the benzene to phenol.
- A fine chemicals company converts phenol to bisphenol A.
- A plastics company polymerizes bisphenol A to polycarbonate.
- Fabricators use polycarbonate to make airplane windows, bullet-proof glass, eyeglasses, baby bottles, compact discs, and football helmets.
- Consumers purchase eyeglasses, baby bottles, and compact discs, use them, and then discard them to the landfill or recycling bin.
- Recyclers reprocess discarded materials into new products.

1.3 Balanced Chemical Reaction Equations

At the heart of most chemical processes lies one or more chemical reactions. If A and B are reactants that undergo a chemical reaction to form products C and D, we write:

$$A + B \rightarrow C + D$$

As an example, in making electronics-grade silicon, silicon tetrachloride ($SiCl_4$) reacts with hydrogen to make pure silicon and hydrogen chloride:

$$SiCl_4 + H_2 \rightarrow Si + HCl$$

The arrow indicates the direction of reaction, from reactants to products. This reaction as written is not balanced.

If we are interested in showing not only the identity but also the quantity of compounds taking part in a chemical reaction, we write a **balanced chemical reaction equation**. *A chemical equation is balanced if the number of atoms of each element on the left-hand side of the equation equals the number of atoms of that element on the right-hand side.* To emphasize that the reaction is balanced, we can replace the arrow with an equals sign. For example, the reaction of silicon tetrachloride with hydrogen to make silicon and hydrogen chloride is balanced if we write

$$SiCl_4 + 2H_2 = Si + 4HCl$$

Because the coefficients are relative rather than absolute quantities, it is also true that

$$2SiCl_4 + 4H_2 = 2Si + 8HCl$$

or

$$\tfrac{1}{2}SiCl_4 + H_2 = \tfrac{1}{2}Si + 2HCl$$

because the coefficients do not have to be integers.

Since the reaction is written as an equation, we can collect all compounds on the right-hand side and write:

$$0 = -\tfrac{1}{2}SiCl_4 - H_2 + \tfrac{1}{2}Si + 2HCl$$

Now let's define **stoichiometric coefficients** ν_i for each chemical compound i, and specify that *ν_i is negative for compounds that are reactants and positive for compounds that are products*. For example, in the above reaction,

Quick Quiz 1.1

What is the numerical value of ν_{H_2}?

$$\nu_{SiCl_4} = -\tfrac{1}{2}$$

and

$$\nu_{HCl} = +2$$

We define

$$\varepsilon_{hi} \equiv \text{number of atoms of the element } h \text{ in molecule } i.$$

For example, $\varepsilon_{Cl,SiCl_4} = 4$, because there are 4 Cl atoms in each molecule of $SiCl_4$. A chemical equation is stoichiometrically balanced with respect to the hth element if and only if

$$\boxed{\sum_i \varepsilon_{hi}\nu_i = 0} \qquad \text{Eq. (1.1)}$$

Helpful Hint
Balance the element that appears in the fewest compounds first.

where the summation is taken over all compounds. In our example, the element Cl appears in two compounds, $SiCl_4$ ($\varepsilon_{Cl,SiCl_4} = 4$) and HCl ($\varepsilon_{Cl,HCl} = 1$), and Eq. (1.1) for the element Cl is simply

$$\varepsilon_{Cl,SiCl_4}\nu_{SiCl_4} + \varepsilon_{Cl,HCl}\nu_{HCl} = 4(-\tfrac{1}{2}) + 1(+2) = 0$$

In addition to Cl, there are two other elements, Si and H, so there are two more similar equations:

$$\varepsilon_{Si,SiCl_4}\nu_{SiCl_4} + \varepsilon_{Si,Si}\nu_{Si} = 1(-\tfrac{1}{2}) + 1(+\tfrac{1}{2}) = 0$$

$$\varepsilon_{H,H_2}\nu_{H_2} + \varepsilon_{H,HCl}\nu_{HCl} = 2(-1) + 1(+2) = 0$$

Eq. (1.1) is very useful because we can use it to systematically find unknown stoichiometric coefficients. For example, suppose the reaction of interest is oxidation of methane (CH_4) to CO_2 and water. Written in an *unbalanced* form the reaction is:

$$CH_4 + O_2 \rightarrow CO_2 + H_2O$$

Quick Quiz 1.2
Why did we set $\nu_{CH_4} = -1$ and not $\nu_{CH_4} = 1$?

There are three elements, (C, H, and O), and four compounds (CH_4, O_2, CO_2, and H_2O), so there are three equations involving four unknown stoichiometric coefficients. Knowing ε_{hi} for each compound and applying Eq. (1.1) to each element, we derive:

$$\text{C:}\quad 1\nu_{CH_4} + 0\nu_{O_2} + 1\nu_{CO_2} + 0\nu_{H_2O} = 0$$

$$\text{H:}\quad 4\nu_{CH_4} + 0\nu_{O_2} + 0\nu_{CO_2} + 2\nu_{H_2O} = 0$$

$$\text{O:}\quad 0\nu_{CH_4} + 2\nu_{O_2} + 2\nu_{CO_2} + 1\nu_{H_2O} = 0$$

Quick Quiz 1.3
Instead of setting $\nu_{CH_4} = -1$, suppose we had chosen to set $\nu_{O_2} = -1$. What would be the balanced chemical reaction equation?

