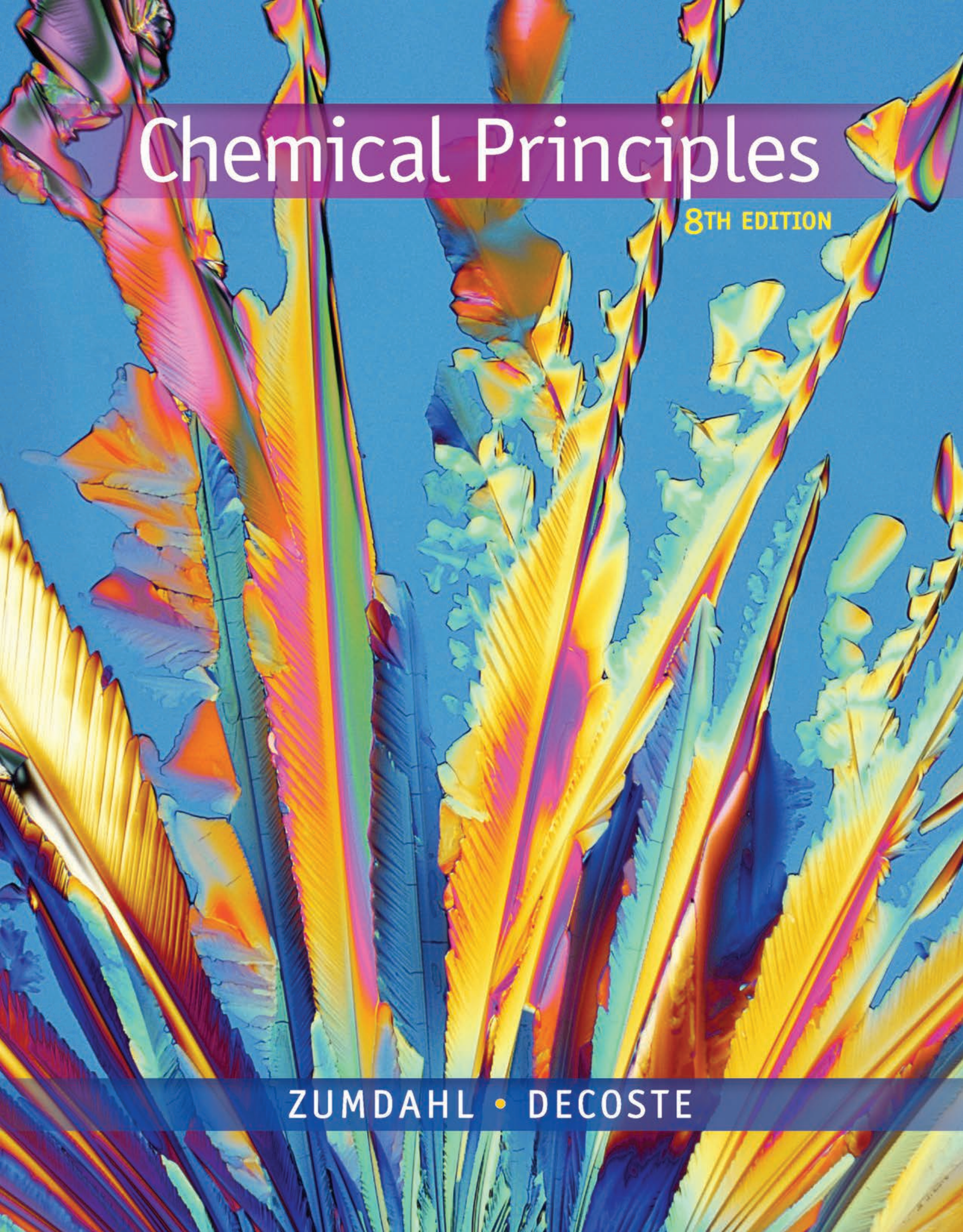


Chemical Principles

8TH EDITION

ZUMDAHL • DECOSTE

Periodic Table of the Elements

Alkaline earth metals

Transition metals

Halogens

Noble gases

Alkali metals

1 1A	2 2A	3	4	5	6	7	8	9	10	11	12	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac†	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

*Lanthanides	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
†Actinides	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

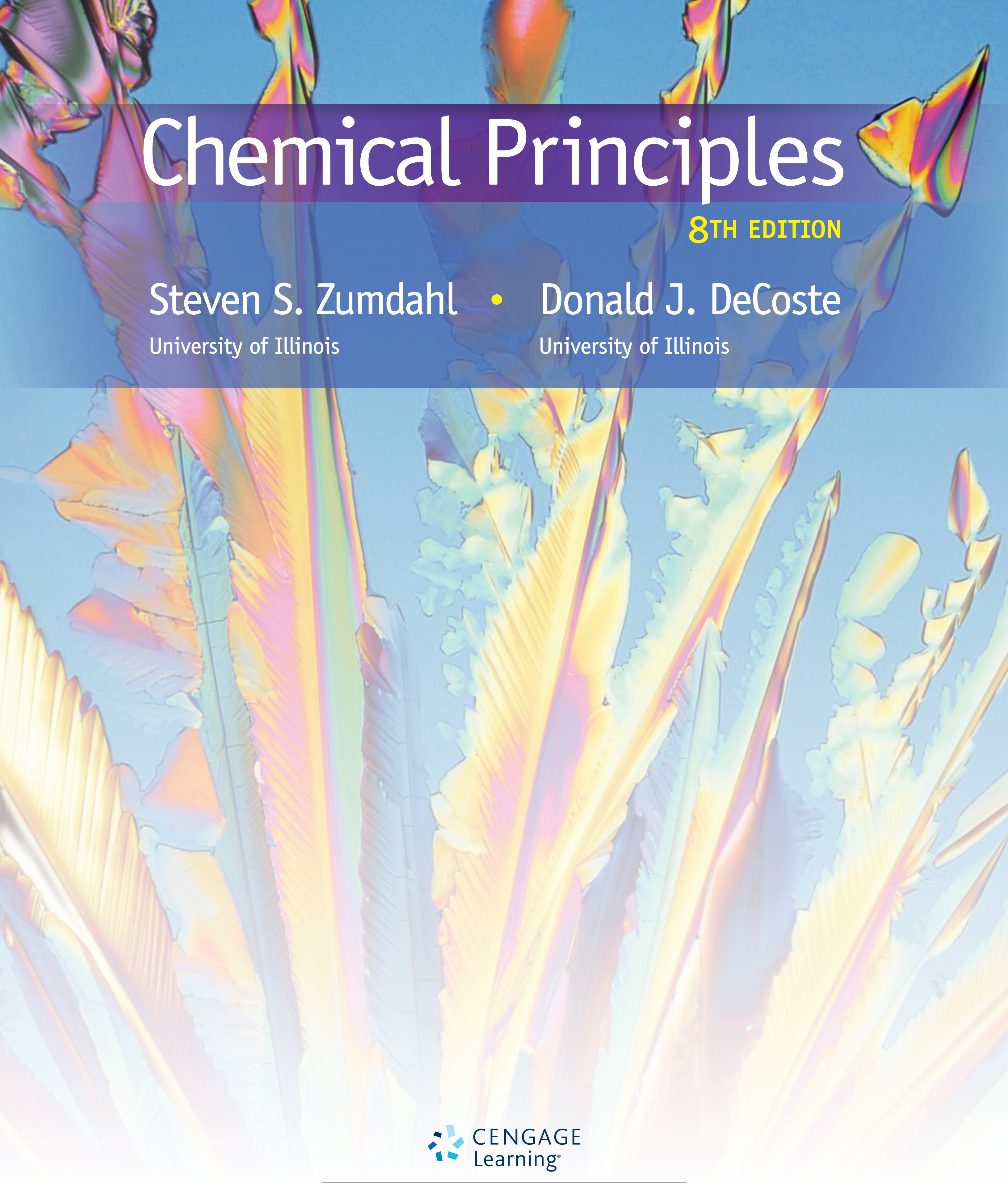
Group numbers 1–18 represent the system recommended by the International Union of Pure and Applied Chemistry.