Since there are four unknowns but only three equations, there are many possible solutions. To proceed, we arbitrarily set one of the stoichiometric coefficients. For example, we can pick ν_{CH_4} as the basis and set $\nu_{CH_4} = -1$. There are now only three unknowns, and we solve to find $\nu_{O_2} = -2$, $\nu_{CO_2} = 1$, $\nu_{H_2O} = 2$. The balanced chemical reaction equation is

$$(1)CH_4 + 2O_2 \rightarrow (1)CO_2 + 2H_2O$$

Example 1.1 Balanced Chemical Reaction Equation: Nitric Acid Synthesis

Nitric acid (HNO_3) is an important industrial acid used, among other things, in the manufacture of nylon. In one of the reactions for making nitric acid, ammonia (NH_3) and oxygen (O_2) react to form NO and H_2O. Write the balanced chemical equation.

Solution

We'll write the unbalanced chemical reaction as

$$NH_3 + O_2 \rightarrow NO + H_2O$$

There are three elements and four compounds, so there are three equations in four unknowns:

$$\text{N:}\quad 1\nu_{NH_3} + 1\nu_{NO} = 0$$

$$\text{H:}\quad 3\nu_{NH_3} + 2\nu_{H_2O} = 0$$

$$\text{O:}\quad 2\nu_{O_2} + 1\nu_{NO} + 1\nu_{H_2O} = 0$$

We'll choose to set $\nu_{NH_3} = -1$. Starting with the N balance, we solve to get $\nu_{NO} = 1$. From the H balance, $\nu_{H_2O} = \frac{3}{2}$. Finally, from the O balance, $\nu_{O_2} = -\frac{5}{4}$. The balanced equation is:

$$NH_3 + \tfrac{5}{4}O_2 \rightarrow NO + \tfrac{3}{2}H_2O$$

[Try choosing to set a different stoichiometric coefficient. Do you get the same balanced equation?]

Example 1.2 Balanced Chemical Reaction Equations: Adipic Acid Synthesis

Adipic acid is an intermediate used in the manufacture of nylon. (We'll discuss this process in greater detail later in this chapter.) Several chemical reaction steps are involved in synthesis of adipic acid:

Reaction 1. Cyclohexane (C_6H_{12}) reacts with oxygen (O_2) to produce cyclohexanol ($C_6H_{12}O$).

Reaction 2. Cyclohexane (C_6H_{12}) reacts with oxygen (O_2) to produce cyclohexanone ($C_6H_{10}O$).

Water (H_2O) is a byproduct of one of these reactions.

Reaction 3. Cyclohexanol reacts with nitric acid to produce adipic acid ($C_6H_{10}O_4$).

Reaction 4. Cyclohexanone reacts with nitric acid to produce adipic acid ($C_6H_{10}O_4$).

NO and H_2O are byproducts of both Reactions 3 and 4.

Write the four balanced chemical equations corresponding to these four reactions.

Solution

Reaction 1. *From the problem statement, water may be a byproduct of this reaction. Let's assume it is,* and see what happens. The unbalanced chemical reaction is

$$C_6H_{12} + O_2 \rightarrow C_6H_{12}O + H_2O$$

There are three elements and four compounds, so we can set one stoichiometric coefficient arbitrarily. C appears in two compounds, O and H in three each, so we apply Eq. (1.1) to the element that appears in the fewest number of compounds:

$$\text{C:}\quad 6\nu_{C_6H_{12}} + 6\nu_{C_6H_{12}O} = 0$$

Helpful Hint
If one of the elements appears in only two compounds, set the stoichiometric coefficient of one of those compounds to a fixed value.

If we choose to set one of these two stoichiometric coefficients, we can solve for the other immediately. Let's set $\nu_{C_6H_{12}O} = +1$. Then

$$\nu_{C_6H_{12}} = -1$$

We then move on to the other two elements:

$$\begin{aligned} \text{H:} \quad & 12\nu_{C_6H_{12}} + 12\nu_{C_6H_{12}O} + 2\nu_{H_2O} = \\ & 12(-1) + 12(1) + 2\nu_{H_2O} = 0 \\ \text{O:} \quad & 2\nu_{O_2} + \nu_{C_6H_{12}O} + \nu_{H_2O} = 2\nu_{O_2} + 1 + \nu_{H_2O} = 0 \end{aligned}$$

These are easily solved to yield

$$\nu_{H_2O} = 0$$

$$\nu_{O_2} = -\tfrac{1}{2}$$

The balanced chemical equation is

$$C_6H_{12} + \tfrac{1}{2}O_2 \rightarrow C_6H_{12}O$$

Finding the stoichiometric coefficients led us to the conclusion that water is not a byproduct of Reaction 1 after all.

Reaction 2. The unbalanced reaction of cyclohexane with oxygen to produce cyclohexanone, with water as a possible byproduct, is

$$C_6H_{12} + O_2 \rightarrow C_6H_{10}O + H_2O$$

Proceeding in a manner similar to that used for Reaction 1, we write three equations:

$$\begin{aligned} \text{C:} \quad & 6\nu_{C_6H_{12}} + 6\nu_{C_6H_{10}O} = 0 \\ \text{H:} \quad & 12\nu_{C_6H_{12}} + 10\nu_{C_6H_{10}O} + 2\nu_{H_2O} = 0 \\ \text{O:} \quad & 2\nu_{O_2} + \nu_{C_6H_{10}O} + \nu_{H_2O} = 0 \end{aligned}$$

We arbitrarily set $\nu_{C_6H_{12}} = -1$ and solve the equations in order to find the other three stoichiometric coefficients. The balanced chemical equation is

$$C_6H_{12} + O_2 \rightarrow C_6H_{10}O + H_2O$$

Reaction 3. In the third chemical reaction, cyclohexanol ($C_6H_{12}O$) and nitric acid (HNO_3) react to make adipic acid ($C_6H_{10}O_4$), with nitric oxide (NO) and water (H_2O) as byproducts. The unbalanced reaction is

$$C_6H_{12}O + HNO_3 \rightarrow C_6H_{10}O_4 + NO + H_2O$$

There are four elements and five compounds:

$$\begin{aligned} \text{C:} \quad & 6\nu_{C_6H_{12}O} + 6\nu_{C_6H_{10}O_4} = 0 \\ \text{H:} \quad & 12\nu_{C_6H_{12}O} + \nu_{HNO_3} + 10\nu_{C_6H_{10}O_4} + 2\nu_{H_2O} = 0 \\ \text{O:} \quad & \nu_{C_6H_{12}O} + 3\nu_{HNO_3} + 4\nu_{C_6H_{10}O_4} + \nu_{NO} + \nu_{H_2O} = 0 \\ \text{N:} \quad & \nu_{HNO_3} + \nu_{NO} = 0 \end{aligned}$$

Starting with either the C or the N balance is a good choice. Let's set $\nu_{C_6H_{12}O} = -1$. We immediately solve the C balance to find $\nu_{C_6H_{12}O_4} = 1$. Substituting these values into the remaining three equations yields

$$\text{H:} \quad -12 + \nu_{HNO_3} + 10 + 2\nu_{H_2O} = 0$$

$$\text{O:} \quad -1 + 3\nu_{HNO_3} + 4 + \nu_{NO} + \nu_{H_2O} = 0$$

$$\text{N:} \quad \nu_{HNO_3} + \nu_{NO} = 0$$

We can't immediately solve any of the remaining equations. To solve "by hand," we

1. Subtract the N balance from the O balance to eliminate ν_{NO}:

$$3 + 2\nu_{HNO_3} + \nu_{H_2O} = 0$$

2. Subtract the H balance from 2× this equation to eliminate ν_{H_2O}:

$$8 + 3\nu_{HNO_3} = 0$$

3. Solve for ν_{HNO_3} and work backwards to find the other stoichiometric coefficients:

$$\nu_{HNO_3} = -\tfrac{8}{3}$$

$$\nu_{NO} = \tfrac{8}{3}$$

$$\nu_{H_2O} = +\tfrac{7}{3}$$

The balanced chemical equation is:

$$C_6H_{12}O + \tfrac{8}{3}HNO_3 \rightarrow C_6H_{10}O_4 + \tfrac{8}{3}NO + \tfrac{7}{3}H_2O$$

Reaction 4. The balanced chemical equation is (details are left for you)

$$C_6H_{10}O + 2\,HNO_3 \rightarrow C_6H_{10}O_4 + 2NO + H_2O$$

Quick Quiz 1.4

In the balanced chemical equation for Reaction 3 of Example 1.2, noninteger coefficients appear. Rewrite the equation, using only integer coefficients.

1.3.1 Using Matrices to Balance Chemical Reactions

Recall that we balance chemical reactions by invoking the element balance equation:

$$\sum_i \varepsilon_{hi}\nu_i = 0 \qquad \text{Eq. (1.1)}$$

where ε_{hi} = the number of atoms of element h in molecule i and ν_i = the (unknown) stoichiometric coefficients. If there are H elements, then H equations must be solved simultaneously to find the unknown ν_i. This is a system of linear equations, and it is straightforward to use matrices to set up and solve these equations.

Suppose we are interested in the reaction of NH_3 and O_2 to NO and H_2O, which is the topic of Example 1.1. There are 3 elements and 4 compounds, so 3 equations must be solved simultaneously to find the 4 unknown stoichiometric coefficients. These 3 equations are given in Example 1.1. We can write this set of equations in matrix form **Ax** = **b**:

$$\begin{matrix} \text{N:} \\ \text{H:} \\ \text{O:} \end{matrix} \begin{bmatrix} 1 & 0 & 1 & 0 \\ 3 & 0 & 0 & 2 \\ 0 & 2 & 1 & 1 \end{bmatrix} \begin{bmatrix} \nu_{NH_3} \\ \nu_{O_2} \\ \nu_{NO} \\ \nu_{H_2O} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

*Notice that each column in matrix **A** represents the chemical formula for one compound*! For example, column 1 represents $N_1H_3O_0$ (NH_3). In other words, we can write this matrix from the known chemical formulas for each compound, without bothering to derive the element balance equation! The vector **x** simply contains the stoichiometric coefficients for each of the 4 compounds.