Table of Atomic Masses*

Element	Symbol	Atomic Number	Atomic Mass	Element	Symbol	Atomic Number	Atomic Mass	Element	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	[227][§]	Germanium	Ge	32	72.59	Potassium	K	19	39.10
Aluminum	Al	13	26.98	Gold	Au	79	197.0	Praseodymium	Pr	59	140.9
Americium	Am	95	[243]	Hafnium	Hf	72	178.5	Promethium	Pm	61	[145]
Antimony	Sb	51	121.8	Hassium	Hs	108	[265]	Protactinium	Pa	91	[231]
Argon	Ar	18	39.95	Helium	He	2	4.003	Radium	Ra	88	226
Arsenic	As	33	74.92	Holmium	Ho	67	164.9	Radon	Rn	86	[222]
Astatine	At	85	[210]	Hydrogen	H	1	1.008	Rhenium	Re	75	186.2
Barium	Ba	56	137.3	Indium	In	49	114.8	Rhodium	Rh	45	102.9
Berkelium	Bk	97	[247]	Iodine	I	53	126.9	Roentgenium	Rg	111	[272]
Beryllium	Be	4	9.012	Iridium	Ir	77	192.2	Rubidium	Rb	37	85.47
Bismuth	Bi	83	209.0	Iron	Fe	26	55.85	Ruthenium	Ru	44	101.1
Bohrium	Bh	107	[264]	Krypton	Kr	36	83.80	Rutherfordium	Rf	104	[261]
Boron	B	5	10.81	Lanthanum	La	57	138.9	Samarium	Sm	62	150.4
Bromine	Br	35	79.90	Lawrencium	Lr	103	[260]	Scandium	Sc	21	44.96
Cadmium	Cd	48	112.4	Lead	Pb	82	207.2	Seaborgium	Sg	106	[263]
Calcium	Ca	20	40.08	Livermorium	Lv	116	[293]	Selenium	Se	34	78.96
Californium	Cf	98	[251]	Lithium	Li	3	6.9419	Silicon	Si	14	28.09
Carbon	C	6	12.01	Lutetium	Lu	71	175.0	Silver	Ag	47	107.9
Cerium	Ce	58	140.1	Magnesium	Mg	12	24.31	Sodium	Na	11	22.99
Cesium	Cs	55	132.90	Manganese	Mn	25	54.94	Strontium	Sr	38	87.62
Chlorine	Cl	17	35.45	Meitnerium	Mt	109	[268]	Sulfur	S	16	32.07
Chromium	Cr	24	52.00	Mendelevium	Md	101	[258]	Tantalum	Ta	73	180.9
Cobalt	Co	27	58.93	Mercury	Hg	80	200.6	Technetium	Tc	43	[98]
Copernicium	Cn	112	[285]	Molybdenum	Mo	42	95.94	Tellurium	Te	52	127.6
Copper	Cu	29	63.55	Neodymium	Nd	60	144.2	Terbium	Tb	65	158.9
Curium	Cm	96	[247]	Neon	Ne	10	20.18	Thallium	Tl	81	204.4
Darmstadtium	Ds	110	[271]	Neptunium	Np	93	[237]	Thorium	Th	90	232.0
Dubnium	Db	105	[262]	Nickel	Ni	28	58.69	Thulium	Tm	69	168.9
Dysprosium	Dy	66	162.5	Niobium	Nb	41	92.91	Tin	Sn	50	118.7
Einsteinium	Es	99	[252]	Nitrogen	N	7	14.01	Titanium	Ti	22	47.88
Erbium	Er	68	167.3	Nobelium	No	102	[259]	Tungsten	W	74	183.9
Europium	Eu	63	152.0	Osmium	Os	76	190.2	Uranium	U	92	238.0
Fermium	Fm	100	[257]	Oxygen	O	8	16.00	Vanadium	V	23	50.94
Flerovium	Fl	114	[289]	Palladium	Pd	46	106.4	Xenon	Xe	54	131.3
Fluorine	F	9	19.00	Phosphorus	P	15	30.97	Ytterbium	Yb	70	173.0
Francium	Fr	87	[223]	Platinum	Pt	78	195.1	Yttrium	Y	39	88.91
Gadolinium	Gd	64	157.3	Plutonium	Pu	94	[244]	Zinc	Zn	30	65.38
Gallium	Ga	31	69.72	Polonium	Po	84	[209]	Zirconium	Zr	40	91.22

*The values given here are to four significant figures where possible.

[§] A value given in brackets denotes the mass of the longest-lived isotope.



Chemical Principles

8TH EDITION

Steven S. Zumdahl
University of Illinois

Donald J. DeCoste
University of Illinois

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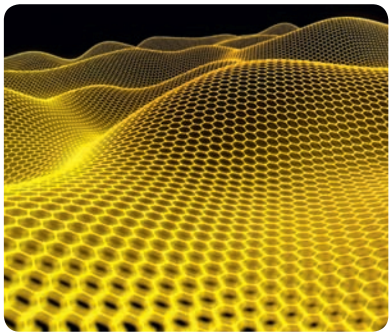

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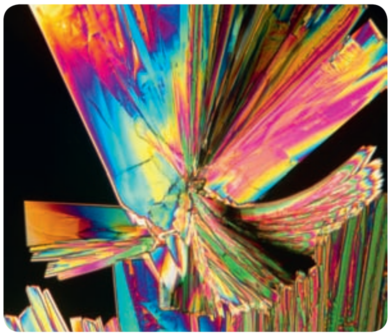

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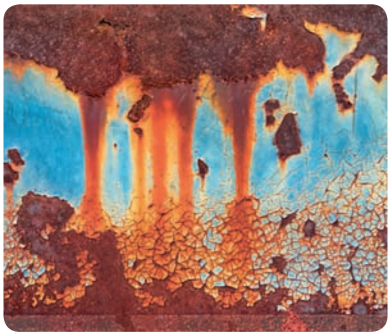

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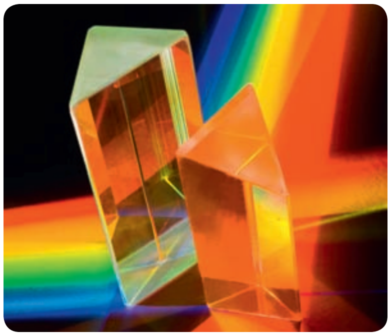

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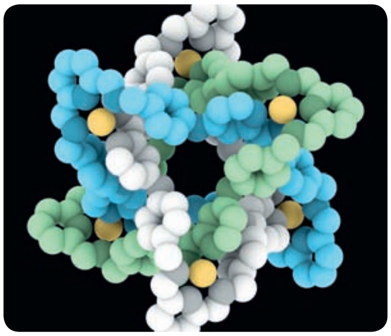

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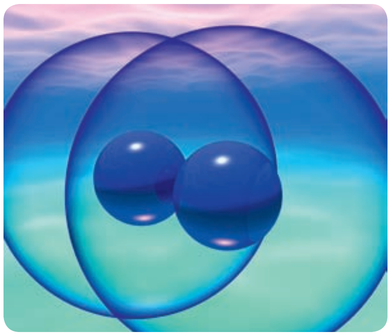

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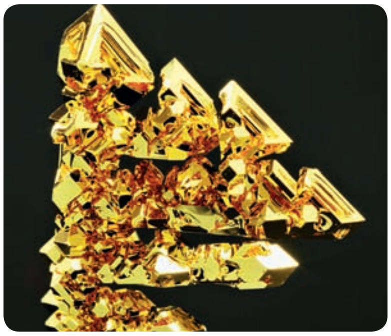

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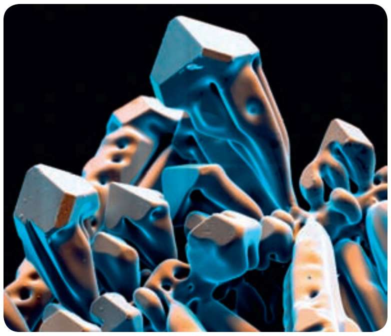

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Learning to Think Like a Chemist

Chemistry is a fascinating and important subject that is challenging to teach and even more challenging to learn. Making this complex subject accessible to students without distortion is the challenge of the chemical educator, especially at the introductory level. *Chemical Principles*, Eighth Edition, provides a rigorous but understandable introduction to chemistry. It emphasizes conceptual understanding, the importance of models, and thoughtful problem solving.

Chemical Principles is based on our experiences at the University of Illinois teaching an accelerated general chemistry course for chemical sciences majors and other students who require a rigorous introductory course. These students typically have excellent credentials and a genuine aptitude for chemistry but only limited understanding of the fundamental concepts of chemistry. Although they may know how to solve stoichiometry and gas problems when they arrive in our courses, these students typically lack a thorough appreciation for the chemical principles that underlie these applications. This is not because they had inadequate preparation in high school; instead, we believe it results from the nature of chemistry itself—a subject that requires several passes before real mastery can take place.