Because there are four variables but only three equations, the matrix **A** is not square. Furthermore, the vector **b** is full of zeros. This system of equations has an infinite number of possible solutions. To find one solution, we arbitrarily specify one of the stoichiometric coefficients of the reactants to equal −1. Let's pick $\nu_{NH_3} = -1$. We'll call NH_3 our basis compound. We then plug this value into the element balance equations and simplify so only terms involving the unknowns are on the left-hand side:

$$\begin{aligned} &\text{N:} \quad \nu_{NO} = 1 \\ &\text{H:} \quad 2\nu_{H_2O} = 3 \\ &\text{O:} \quad 2\nu_{O_2} + \nu_{NO} + \nu_{H_2O} = 0 \end{aligned}$$

(Of course it would be easy to solve this set of equations, but we continue on for illustration purposes.) We write this new set of three equations in three unknowns in matrix form:

$$\begin{matrix} \text{N:} \\ \text{H:} \\ \text{O:} \end{matrix} \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 2 \\ 2 & 1 & 1 \end{bmatrix} \begin{bmatrix} \nu_{O_2} \\ \nu_{NO} \\ \nu_{H_2O} \end{bmatrix} = \begin{bmatrix} 1 \\ 3 \\ 0 \end{bmatrix}$$

Notice three things. First, we now have a 3 × 3, or square matrix. This is a necessary (but not sufficient) condition for finding a unique solution. Second, matrix **A** can be written down by inspection: Each column is simply the chemical formula of the compounds for which the stoichiometric coefficient is not known. Third, vector **b** can be written down by inspection: it is simply the chemical formula for the compound (NH_3) chosen as the basis! The solution is straightforward; you can solve by using matrix functions on a calculator or by using equation-solving software.

Let's recap how we use matrices to balance a chemical equation involving *I* compounds and *H* elements:

1. List the elements involved (e.g., C, H, O, N).
2. Choose one of the reactants to serve as a basis. Set its stoichiometric coefficient equal to −1.

3. List the chemical composition of all other compounds except the basis compound in a column in a matrix **A**. Be sure to list the elements in the order chosen in step 1, and do not forget the zeros. The matrix will have H rows (corresponding to the H elements) and $I - 1$ columns (I compounds $- 1$ basis compound).
4. List the unknown stoichiometric coefficients in vector **x**. The vector will have $I - 1$ entries. Be sure to list the coefficients in the same order as the compounds were entered into the matrix.
5. List the chemical composition of the basis compound in vector **b**. Be sure to list the elements in the order chosen in step 1, and do not forget the zeros.
6. Find the solution to the matrix equation, using a calculator or an equation-solving program.

Example 1.3 **Balancing Chemical Equations with Matrix Math: Adipic Acid Synthesis**

Cyclohexanol ($C_6H_{12}O$) and nitric acid (HNO_3) react to make adipic acid ($C_6H_{10}O_4$), with nitrogen oxide (NO) and water (H_2O) as byproducts. Find the stoichiometric coefficients using a matrix equation.

Solution

We solved this already in Example 1.2 (Reaction 3), but this time we will solve using the matrix method. We select $C_6H_{12}O$ as the basis compound, set $\nu_{C_6H_{12}O} = -1$, and proceed to write by inspection:

$$\begin{matrix} \text{C:} \\ \text{H:} \\ \text{O:} \\ \text{N:} \end{matrix} \begin{bmatrix} 0 & 6 & 0 & 0 \\ 1 & 10 & 0 & 2 \\ 3 & 4 & 1 & 1 \\ 1 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} \nu_{HNO_3} \\ \nu_{C_6H_{10}O_4} \\ \nu_{NO} \\ \nu_{H_2O} \end{bmatrix} = \begin{bmatrix} 6 \\ 12 \\ 1 \\ 0 \end{bmatrix}$$

The solution is

$$\begin{bmatrix} \nu_{HNO_3} \\ \nu_{C_6H_{10}O_4} \\ \nu_{NO} \\ \nu_{H_2O} \end{bmatrix} = \begin{bmatrix} -8/3 \\ 1 \\ 8/3 \\ 7/3 \end{bmatrix}$$

(Compare to the solution given in Example 1.2.)

1.4 Generation-Consumption Analysis

Choosing the raw materials and writing balanced chemical reaction equations are early steps in chemical process synthesis. Many chemical processes require that we combine multiple chemical reactions together, in order to convert available raw materials to the desired products. This is done, in order to make the most product out of the least (and least expensive) raw material. We also want to avoid making waste byproducts, especially if those materials are toxic or hazardous.

Generation-consumption analysis is a systematic method for synthesizing reaction pathways involving multiple chemical reactions with these goals in mind. This analysis allows us to calculate the moles of raw materials consumed in generating a given quantity of product, and the moles of byproducts generated per mole of product.

As an example, suppose a company has developed a fermentation process that produces isobutanol ($C_4H_{10}O$) from glucose, which was derived sustainably from agricultural waste products. The balanced reaction is:

$$C_6H_{12}O_6 \rightarrow C_4H_{10}O + 2CO_2 + H_2O \qquad \text{(R1)}$$

The company's goal is to use isobutanol as a "platform" chemical—a chemical that serves as an intermediate toward making other chemicals from renewable resources that are currently made from fossil fuels. One idea is to make xylene (C_8H_{10}), a chemical that is blended into high-octane gasoline, used to make plastic bottles, and used as a solvent for waxes (even ear wax!). Xylene is produced from isobutanol in two steps. First isobutanol is dehydrated to isobutene (C_4H_8)

$$C_4H_{10}O \rightarrow C_4H_8 + H_2O \qquad \text{(R2)}$$

And then isobutene reacts to make xylene, with hydrogen as a byproduct

$$2C_4H_8 \rightarrow C_8H_{10} + 3H_2 \qquad \text{(R3)}$$

Let's focus first on just reactions (R2) and (R3). In reaction (R2), one mole of C_4H_8 is *generated* for every mole of isobutanol *consumed*. In reaction (R3), one mole of xylene is generated for every two moles of isobutene consumed. Isobutanol is the desired reactant and xylene is the desired product: we want no net generation or consumption of isobutene. So we need two moles of isobutene generated in (R2). This can easily be achieved by simply multiplying (R2) by 2!