Our mission in writing this text was to produce a book that does not assume that students already know how to think like chemists. These students will eventually do complicated and rigorous thinking, but they must be brought to that point gradually. Thus this book covers the advanced topics (in gases, atomic theory, thermodynamics, and so on) that one expects in a course for chemical sciences majors, but it starts with the fundamentals and then builds to the level required for more complete understanding. Chemistry is not the result of an inspired vision. It is the product of countless observations and many attempts, using logic and trial and error, to account for these observations. In this book we develop key chemical concepts in the same way—to show the observations first and then discuss the models that have been constructed to explain the observed behavior. We hope students will practice "thinking like a chemist" by carefully studying the observations to see if they can follow the thought process, rather than just jumping ahead to the equation or model that will follow.

In *Chemical Principles,* Eighth Edition, we take advantage of the excellent math skills that these students typically possess. As a result, there are fewer worked-out examples than would be found in most mainstream books. The end-of-chapter problems cover a wide range—from drill exercises to difficult problems, some of which would challenge the average senior chemistry major. Thus instructors can tailor the problem assignments to the level appropriate for their students.

This text maintains a student-friendly approach without being patronizing. In addition, to demonstrate the importance of chemistry in real life, we have incorporated throughout the book a number of applications and recent advances in essay form.

New to This Edition

We continue to be pleased that the previous editions of the text have been well received. In response to comments from users, however, we have made some significant changes for the eighth edition.

- We have expanded Section 3.4 “Conceptual Problem Solving” to increase the emphasis on the importance of having students think their way through a problem.
- We have increased the discussion of how to use our problem-solving approach in the examples in Chapters 3 through 5 to model for the students the types of questions they should be asking and answering when solving problems.
- All examples have been checked and revised as needed, with titles being added.
- In the new Section 3.11, “Solving a Complex Problem,” we discuss at length a complex problem (that is, one which requires the students to utilize knowledge and understanding of many concepts). We also consider an alternative solution to show students that there is always more than one method to solve a complex problem.
- A more rigorous discussion of the mathematics involved in relating the number of microstates to the concept of entropy is included in Section 10.1.
- *Critical Thinking* questions have been added throughout the text to emphasize the importance of conceptual learning.
- Several *Chemical Insights and Chemistry Explorers* features have been added or revised.
- Calculus-based derivations of integrated rate laws for zero-, first-, and second-order reactions have been added in Appendix 6.
- New end-of-chapter questions and problems have been added throughout the text.
- *ChemWork* problems have been added to the end-of-chapter problems throughout the text. These problems test the students’ understanding of core concepts from each chapter. Students who solve a particular problem with no assistance can proceed directly to the answer. However, students who need help can get assistance through a series of online hints. The online procedure for assisting students is modeled after the way a teacher would help with homework problems in his or her office. The hints are usually in the form of interactive questions that guide students through the problem-solving process. Students cannot receive the correct answer from the computer; rather, it encourages students to continue working through the hints to arrive at the answer. *ChemWork* problems in the text can be worked using the online system or as pencil-and-paper problems.
- All end-of-chapter questions and problems have been checked, rewritten, and updated as needed to comply with OWL v.2.
- The art program has been modified and updated as needed.

Organization

The early chapters in this book deal with chemical reactions. Stoichiometry is covered in Chapters 3 and 4, with special emphasis on reactions in aqueous solutions. The properties of gases are treated in Chapter 5, followed by coverage of gas phase equilibria in Chapter 6. Acid–base equilibria are covered in Chapter 7, and Chapter 8 deals with additional aqueous equilibria. Thermodynamics is covered in two chapters: Chapter 9 deals with thermochemistry and the first law of thermodynamics; Chapter 10 treats the topics associated with the second law of thermodynamics. The discussion of electrochemistry follows in Chapter 11. Atomic theory and quantum mechanics are covered in

Chapter 12, followed by two chapters on chemical bonding and modern spectroscopy (Chapters 13 and 14). Chemical kinetics is discussed in Chapter 15, followed by coverage of solids and liquids in Chapter 16 and the physical properties of solutions in Chapter 17. A systematic treatment of the descriptive chemistry of the representative elements is given in Chapter 18 and of the transition metals in Chapter 19. Chapter 20 covers topics in nuclear chemistry, and Chapter 21 provides an introduction to organic chemistry and to the most important biomolecules.

Flexibility of Topic Order

We recognize that the order of the chapters in this text may not fit the order of the topics in your course. Therefore, we have tried to make the order as flexible as possible. In the courses that we have taught using the text, we have successfully used it in a very different order from the one the text follows. We would encourage you to use it in whatever order that serves your purposes.

Instructors have several options for arranging the material to complement their syllabi. For example, the section on gas phase and aqueous equilibria (Chapters 6–8) could be moved to any point later in the course. The chapters on thermodynamics can be separated: Chapter 9 can be used early in the course with Chapter 10 later. In addition, the chapters on atomic theory and bonding (Chapters 12–14) can be used near the beginning of the course. In summary, an instructor who wants to cover atomic theory early and equilibrium later might prefer the following order of chapters: 1–5, 9,

Two approaches for teaching atomic theory earlier and equilibrium later in the course

APPROACH 1		***APPROACH 2***	
Chapter 1	*Chemists and Chemistry*	**Chapter 1**	*Chemists and Chemistry*
Chapter 2	*Atoms, Molecules, and Ions*	**Chapter 2**	*Atoms, Molecules, and Ions*
Chapter 3	*Stoichiometry*	**Chapter 3**	*Stoichiometry*
Chapter 4	*Types of Chemical Reactions and Solution Stoichiometry*	**Chapter 4**	*Types of Chemical Reactions and Solution Stoichiometry*
Chapter 5	*Gases*	**Chapter 5**	*Gases*
Chapter 9	*Energy, Enthalpy, and Thermochemistry*	**Chapter 9**	*Energy, Enthalpy, and Thermochemistry*
Chapter 12	*Quantum Mechanics and Atomic Theory*	**Chapter 12**	*Quantum Mechanics and Atomic Theory*
Chapter 13	*Bonding: General Concepts*	**Chapter 13**	*Bonding: General Concepts*
Chapter 14	*Covalent Bonding: Orbitals*	**Chapter 14**	*Covalent Bonding: Orbitals*
Chapter 10	*Spontaneity, Entropy, and Free Energy*	**Chapter 6**	*Chemical Equilibrium*
Chapter 11	*Electrochemistry*	**Chapter 7**	*Acids and Bases*
Chapter 6	*Chemical Equilibrium*	**Chapter 8**	*Applications of Aqueous Equilibria*
Chapter 7	*Acids and Bases*	**Chapter 10**	*Spontaneity, Entropy, and Free Energy*
Chapter 8	*Applications of Aqueous Equilibria*	**Chapter 11**	*Electrochemistry*
Chapter 15	*Chemical Kinetics*	**Chapter 15**	*Chemical Kinetics*
Chapter 16	*Liquids and Solids*	**Chapter 16**	*Liquids and Solids*
Chapter 17	*Properties of Solutions*	**Chapter 17**	*Properties of Solutions*
Chapter 18	*The Representative Elements*	**Chapter 18**	*The Representative Elements*
Chapter 19	*Transition Metals and Coordination Chemistry*	**Chapter 19**	*Transition Metals and Coordination Chemistry*
Chapter 20	*The Nucleus: A Chemist's View*	**Chapter 20**	*The Nucleus: A Chemist's View*
Chapter 21	*Organic and Biochemical Molecules*	**Chapter 21**	*Organic and Biochemical Molecules*

12, 13, 14, 10, 11, 6, 7, 8, 15–21. An alternative order might be: 1–5, 9, 12, 13, 14, 6, 7, 8, 10, 11, 15–21. The point is that the chapters on atomic theory and bonding (12–14), thermodynamics (9, 10), and equilibrium (6, 7, 8) can be moved around quite easily. In addition, the kinetics chapter (Chapter 15) can be covered at any time after bonding. It is also possible to use Chapter 20 (on nuclear chemistry) much earlier—after Chapter 12, for example—if desired.

Mathematical Level

This text assumes a solid background in algebra. All of the mathematical operations required are described in Appendix One or are illustrated in worked-out examples. A knowledge of calculus is not required for use of this text. Differential and integral notions are used only where absolutely necessary and are explained when they are used.