$$2C_4H_{10}O \rightarrow 2C_4H_8 + 2H_2O \qquad 2 \times \text{(R2)}$$

These concepts can be expressed mathematically. We define

$$\nu_{ik} \equiv \text{stoichiometric coefficient of compound } i \text{ in reaction } k.$$

For example, $\nu_{H_2,3} = +3$. We define

$$\chi_k \equiv \text{multiplying factor for reaction } k.$$

For example, we used $\chi_2 = 2$ to ensure no net generation or consumption of isobutene when combining (R2) and (R3).

The net generation or consumption of a compound i from a system of reactions is then

$$\boxed{\nu_{i,\text{net}} = \sum_{\text{all } k} \nu_{ik}\chi_k} \qquad \text{Eq. (1.2)}$$

For a compound that is an overall *product* (net generated) of a reaction pathway, $\nu_{i,\text{net}} > 0$.

For a compound that is an overall *reactant* (net consumed) of a reaction pathway, $\nu_{i,\text{net}} < 0$.

For a compound that serves as an intermediate, with no net generation or consumption,

$$\nu_{i,\text{net}} = 0. \qquad \text{Eq. (1.3)}$$

This equality is used to find the correct multiplying factors when combining a system of chemical reactions into a pathway. In the example of making xylene from glucose ((R1) through (R3)), both isobutanol and isobutene serve as intermediates and therefore ideally have no net generation or consumption. Applying Eqs. (1.2) and (1.3) to these two intermediates yields a system of two equations involving three multiplying factors:

$$\nu_{\text{isobutanol,net}} = \nu_{\text{isobutanol,1}}\chi_1 + \nu_{\text{isobutanol,2}}\chi_2 + \nu_{\text{isobutanol,3}}\chi_3 = 0$$
$$\nu_{\text{isobutene,net}} = \nu_{\text{isobutene,1}}\chi_1 + \nu_{\text{isobutene,2}}\chi_2 + \nu_{\text{isobutene,3}}\chi_3 = 0$$

Inserting the known stoichiometric coefficients yields

$$\nu_{\text{isobutanol,net}} = (+1)\chi_1 + (-1)\chi_2 + (0)\chi_3 = 0$$
$$\nu_{\text{isobutene,net}} = (0)\chi_1 + (+1)\chi_2 + (-2)\chi_3 = 0$$

Since there is one more unknown than equation, we cannot yet solve for χ_k. To proceed, we pick one of the multiplying factors and set it arbitrarily to a specific value. Let's pick $\chi_3 = 1$. Then the system of equations becomes

$$(+1)\chi_1 + (-1)\chi_2 = 0$$
$$(+1)\chi_2 = 2$$

This system of equations can be solved to find: $\chi_1 = 2$ and $\chi_2 = 2$.

We can generalize this method as follows. Suppose we have K reactions involving I compounds. To complete a generation-consumption analysis, we

1. Write balanced chemical equations for all K reactions.
2. Make a (vertical) list of all I compounds (reactants and products) in a column.
3. For each reaction k, write ν_{ik} associated with each compound in a column. There will be I rows, one for each compound, and K columns, one for each reaction.
4. Adjust the net generation or consumption of compounds by finding multiplying factors χ_k. If we wish to have zero net generation or consumption of compound i, we find χ_k such that

$$\nu_{i,\text{net}} = \sum_{\text{all } k} \chi_k \nu_{ik} = 0 \qquad \text{Eq. (1.3)}$$

5. Calculate the net generation or consumption of all compounds using Eq. (1.2) and the χ_k that you found in step 4.

Why *can* we do step 4? Because stoichiometric coefficients give relative quantities, or ratios, of reactants and products, not absolute quantities. If we multiply a balanced chemical equation by a common factor, the equation is still balanced.

Why *should* we do step 4? There are many reasons; for example, we may want to avoid net consumption of an expensive compound, or net generation of a toxic or hazardous byproduct.

Note: it is not always possible to find χ_k that will satisfy Eq. (1.3). In that case, we may need to search for additional or different chemical reactions to achieve our goals.

Generation-consumption analysis is illustrated in the next two examples.

Example 1.4 Generation-Consumption Analysis: Ammonia Synthesis

Ammonia is one of the largest-tonnage chemicals produced today. Ammonia synthesis proceeds by reacting steam (H_2O) with methane (CH_4) to make carbon monoxide and hydrogen. Then CO and water react to make CO_2 and more H_2. Finally nitrogen (N_2) and hydrogen combine to produce ammonia, NH_3.

How can we combine these reactions so there is no net generation or consumption of CO or H_2?

Solution

We start with balanced chemical equations:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{R1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{R2}$$

$$N_2 + 3H_2 \rightarrow 2NH_3 \tag{R3}$$

Let's look at the generation-consumption table, using these balanced chemical equations as written, without yet considering multiplying factors.