Supporting Materials

Please visit http://www.cengage.com/chemistry/zumdahl/chemprin8e for more information about student and instructor resources for this book and about custom versions.

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Professor Zumdahl is known at the University of Illinois for his rapport with students and for his outstanding teaching ability. During his tenure at the University, he received the University of Illinois Award for Excellence in Teaching, the Liberal Arts and Sciences College Award for Distinguished Teaching, and the School of Chemical Sciences Teaching Award (five times).

Dr. Z., as he is known to his students, greatly enjoys "mechanical things," including bicycles and cars. He collects and restores classic automobiles, having a special enthusiasm for vintage Corvettes and Packards.

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At UIUC he teaches courses in introductory chemistry and the teaching of chemistry and has developed chemistry courses for nonscience majors, preservice secondary teachers, and preservice elementary teachers. He has received the LAS Award for Excellence in Undergraduate Teaching by Instructional Staff Award, the Provost's Excellence in Undergraduate Teaching Award, and the School of Chemical Sciences Teaching Award four times.

Don has led workshops for secondary teachers and graduate student teaching assistants, discussing the methods and benefits of getting students more actively involved in class. When not involved in teaching and advising, Don enjoys spending time with his wife and three children.

chapter 1 Chemists and Chemistry

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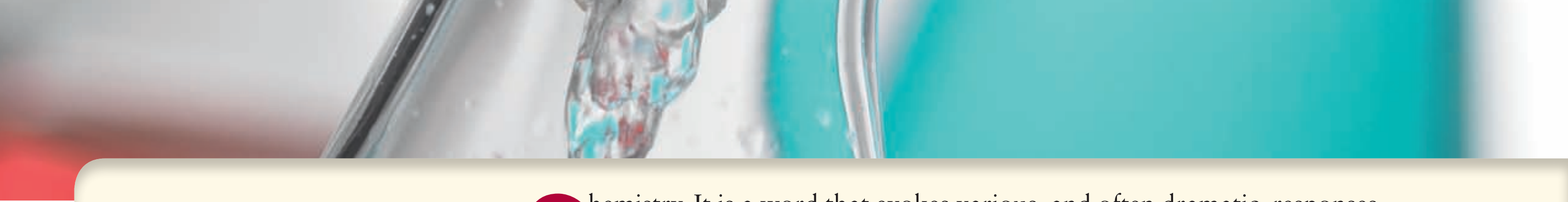


Chemistry. It is a word that evokes various, and often dramatic, responses. It is a word that is impossible to define concisely, because the field is so diverse and its practitioners perform such an incredible variety of jobs. Chemistry mainly deals with situations in which the nature of a substance is changed by altering its composition; entirely new substances are synthesized, or the properties of existing substances are enhanced.

There are many misconceptions about the practitioners of chemistry. Many people picture a chemist as a solitary figure who works in a laboratory and does not talk to anyone else for days at a time. Nothing could be further from the truth. Many chemists do indeed work in laboratories, but rarely by themselves. A typical day for a modern chemist would be spent as a member of a team solving a particular problem important to his or her company. This team might consist of chemists from various specialties, chemical engineers, development specialists, and possibly even lawyers. Figure 1.1 ▼ represents the people and organizations with which typical laboratory chemists might expect to interact in the course of their jobs.

On the other hand, many persons trained as chemists do not perform actual laboratory work but may work as patent lawyers, financial analysts, plant managers, salespeople, personnel managers, and so on. Also, it is quite common for a person trained as a chemist to have many different jobs during a career.

In Chapters 2 through 21 of this text we will concentrate on the formal discipline of chemistry—its observations, theories, and applications. The goal of Chapter 1 is to introduce some of the important aspects of chemistry not typically discussed in connection with learning chemistry. The chapter includes an introduction to the world of commercial chemistry and provides a couple

Figure 1.1

Typical chemists interact with a great variety of other people while doing their jobs. (Center photo: Photograph Courtesy of Argonne National Laboratory)

USDA Photo by Scott Bauer

Jim Arbogast/Getty Images

B. Busco/Getty Images

Will & Deni McIntyre/Photo Researchers, Inc.

of specific examples of the types of problems confronting the practitioners of the "chemical arts." We begin by considering the chemical scientist as a problem solver.

1.1 Thinking Like a Chemist

Much of your life, both personal and professional, will involve problem solving. Most likely, the more creative you are at solving problems, the more effective and successful you will be. Chemists are usually excellent problem solvers because they get a lot of practice. Chemical problems are frequently very complicated—there is usually no neat and tidy solution. Often it is difficult to know where to begin. In response to this dilemma, a chemist makes an educated guess (formulates a hypothesis) and then tests it to see if the proposed solution correctly predicts the observed behavior of the system. This process of trial and error is virtually a way of life for a chemist. Chemists rarely solve a complex problem in a straightforward, elegant manner. More commonly, they poke and prod the problem and make progress only in fits and starts.

It's very important to keep this in mind as you study chemistry. Although "plug and chug" exercises are necessary to familiarize you with the relationships that govern chemical behavior, your ultimate goal should be to advance beyond this stage to true problem solving. Unfortunately, it is impossible to give a formula for becoming a successful problem solver. Creative problem solving is a rather mysterious activity that defies simple analysis. However, it is clear that practice helps. That's why we will make every attempt in this text to challenge you to be creative with the knowledge of chemistry you will be acquiring. Although this process can be frustrating at times, it is definitely worth the struggle—both because it is one of the most valuable skills you can develop and because it helps you test your understanding of chemical concepts. If your understanding of these concepts is not sufficient to allow you to solve problems involving "twists" that you have never encountered before, your knowledge is not very useful to you. The only way to develop your creativity is to expose yourself to new situations in which you need to make new connections. A substantial part of creative problem solving involves developing the confidence necessary to think your way through unfamiliar situations. You must recognize that the entire solution to a complex problem is almost never visible in the beginning. Typically, one tries first to understand pieces of the problem and then puts those pieces together to form the solution.

1.2 A Real-World Chemistry Problem

As discussed, the professional chemist is primarily a problem solver—one who daily confronts tough, but fascinating, situations that must be understood. To illustrate, we will consider an important current problem that requires chemical expertise to solve: the crumbling of the paper in many of the books published in the past century. The pages of many of these books are literally falling apart. To give some perspective on the magnitude of the problem, if the books in the New York Public Library were lined up, they would stretch for almost 100 miles. Currently, about 40 miles of these books are quietly crumbling to dust.

Because of the magnitude of this problem, the company that develops a successful preservation process will reap considerable financial rewards, in addition to performing an important service to society. Assume that you work for a company that is interested in finding a method for saving the crumbling paper in books and that you are put in charge of your company's efforts to develop such a process. What do you know about paper? Probably not much. So the first step is to go to the library to learn all you can about paper. Because

Gamma Rapho/Getty Images

Acid-damaged paper.

CHEMICAL EXPLORERS

Alison Williams's Focus: The Structure of Nucleic Acids

Alison Williams started her scientific career as a high school student when she worked part-time at the Ohio State Agricultural Research and Development Center in Wooster, Ohio. She subsequently received her undergraduate degree from Wesleyan University, and then her master's degree and Ph.D. in biophysical chemistry. Dr. Williams has taught at Swarthmore College, Wesleyan University, Princeton University, Barnard College, and is now at Oberlin College.

Dr. Williams's primary interest is to understand the thermodynamic and kinetic behavior of nucleic acid structure. Nucleic acids, in the form of the huge polymers DNA and RNA, are central to the genetic machinery of cells. In 2012, Dr. Williams was appointed as Director of the Multicultural Resource Center (MRC) and Associate Dean of Academic Diversity at Oberlin College in Ohio. At Oberlin, Dr. Williams works on curricular and faculty diversity initiatives with emphasis on student inclusion and faculty support.


Barnard College/Asiya Khaki

Alison Williams.

paper manufacturing is a mature industry, a great deal of information is available. Research at the library will show that paper is made of cellulose obtained from wood pulp and that the finished paper is "sized" to give it a smooth surface that prevents ink from "fuzzing." The agent typically used for sizing is alum [$Al_2(SO_4)_3$], which is the cause of the eventual decomposition of the paper. This happens as follows: In the presence of moisture, the Al^{3+} ions from alum become hydrated, forming $Al(H_2O)_6{}^{3+}$. The $Al(H_2O)_6{}^{3+}$ ion acts as an acid because the very strong Al^{3+}—O bond causes changes in the O—H bonds of the attached water molecules, thus allowing H^+ ions to be produced by the following reaction:

$$Al(H_2O)_6{}^{3+} \rightleftharpoons [Al(OH)(H_2O)_5]^{2+} + H^+$$

Therefore, paper sized with alum contains significant numbers of H^+ ions. This is important because the H^+ assists in the breakdown of the polymeric cellulose structure of paper. Cellulose is composed of glucose molecules ($C_6H_{12}O_6$) bonded together to form long chains. A segment of cellulose is shown in Fig. 1.2 ►. When the long chains of glucose units in cellulose are broken into shorter pieces, the structural integrity of the paper fails and it crumbles.