Compound	**R1** ν_{i1}	**R2** ν_{i2}	**R3** ν_{i3}	**Net** $\nu_{i,\text{net}}$
CH_4	−1			−1
H_2O	−1	−1		−2
CO	+1	−1		0
H_2	+3	+1	−3	+1
CO_2		+1		+1
N_2			−1	−1
NH_3			+2	+2

This solution does satisfy the constraint that net CO = 0, but doesn't satisfy the requirement that net H_2 = 0. Let's write Eq. (1.3) for these two intermediates:

$$\text{CO:} \quad \chi_1 - \chi_2 = 0$$

$$H_2\text{:} \quad 3\chi_1 + \chi_2 - 3\chi_3 = 0$$

All we need to do is find a set of values for (χ_1,χ_2,χ_3) that satisfies these two equations. Since there are two equations but three variables, there is more than one valid solution. Because there is more than one valid solution, we can pick any number greater than zero for the value of one of the multiplying factors, and then solve for the other two. Let's pick

$$\chi_1 = 1$$

Then,

$$\chi_2 = 1, \chi_3 = \tfrac{4}{3}$$

By multiplying all entries in the (R1), (R2), and (R3) columns by these values for χ_1, χ_2, and χ_3, respectively, we get the result we want:

Compound	$\chi_1\nu_{i1}$	$\chi_2\nu_{i2}$	$\chi_3\nu_{i3}$	$\nu_{i,\text{net}}$
CH_4	−1			−1
H_2O	−1	−1		−2
CO	+1	−1		0
H_2	+3	+1	−4	0
CO_2		+1		+1
N_2			−4/3	−4/3
NH_3			+8/3	+8/3

Quick Quiz 1.5

In Example 1.4, what's the net reaction if you set $\chi_2 = 3$ and solve for χ_1 and χ_3?

Would it be possible to combine the set of reactions in Example 1.4 such that there is no net generation or consumption of CO_2?

The net reaction for ammonia synthesis is read from the last column:

$$CH_4 + 2H_2O + \tfrac{4}{3}N_2 \rightarrow CO_2 + \tfrac{8}{3}NH_3$$

Example 1.5 Generation-Consumption Analysis: The Solvay Process

Limestone ($CaCO_3$) decomposes to lime (CaO), and lime reacts with water to form "milk of lime," $Ca(OH)_2$

$$CaCO_3 \rightarrow CaO + CO_2 \quad \text{(R1)}$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad \text{(R2)}$$

Milk of lime reacts with ammonium chloride to make ammonia and calcium chloride:

$$Ca(OH)_2 + 2NH_4Cl \rightarrow 2NH_3 + CaCl_2 + 2H_2O \quad \text{(R3)}$$

Ammonia dissolved in water makes ammonium hydroxide, which reacts with CO_2 to make ammonium carbonate and then ammonium bicarbonate:

$$NH_3 + H_2O \rightarrow NH_4OH \quad \text{(R4)}$$

$$2NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O \quad \text{(R5)}$$

$$(NH_4)_2CO_3 + CO_2 + H_2O \rightarrow 2NH_4HCO_3 \quad \text{(R6)}$$

Ammonium bicarbonate reacts with sodium chloride to produce sodium bicarbonate and generate more ammonium chloride:

$$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3 \tag{R7}$$

Finally, sodium bicarbonate ($NaHCO_3$, common baking soda) decomposes to the desired product, sodium carbonate, releasing carbon dioxide and water as byproducts:

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O \tag{R8}$$

Can we use these reactions to come up with a process for making sodium carbonate from limestone and salt that makes efficient use of raw materials?

Solution

These 8 reactions involve 14 different compounds. Let's use the generation-consumption analysis in Table 1.1a to evaluate this set of chemical reactions, without yet considering any multiplying factors.

Table 1.1a Generation-Consumption Analysis of the Solvay Process (first try)

Compound	R1 ν_{i1}	R2 ν_{i2}	R3 ν_{i3}	R4 ν_{i4}	R5 ν_{i5}	R6 ν_{i6}	R7 ν_{i7}	R8 ν_{i8}	Net $\nu_{i,\text{net}} = \sum \nu_{ik}$
$CaCO_3$	−1								−1
CaO	+1	−1							0
CO_2	+1				−1	−1		+1	0
H_2O		−1	+2	−1	+1	−1		+1	+1
$Ca(OH)_2$		+1	−1						0
NH_4Cl			−2				+1		−1
NH_3			+2	−1					+1
NH_4OH				+1	−2				−1
$(NH_4)_2CO_3$					+1	−1			0
NH_4HCO_3						+2	−1		+1
$NaCl$							−1		−1
$NaHCO_3$							+1	−2	−1
$CaCl_2$			+1						+1
Na_2CO_3								+1	+1

We are using 1 mole $CaCO_3$ and 1 mole NaCl to make 1 mole Na_2CO_3 (the desired product), but we are also consuming or generating a lot of other chemicals. Could we synthesize a reaction pathway with no net consumption of any raw materials other than $CaCO_3$ and NaCl, and no net generation or consumption of any of the ammonia-containing compounds? In other words, can we find multiplying factors χ_k such that the entry in the Net column equals zero for NH_4Cl, NH_3, NH_4OH, $(NH_4)_2CO_3$, NH_4HCO_3, and $NaHCO_3$? Applying Eq. (1.3) to these six compounds gives

$$\begin{aligned} &NH_4Cl: && -2\chi_3 + \chi_7 = 0 \\ &NH_3: && 2\chi_3 - \chi_4 = 0 \\ &NH_4OH: && \chi_4 - 2\chi_5 = 0 \\ &(NH_4)_2CO_3: && \chi_5 - \chi_6 = 0 \\ &NH_4HCO_3: && 2\chi_6 - \chi_7 = 0 \\ &NaHCO_3: && \chi_7 - 2\chi_8 = 0 \end{aligned}$$

One solution that satisfies all these constraints is

$$\chi_3 = \chi_5 = \chi_6 = \chi_8 = 1$$

$$\chi_4 = \chi_7 = 2$$

Let's see what happens if we multiply the stoichiometric coefficients for reactions (R4) and (R7) by 2 and multiply all other reactions by 1 (Table 1.1b):

Table 1.1b Generation-Consumption Analysis of the Solvay Process (second try)*

Compound	**R1** ν_{i1}	**R2** ν_{i2}	**R3** ν_{i3}	**R4** $\chi_4\nu_{i4}$	**R5** ν_{i5}	**R6** ν_{i6}	**R7** $\chi_7\nu_{i7}$	**R8** ν_{i8}	**Net** $\nu_{i,net} = \sum \chi_k \nu_{ik}$
$CaCO_3$	−1								−1
CaO	+1	−1							0
CO_2	+1				−1	−1		+1	0
H_2O		−1	+2	**−2**	+1	−1		+1	**0**
$Ca(OH)_2$		+1	−1						0
NH_4Cl			−2				**+2**		**0**
NH_3			+2	**−2**					**0**
NH_4OH				**+2**	−2				**0**
$(NH_4)_2CO_3$					+1	−1			0
NH_4HCO_3						+2	**−2**		**0**
$NaCl$							**−2**		**−2**
$NaHCO_3$							**+2**	−2	**0**
$CaCl_2$			+1						+1
Na_2CO_3								+1	+1

*Changes are shown in bold.

Perfect! All of the ammonia-containing compounds are now strictly intermediates, with no net generation or consumption. Furthermore, there is no net consumption of $NaHCO_3$. Remarkably, the net effect of this pathway of 8 chemical reactions involving 14 compounds is simply (from the last column of Table 1.1b):

$$CaCO_3 + 2NaCl \rightarrow Na_2CO_3 + CaCl_2$$

1.4.1 Using Matrices in Generation-Consumption Analysis

Matrix math can be used to find the correct values of x_k in Eq. (1.2) and (1.3). These methods are particularly useful for systems of large numbers of reactions, because the matrix equation can be developed by inspection. Matrix methods are even useful in cases where it is not obvious whether the reactions can be combined in such a way that a compound can serve as an intermediate or must be a byproduct! Our goal is to find an equation $\mathbf{Ax} = \mathbf{b}$, where $\mathbf{A}$ is a matrix containing the stoichiometric coefficients of all compounds that have net-zero generation/consumption, $\mathbf{x}$ is the vector containing the (unknown) multiplying factors, and $\mathbf{b}$ is a vector containing the stoichiometric coefficients for one reaction chosen as the basis reaction. Then we solve for $\mathbf{x}$ and complete the generation-consumption analysis. Here is the procedure to follow:

1. List all the compounds that appear in any reaction. To write the matrix $\mathbf{A}$, list the stoichiometric coefficients for each reaction in a column, in the order of the compounds in your list. $\mathbf{A}$ will have I rows (one for each compound) and K columns (one for each reaction). There should be at least as many compounds as there are reactions.
2. Scan the rows of $\mathbf{A}$. Cross out any rows that have only a single nonzero entry. These rows correspond to compounds that appear in only a single reaction in the reaction system. Such compounds *cannot* have net-zero generation/consumption and so cannot be intermediates: They must be either a reactant or a product.
3. If there is one fewer row than column in matrix $\mathbf{A}$, go to step 4. If not, scan the remaining rows of $\mathbf{A}$ and identify any compounds that are acceptable as raw materials and/or products. Such compounds may be "acceptable" because they are nontoxic, or because they are cheap raw materials or valuable byproducts. Continue crossing out rows of acceptable compounds until there is one fewer row than column in $\mathbf{A}$ (equivalently, there is one fewer compound than reaction).
4. Choose one of the reactions (one of the columns) to serve as a basis reaction. Let $\mathbf{b}$ = a column vector containing the negative of the stoichiometric coefficients of the basis reaction. Delete that column from matrix $\mathbf{A}$.
5. Check that you now have a square coefficient matrix $\mathbf{A}$ with an equal number of rows and columns, a variable vector $\mathbf{x}$ that is the unknown multiplying factors, and a vector $\mathbf{b}$ that describes your basis reaction. Solve for $\mathbf{x}$. Use the solution to complete the generation-consumption analysis.

The procedure sounds more complicated than it is. Example 1.6 illustrates the idea.