Although library research helps you to understand the fundamentals of the problem, now the tough part (and the most interesting part) begins. Can you find a creative solution to the problem? Can the paper in existing books be treated to stop the deterioration in a way that is economical, permanent, and safe?

The essence of the problem seems to be the H^+ present in the paper. How can it be removed or at least rendered harmless?

Your general knowledge of chemistry tells you that some sort of base (a substance that reacts with H^+) is needed. One of the most common and least expensive bases is sodium hydroxide. Why not dip the affected books in a solution of sodium hydroxide and remove the H^+ by the reaction: $H^+ + OH^- \rightarrow H_2O$? This seems to be a reasonable first idea, but as you consider it further and discuss it with your colleagues, several problems become apparent:

1. The NaOH(*aq*) is a strong base and is therefore quite corrosive. It will destroy the paper by breaking down the cellulose just as acid does.

Stephanie Burns: Chemist, Executive

CHEMICAL EXPLORERS

Stephanie Burns was always interested in science, even as a little girl. This interest intensified over the years until she obtained a Ph.D. in organic chemistry from Iowa State University, where she specialized in the organic chemistry of silicon. Her career path led her to a job with Dow Corning Company, where she developed useful products containing silicon. Eventually her career path led to several positions involving product development, marketing, and business management. Her outstanding performance in these positions resulted in her appointment as an executive vice president. In early 2003, Dr. Burns, at age 48, was promoted to President and Chief Operating Officer for Dow Corning. In 2004 she became Chief Executive Officer, and in 2006 she was elected Chairman. She has repeatedly been on *Forbes*'s list of the 100 most powerful women.

Dr. Burns says "there was no magic" in reaching the position of Chairman and Chief Executive Officer of Dow Corning. "I'm driven by the science and technology of the company. It's in my blood," she says. Burns says her top priority is to encourage her company's scientists to develop innovative products and expand business built on silicon-based chemistry.


Courtesy Dow Corning. Photo by Jeffrey Glen.

Stephanie Burns.

2. The book bindings will be destroyed by dipping the books in water, and the pages will stick together after the books dry.
3. The process will be very labor-intensive, requiring the handling of individual books.

Some of these difficulties can be addressed. For example, a much weaker base than sodium hydroxide could be used. Also, the pages could be removed from the binding, soaked one at a time, dried, and then rebound. In fact, this process is used for some very rare and valuable books, but the labor involved makes it very expensive—much too expensive for the miles of books in the

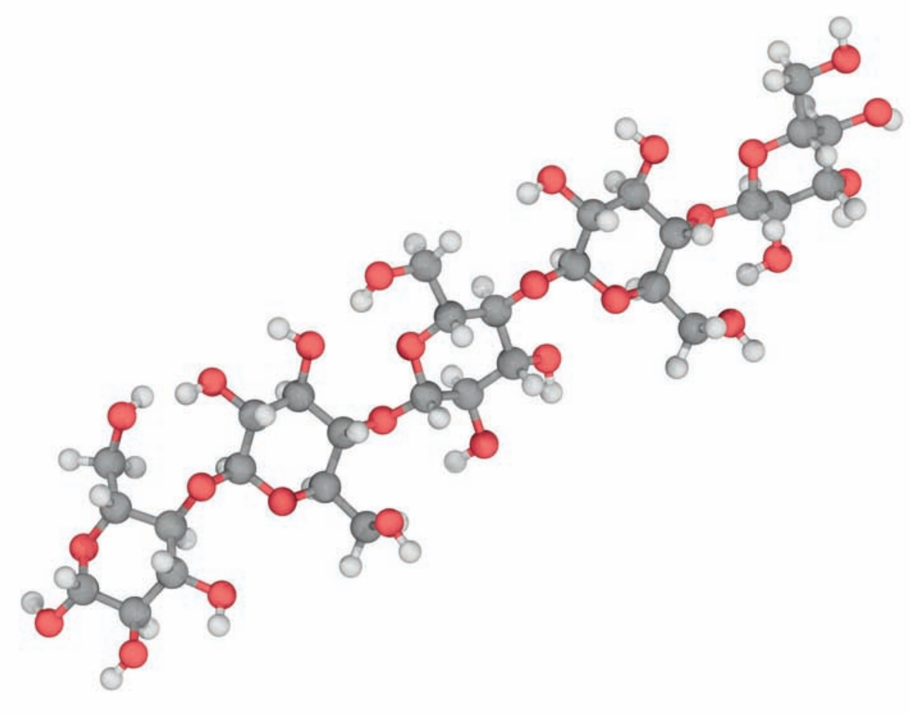


Figure 1.2
The polymer cellulose, which consists of β-D-glucose monomers. (Source: Laguna Design/Science Source)

New York Public Library. Obviously, this process is not what your company is seeking.

You need to find a way to treat large numbers of books without disassembling them. How about using a gaseous base? The books could be sealed in a chamber and the gaseous base allowed to permeate them. The first candidate that occurs to you is ammonia, a readily available gaseous base that reacts with H^+ to form NH_4^+:

$$NH_3 + H^+ \longrightarrow NH_4^+$$

This seems like a very promising idea, so you decide to construct a pilot treatment chamber. To construct this chamber, you need some help from coworkers. For example, you might consult a chemical engineer for help in the design of the plumbing and pumps needed to supply ammonia to the chamber. You might also consult a mechanical engineer about the appropriate material to use for the chamber and then discuss the actual construction of the chamber with machinists and other personnel from the company's machine shop. In addition, you probably would consult a safety specialist and possibly a toxicologist about the hazards associated with ammonia.

Before the chamber is built, you also have to think carefully about how to test the effectiveness of the process. How could you evaluate, in a relatively short time, how well the process protects paper from deterioration? At this stage, you would undoubtedly do more library research and consult with other experts, such as a paper chemist your company hires as an outside consultant.

Assume now that the chamber has been constructed and that the initial tests look encouraging. At first the H^+ level is greatly reduced in the treated paper. However, after a few days the H^+ level begins to rise again. Why? The fact that ammonia is a gas at room temperature (and pressure) is an advantage because it allows you to treat many books simultaneously in a dry chamber. However, the volatility of ammonia works against you after the treatment. The process

$$NH_4^+ \longrightarrow NH_3\uparrow + H^+$$

allows the ammonia to escape after a few days. Thus this treatment is too temporary. Even though this effort failed, it was still useful because it provided an opportunity to understand what is required to solve this problem. You need a gaseous substance that *permanently* reacts with the paper and that also consumes H^+.

In discussing this problem over lunch, a colleague suggests the compound diethyl zinc [$(C_2H_5)_2Zn$], which is quite volatile (boiling point = 117°C) and which reacts with water (moisture is present in paper) as follows:

$$(C_2H_5)_2Zn + H_2O \longrightarrow ZnO + 2C_2H_6$$

The C_2H_6 (ethane) is a gas that escapes, but the white solid, ZnO, becomes an integral part of the paper. The important part of ZnO is the oxide ion, O^{2-}, which reacts with H^+ to form water:

$$O^{2-} + 2H^+ \longrightarrow H_2O$$

Thus the ZnO is a nonvolatile base that can be placed in the paper by a gaseous substance. This process seems very promising. However, the major disadvantage of this process (there are always disadvantages) is that diethyl zinc is *very* flammable and great care must be exercised in its use. This leads to another question: Is the treatment effective enough to be worth the risks involved? As it turns out, the Library of Congress used diethyl zinc until 1994, but the process was discontinued because of its risks. Since then, a process known as Bookkeeper has been used. In this process, the book is immersed into a suspension of magnesium oxide (MgO). Small particles (submicron) of MgO are deposited in the pages, and these neutralize the acid and, like ZnO

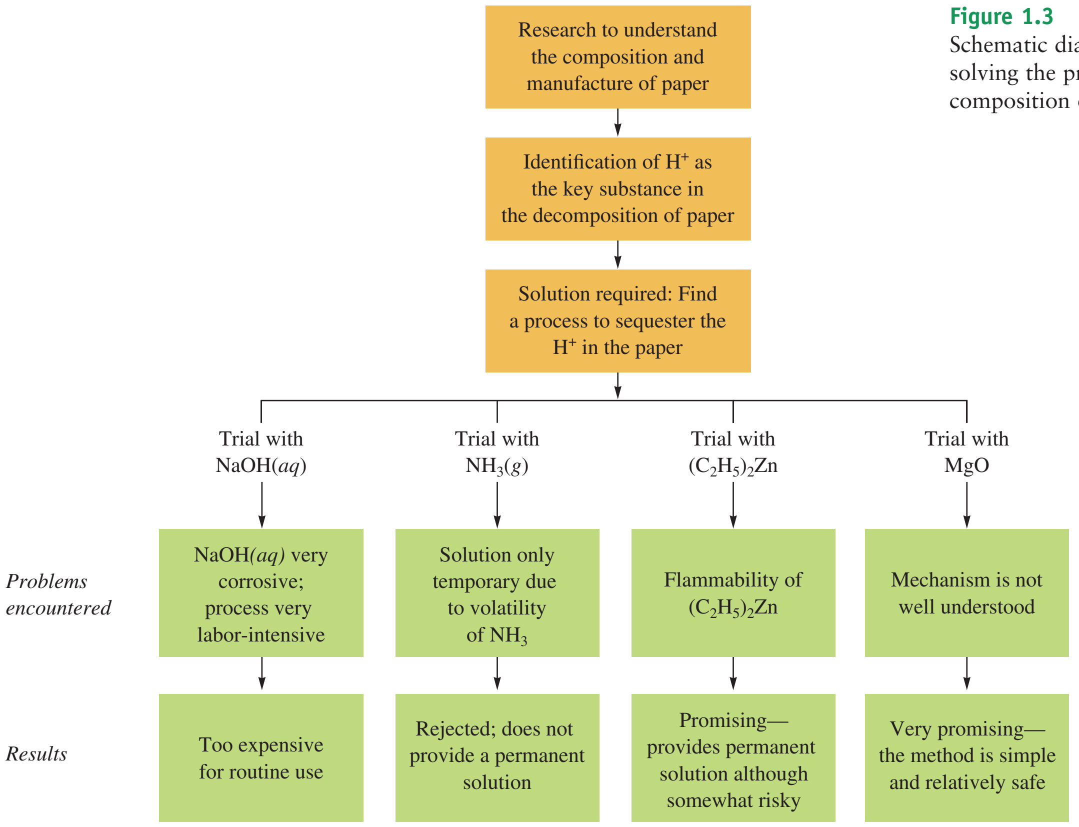


Figure 1.3
Schematic diagram of the strategy for solving the problem of the acid decomposition of paper.

formed from diethyl zinc, become an integral part of the paper. The advantages are the simplicity of the application and the safety of the method.

The type of problem solving illustrated by investigation of the acid decomposition of paper is quite typical of that which a practicing chemist confronts daily. The first step in successful problem solving is to identify the exact nature of the problem. Although this may seem trivial, it is often the most difficult and most important part of the process. Poor problem solving often results from a fuzzy definition of the problem. You cannot efficiently solve a problem if you do not understand the essence of the problem. Once the problem is well defined, then solutions can be advanced, usually by a process of intelligent trial and error. This process typically involves starting with the simplest potential solution and iterating to a final solution as the feedback from earlier attempts is used to refine the approach. Rarely, if ever, is the solution to a complex problem obvious immediately after the problem is defined. The best solution becomes apparent only as the results from various trial solutions are evaluated. A schematic summarizing the approach for dealing with the acid decomposition of paper is shown in Fig. 1.3 ▲.

1.3 The Scientific Method

Science is a framework for gaining and organizing knowledge. Science is not simply a set of facts but is also a plan of action—a *procedure* for processing and understanding certain types of information. Scientific thinking is useful in all aspects of life, but in this text we will use it to understand how the chemical world operates. The process that lies at the center of scientific inquiry is called the **scientific method.** There are actually many scientific methods depending on the nature of the specific problem under study and on the particular investigator involved. However, it is useful to consider the following general framework for a generic scientific method:

STEPS Steps in the Scientific Method

1 *Making observations.* Observations may be *qualitative* (the sky is blue; water is a liquid) or *quantitative* (water boils at 100°C; a certain chemistry book weighs 2 kilograms). A qualitative observation does not involve a number. A quantitative observation (called a **measurement**) involves both a number and a unit. ◀

2 *Formulating hypotheses.* A hypothesis is a *possible* explanation for the observation.

3 *Making predictions.* The hypothesis then is used to make a prediction that can be tested by performing an experiment.

4 *Performing experiments.* An experiment is carried out to test the hypothesis. This involves gathering new information that enables a scientist to decide whether the hypothesis is correct—that is, whether it is supported by the new information learned from the experiment. Experiments always produce new observations, and this brings the process back to the beginning again.

See Appendix A1.6 for conventions regarding the use of significant figures in connection with measurements and the calculations involving measurements. Appendix 2 discusses methods for converting among various units.

Critical Thinking

What if everyone in the government used the scientific method to analyze and solve society's problems, and politics were never involved in the solutions? How would this be different from the present situation, and would it be better or worse?

To understand a given phenomenon, these steps are repeated many times, gradually accumulating the knowledge necessary to provide a possible explanation of the phenomenon.

As scientists observe nature, they often see that the same observation applies to many different systems. For example, innumerable chemical changes have shown that the total observed mass of the materials involved is the same before and after the change. Such generally observed behavior is formulated into a statement called a **natural law.** For example, the observation that the total mass of materials is not affected by a chemical change in those materials is called the law of conservation of mass. This law tells us *what* happens, but it does not tell us *why.* To try to explain why, we continue to make observations, formulate hypotheses, and test these against observations.

Once a set of hypotheses that agree with the various observations is obtained, the hypotheses are assembled into a theory. A **theory,** which is often called a *model,* is a set of tested hypotheses that gives an overall explanation of some natural phenomenon. ◀

This portrayal of the classical scientific method probably overemphasizes the importance of observations in current scientific practice. Now that we know a great deal about the nature of matter, scientists often start with a hypothesis that they try to refute as they push forward the frontiers of science. See the writings of Karl Popper for more information on this view.

It is very important to distinguish between observations and theories. An observation is something that is witnessed and can be recorded. A theory is an *interpretation*—a possible explanation of *why* nature behaves in a particular way. For example, in Chapter 2 we will read about Dalton's atomic theory, in which John Dalton proposed that a chemical reaction is a reorganization of atoms in reacting substances to produce new substances. As we discussed, we know that mass is conserved (it is a natural law), and we can explain it by claiming that all matter is made of nonchanging atoms (the theory).

Theories inevitably change as more information becomes available. For example, we will also see in Chapter 2 that with further experimentation and observations, the atomic theory came to include subatomic particles—electrons,

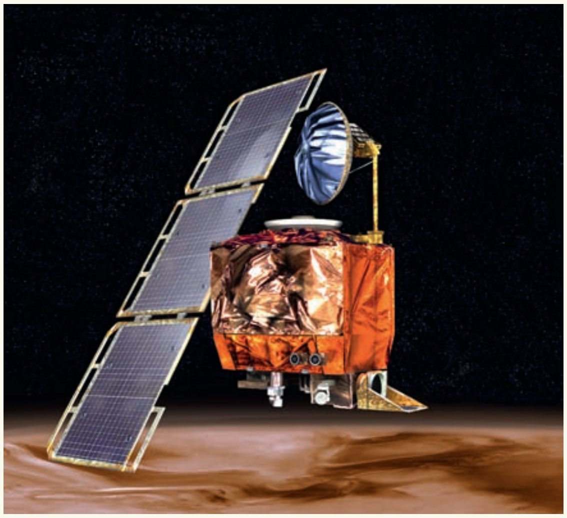
CHEMICAL INSIGHTS

Critical Units!

How important are conversions from one unit to another? If you ask the National Aeronautics and Space Administration (NASA), very important! In 1999 NASA lost a $125 million Mars Climate Orbiter because of a failure to convert from English to metric units.