Example 1.6 Generation-Consumption Analysis Using Matrix Math: Nitric Acid Synthesis

We want to develop a reaction pathway to make nitric acid (HNO_3) from readily available and cheap raw materials. We think some combination of the following reactions might be useful:

$$O_2 + 2CH_4 \rightarrow 2CO + 4H_2 \qquad \text{(R1)}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{(R2)}$$

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad \text{(R3)}$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad \text{(R4)}$$

$$2NO + O_2 \rightarrow 2NO_2 \qquad \text{(R5)}$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \qquad \text{(R6)}$$

Use matrix methods to combine these reactions into a pathway to make nitric acid. Preferably, we'd like to use inexpensive and readily available raw materials like water, methane (CH_4), and oxygen and nitrogen from air, and we want to avoid any net generation of toxic or environmentally damaging compounds such as NO, NO_2, NH_3, and CO.

Solution

1. We list the compounds involved and immediately write down the matrix of stoichiometric coefficients from the balanced chemical reactions:

	R1	R2	R3	R4	R5	R6
O_2	−1	0	0	−5	−1	0
N_2	0	0	−1	0	0	0
CH_4	−2	0	0	0	0	0
H_2O	0	−1	0	6	0	−1
CO	2	−1	0	0	0	0
CO_2	0	1	0	0	0	0
H_2	4	1	−3	0	0	0
NH_3	0	0	2	−4	0	0
NO	0	0	0	4	−2	1
NO_2	0	0	0	0	2	−3
HNO_3	0	0	0	0	0	2

2. Next we scan the list and eliminate any rows (compounds) with just one entry. This includes necessary reactants N_2 and CH_4 and the desired product HNO_3.

We also observe that CO_2 *must* be a product of this reaction pathway, because it appears in only one reaction. Our matrix becomes:

$$\begin{array}{c} \\ O_2 \\ H_2O \\ CO \\ H_2 \\ NH_3 \\ NO \\ NO_2 \end{array}\begin{array}{c} \begin{array}{cccccc} R1 & R2 & R3 & R4 & R5 & R6 \end{array} \\ \begin{bmatrix} -1 & 0 & 0 & -5 & -1 & 0 \\ 0 & -1 & 0 & 6 & 0 & -1 \\ 2 & -1 & 0 & 0 & 0 & 0 \\ 4 & 1 & -3 & 0 & 0 & 0 \\ 0 & 0 & 2 & -4 & 0 & 0 \\ 0 & 0 & 0 & 4 & -2 & 1 \\ 0 & 0 & 0 & 0 & 2 & -3 \end{bmatrix} \end{array}$$

3. We have seven compounds but only six reactions; according to our procedure we need to have one fewer compound than reaction. We look for two materials that are acceptable raw materials or byproducts. O_2 and H_2O fit the bill. We eliminate them from consideration. The remaining five compounds can all be net-zero compounds! The matrix becomes:

$$\begin{array}{c} \\ CO \\ H_2 \\ NH_3 \\ NO \\ NO_2 \end{array}\begin{array}{c} \begin{array}{cccccc} R1 & R2 & R3 & R4 & R5 & R6 \end{array} \\ \begin{bmatrix} 2 & -1 & 0 & 0 & 0 & 0 \\ 4 & 1 & -3 & 0 & 0 & 0 \\ 0 & 0 & 2 & -4 & 0 & 0 \\ 0 & 0 & 0 & 4 & -2 & 1 \\ 0 & 0 & 0 & 0 & 2 & -3 \end{bmatrix} \end{array}$$

4. We arbitrarily choose one of the reactions to serve as the basis reaction—let's choose (R1). We create the **b** vector by multiplying the column corresponding to (R1) by −1, and then we delete that column from **A**. The **x** vector is simply the listing of the multiplying factors for the remaining reactions. We end up with

$$\begin{bmatrix} -1 & 0 & 0 & 0 & 0 \\ 1 & -3 & 0 & 0 & 0 \\ 0 & 2 & -4 & 0 & 0 \\ 0 & 0 & 4 & -2 & 1 \\ 0 & 0 & 0 & 2 & -3 \end{bmatrix}\begin{bmatrix} \chi_2 \\ \chi_3 \\ \chi_4 \\ \chi_5 \\ \chi_6 \end{bmatrix} = \begin{bmatrix} -2 \\ -4 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

5. The columns in the matrix **A** correspond to the five remaining reactions, (R2) through (R6). The rows in the matrix correspond to the stoichiometric coefficients of the remaining compounds: CO, H_2, NH_3, NO, and NO_2. These

are the compounds where we want to have no net generation or consumption. We solve, by calculator or by computer, and find the multiplying factors:

$$\mathbf{x} = \begin{bmatrix} 2 \\ 2 \\ 1 \\ 3 \\ 2 \end{bmatrix}$$

Finally, we multiply the stoichiometric coefficients ν_{ik} by the corresponding multiplying factor x_k to complete the generation-consumption table:

Compound	R1	R2	R3	R4	R5	R6	Net
O_2	−1			−5	−3		−9
N_2			−2				−2
CH_4	−2						−2
H_2O		−2		+6		−2	+2
CO	+2	−2					0
CO_2		+2					+2
H_2	+4	+2	−6				0
NH_3			+4	−4			0
NO				+4	−6	+2	0
NO_2					+6	−6	0
HNO_3						+4	+4

The net overall reaction is

$$9O_2 + 2N_2 + 2CH_4 \rightarrow 2H_2O + 2CO_2 + 4HNO_3$$

1.5 A First Look at Material Balances and Process Economics

In this section, we'll examine how to use the results from a generation-consumption analysis to calculate the mass of raw materials needed to produce a specified mass of product, the mass of byproducts produced per mass of desired product,