The problem arose because two teams working on the Mars mission were using different sets of units. NASA's scientists at the Jet Propulsion Laboratory in Pasadena, California, assumed that the thrust data for the rockets on the orbiter they received from Lockheed Martin Astronautics in Denver, which built the spacecraft, were in metric units. In reality, the units were English. As a result the orbiter dipped 100 kilometers lower into the Mars atmosphere than planned, and the friction from the atmosphere caused the craft to burn up.

NASA's mistake refueled the controversy over whether Congress should require the United States to switch to the metric system. About 95% of the world now uses the metric system, and the United States is slowly switching from English to metric. For example, the automobile industry has adopted metric fasteners, and we buy our soda in 2-liter bottles.


NASA

Artist's conception of the lost Mars Climate Orbiter.

Units can be very important. In fact, they can mean the difference between life and death on some occasions. In 1983, for example, a Canadian jetliner almost ran out of fuel when someone pumped 22,300 pounds of fuel into the aircraft instead of 22,300 kilograms. Remember to watch your units!

protons, and neutrons. The "indivisible" atom of Dalton is not indivisible after all. We see the idea of changing theories in all realms of science. For example, the motions of the sun and stars have remained virtually the same over the thousands of years during which humans have been observing them, but our explanations—our theories—for these motions have changed greatly since ancient times.

The point is that scientists do not stop asking questions just because a given theory seems to account satisfactorily for some aspect of natural behavior. They continue doing experiments to refine or replace the existing theories. This is generally done by using the currently accepted theory to make a prediction and then performing an experiment (making a new observation) to see whether the results bear out this prediction.

Always remember that theories (models) are human inventions. They represent attempts to explain observed natural behavior in terms of human experiences. A theory is actually an educated guess. We must continue to do experiments and to refine our theories (making them consistent with new knowledge) if we hope to approach a more nearly complete understanding of nature.

In this section we have described the scientific method as it might ideally be applied (► Fig. 1.4). However, it is important to remember that science does not always progress smoothly and efficiently. For one thing, hypotheses and observations are not totally independent of each other, as we have assumed in the description of the idealized scientific method. The coupling of

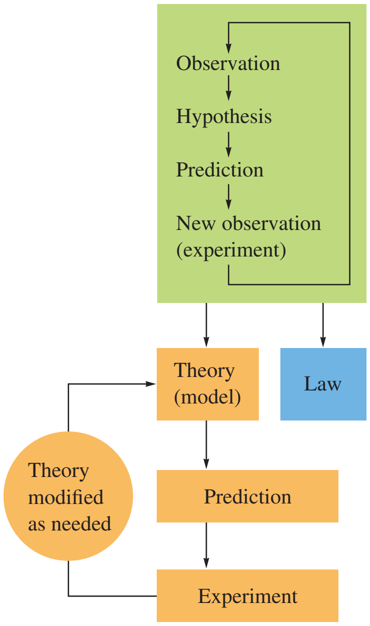


Figure 1.4
The various parts of the scientific method.

observations and hypotheses occurs because once we begin to proceed down a given theoretical path, our hypotheses are unavoidably couched in the language of those theoretical underpinnings. In other words, we tend to see what we expect to see and often fail to notice things that we do not expect. Thus the theory we are testing helps us because it focuses our questions. However, at the very same time, this focusing process may limit our ability to see other possible explanations.

It is also important to keep in mind that scientists are human. They have prejudices; they misinterpret data; they become emotionally attached to their theories and thus lose objectivity; and they play politics. Science is affected by profit motives, budgets, fads, wars, and religious beliefs. Galileo, for example, was forced to recant his astronomical observations in the face of strong religious resistance. Lavoisier, the father of modern chemistry, was beheaded because of his political affiliations. And great progress in the chemistry of nitrogen fertilizers resulted from the desire to produce explosives to fight wars. The progress of science is often affected more by the frailties of humans and their institutions than by the limitations of scientific measuring devices. The scientific methods are only as effective as the humans using them. They do not automatically lead to progress.

1.4 | Industrial Chemistry


Christian Lagerek/
Shutterstock.com #56046928

Industrial processes require large plants for the production of chemicals.

The impact of chemistry on our lives is due in no small measure to the many industries that process and manufacture chemicals to provide the fuels, fabrics, fertilizers, food preservatives, detergents, and many other products that affect us daily. The chemical industry can be subdivided in terms of three basic types of activities:

1. The isolation of naturally occurring substances for use as raw materials
2. The processing of raw materials by chemical reactions to manufacture commercial products
3. The use of chemicals to provide services

A given industry may participate in one, two, or all three of these activities.

Producing chemicals on a large industrial scale is very different from an academic laboratory experiment. Some of the important differences are described below.

- In the academic laboratory, practicality is typically the most important consideration. Because the amounts of substances used are usually small, hazardous materials can be handled by using fume hoods, safety shields, and so on; expense, although always a consideration, is not a primary factor. However, for any industrial process, economy and safety are critical.
- In industry, containers and pipes are metal rather than glass, and corrosion is a constant problem. In addition, because the progress of reactions cannot be monitored visually, gauges must be used.
- In the laboratory, any by-products of a reaction are simply disposed of; in industry, they are usually recycled or sold. If no current market exists for a given by-product, the manufacturer tries to develop such a market.
- Industrial processes often run at very high temperatures and pressures and ideally are *continuous flow,* meaning that reactants are added and products are extracted continuously. In the laboratory, reactions are run in batches and typically at much lower temperatures and pressures.

The many criteria that must be satisfied to make a process feasible on the industrial scale require that great care be taken in the development of each

A Note-able Achievement

CHEMICAL INSIGHTS

Post-it Notes, a product of the 3M Corporation, revolutionized casual written communications and personal reminders. Introduced in the United States in 1980, these sticky-but-not-too-sticky notes have now found countless uses in offices, cars, and homes throughout the world.

The invention of sticky notes occurred over a period of about 10 years and involved a great deal of serendipity. The adhesive for Post-it Notes was discovered by Dr. Spencer F. Silver of 3M in 1968. Silver found that when an acrylate polymer material was made in a particular way, it formed cross-linked microspheres. When suspended in a solvent and sprayed on a sheet of paper, this substance formed a "sparse monolayer" of adhesive after the solvent evaporated. Scanning electron microscope images of the adhesive show that it has an irregular surface, a little like the surface of a gravel road. In contrast, the adhesive on cellophane tape looks smooth and uniform, like a superhighway. The bumpy surface of Silver's adhesive caused it to be sticky but not so sticky as to produce permanent adhesion because the number of contact points between the binding surfaces was limited.

When he invented this adhesive, Silver had no specific ideas for its use, so he spread the word of his discovery to his fellow employees at 3M to see if anyone had an application for it. In addition, over the next several years development was carried out to improve the adhesive's properties. It was not until 1974 that the idea for Post-it Notes popped up. One Sunday, Art Fry, a chemical engineer for 3M, was singing in his church choir when he became annoyed that the bookmark in his hymnal kept falling out. He thought to himself that it would be nice if the bookmark were sticky enough to stay in place but not so sticky that it couldn't be moved. Luckily, he remembered Silver's glue—and the Post-it Note was born.

For the next three years, Fry worked to overcome the manufacturing obstacles associated with the product. By 1977 enough Post-it Notes were being produced to supply 3M's corporate headquarters, where the employees quickly became addicted to their many uses. Post-it Notes are now available in more than 60 colors and 25 shapes.

In the years since their introduction, 3M has heard some remarkable stories connected to the use of these notes. For example, a Post-it Note was applied to the nose of a corporate jet, where it was intended to be read by the plane's Las Vegas ground crew. Someone forgot to remove it, however. The note was still on the nose of the plane when it landed in Minneapolis, having survived a takeoff and landing and speeds of 500 miles per hour at temperatures as low as −56°F. Stories on the 3M website also describe how a Post-it Note on the front door of a home survived the 140 mile per hour winds of Hurricane Hugo and how a foreign official accepted Post-it Notes in lieu of cash when a small bribe was needed to cut through bureaucratic hassles.

Post-it Notes have definitely changed the way we communicate and remember things.

process to ensure safe and economical operation. The development of an industrial chemical process typically involves the following steps:

Step 1: A need for a particular product is identified.

Step 2: The relevant chemistry is studied on a small scale in a laboratory. Various ways of producing the desired material are evaluated in terms of costs and potential hazards.

Step 3: The data are evaluated by chemists, chemical engineers, business managers, safety engineers, and others to determine which possibility is most feasible.

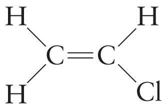
Step 4: A *pilot-plant test* of the process is carried out. The scale of the pilot plant is between that of the laboratory and that of a manufacturing plant. This test has several purposes: to make sure that the reaction is efficient at a larger scale, to test reactor (reaction container) designs, to determine the costs of the process, to evaluate the hazards, and to gather information on environmental impact.

1.5 Polyvinyl Chloride (PVC): Real-World Chemistry

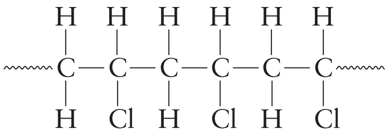
To get a little better feel for how the world of industrial chemistry operates, we will now consider a particular product, polyvinyl chloride (PVC), to see what types of considerations have been important in making this a successful and important consumer product.

When you put on a nylon jacket, use a polyethylene wash bottle in the lab, wear contact lenses, or accidentally drop your telephone (and it doesn't break), you are benefiting from the properties of polymers. Polymers are very large molecules that are assembled from small units (called monomers). Because of their many useful properties, polymers are manufactured in huge quantities. In fact, it has been estimated that more than 50% of all industrial chemists have jobs that are directly related to polymers.

One particularly important polymer is PVC, which is made from the molecule commonly called vinyl chloride:

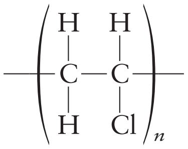


When many of these units are joined together, the polymer PVC results:



$$\sim\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{Cl}}{\mathrm{C}}}\sim$$

This can be represented as



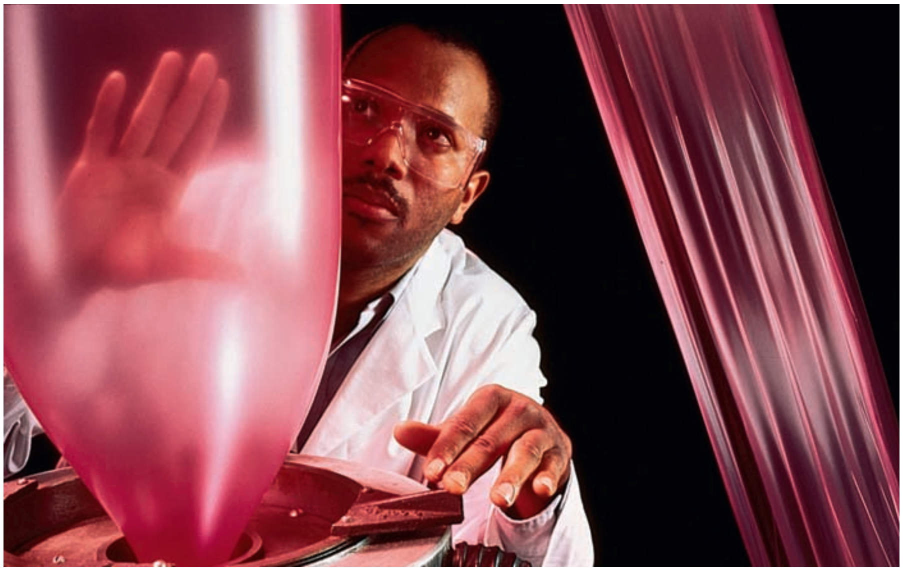
$$-\!\left(\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{Cl}}{\mathrm{C}}}\right)_{n}\!-$$

where n is usually greater than 1000.

Because the development of PVC into a useful, important material is representative of the type of problem solving encountered in industrial chemistry, we will consider it in some detail.

In pure form PVC is a hard, brittle substance that decomposes easily at the high temperatures necessary to process it. This makes it almost useless. The fact that it has become a high-volume plastic (≈10 billion pounds per year produced in the United States) is a tribute to chemical innovation. Depending on the additives used, PVC can be made rigid or highly flexible, and it can be tailored for use in inexpensive plastic novelty items or for use in precision engineering applications.

The development of PVC illustrates the interplay of logic and serendipity, as well as the importance of optimizing properties both for processing and for applications. PVC production has been beset with difficulties from the beginning, but solutions have been found for each problem through a combination of chemical deduction and trial and error. For example, many additives have been found that provide temperature stability so that PVC can be processed as a melt (liquid) and so that PVC products can be used at high temperatures. However, there is still controversy among chemists about exactly how PVC decomposes thermally, and thus the reason these stabilizers work is not well understood. Also, there are approximately 100 different plasticizers (softeners) available for



Brownie Harris/Stock Market/Corbis

A scientist inspecting a product being formed from polyvinyl plastic.

PVC, but the theory of its plasticization is too primitive to predict accurately which compounds might produce even better results.

PVC was discovered by a German chemical company in 1912, but its brittleness and thermal instability proved so problematic that in 1926 the company stopped paying the fees to maintain its patents. That same year Waldo Semon, a chemist at B. F. Goodrich, found that PVC could be made flexible by the addition of phosphate and phthalate esters. Semon also found that white lead [$Pb_3(OH)_2(CO_3)_2$] provided thermal stability to PVC. These advances led to the beginning of significant U.S. industrial production of PVC (≈4 million pounds per year by 1936). In an attempt to further improve PVC, T. L. Gresham (also a chemist at B. F. Goodrich) tried approximately 1000 compounds, searching for a better plasticizer. The compound that he found (its identity is not important here) remains the most common plasticizer added to PVC. The types of additives commonly used in the production of PVC are listed in Table 1.1 ▼.

Although the exact mechanism of the thermal, heat-induced decomposition of PVC remains unknown, most chemists agree that the chlorine atoms present in the polymer play an important role. Lead salts are added to PVC both to provide anions less reactive than chloride and to provide lead ions to combine with the released chloride ions. As a beneficial side effect, the lead chloride formed gives PVC enhanced electrical resistance, making lead stabilizers particularly useful in producing PVC for electrical wire insulation.

One major use of PVC is for pipes in plumbing systems. Here, even though the inexpensive lead stabilizers would be preferred from an economic standpoint, the possibility that the toxic lead could be leached from the pipes into the drinking water necessitates the use of more expensive tin and antimony compounds as

Table 1.1

Types of Additives Commonly Used in the Production of PVC

Type of Additive	Effect
Plasticizer	Softens the material
Heat stabilizer	Increases resistance to thermal decomposition
Ultraviolet absorber	Prevents damage by sunlight
Flame retardant	Lowers flammability
Biocide	Prevents bacterial or fungal attack

thermal stabilizers. Because about one-half of the annual U.S. production of PVC is formed into piping, the PVC formulation used for pipes represents a huge market for companies that manufacture additives, and the competition is very intense. A recently developed low-cost thermal stabilizer for PVC is a mixture of antimony and calcium salts. This mixture has replaced stabilizers containing tin compounds that have become increasingly costly in recent years.

Outdoor applications of PVC often require that it contain ultraviolet light absorbers to protect against damage from sunlight. For pigmented applications such as vinyl siding, window frames, and building panels, titanium(IV) oxide (TiO_2) is usually used. For applications in which the PVC must be transparent, other compounds are needed.

The additives used in PVC in the largest amounts are plasticizers, but one detrimental effect of these additives is an increase in flammability. Rigid PVC, which contains little plasticizer, is quite flame resistant because of its high chloride content. However, as more plasticizer is added for flexibility, the flammability increases to the point where fire retardants must be added, the most common being antimony(III) oxide (Sb_2O_3). As the PVC is heated, this oxide forms antimony(III) chloride ($SbCl_3$), which migrates into the flame, where it inhibits the burning process. Because antimony(III) oxide is a white salt, it cannot be used for transparent or darkly colored PVC. In these cases sodium antimonate (Na_3SbO_4), a transparent salt, is used.

Once the additives have been chosen for a particular PVC application, the materials must be blended. This is often done in a dry-blending process, which produces a powder that is then used for fabrication of the final product. The powdered mixture also can be melted and formed into pellets, which are easily shipped to manufacturing plants, where they are remelted and formed into the desired products.

The production of PVC provides a good case study of an industrial process. It illustrates many of the factors that must be taken into account when any product is manufactured: effectiveness of the product, cost, ease of production, safety, and environmental impact. The last issue is becoming ever more important as our society struggles both to reduce the magnitude of the waste stream by recycling and to improve our waste disposal methods.

Key Terms

Section 1.3

scientific method
measurement
natural law
theory

For Review

Thinking like a chemist

- Problem solving often requires trial and error.
- Practice helps one become a better problem solver.

Scientific method

- Make observations.
- Formulate hypotheses.
- Make predictions.
- Perform experiments.

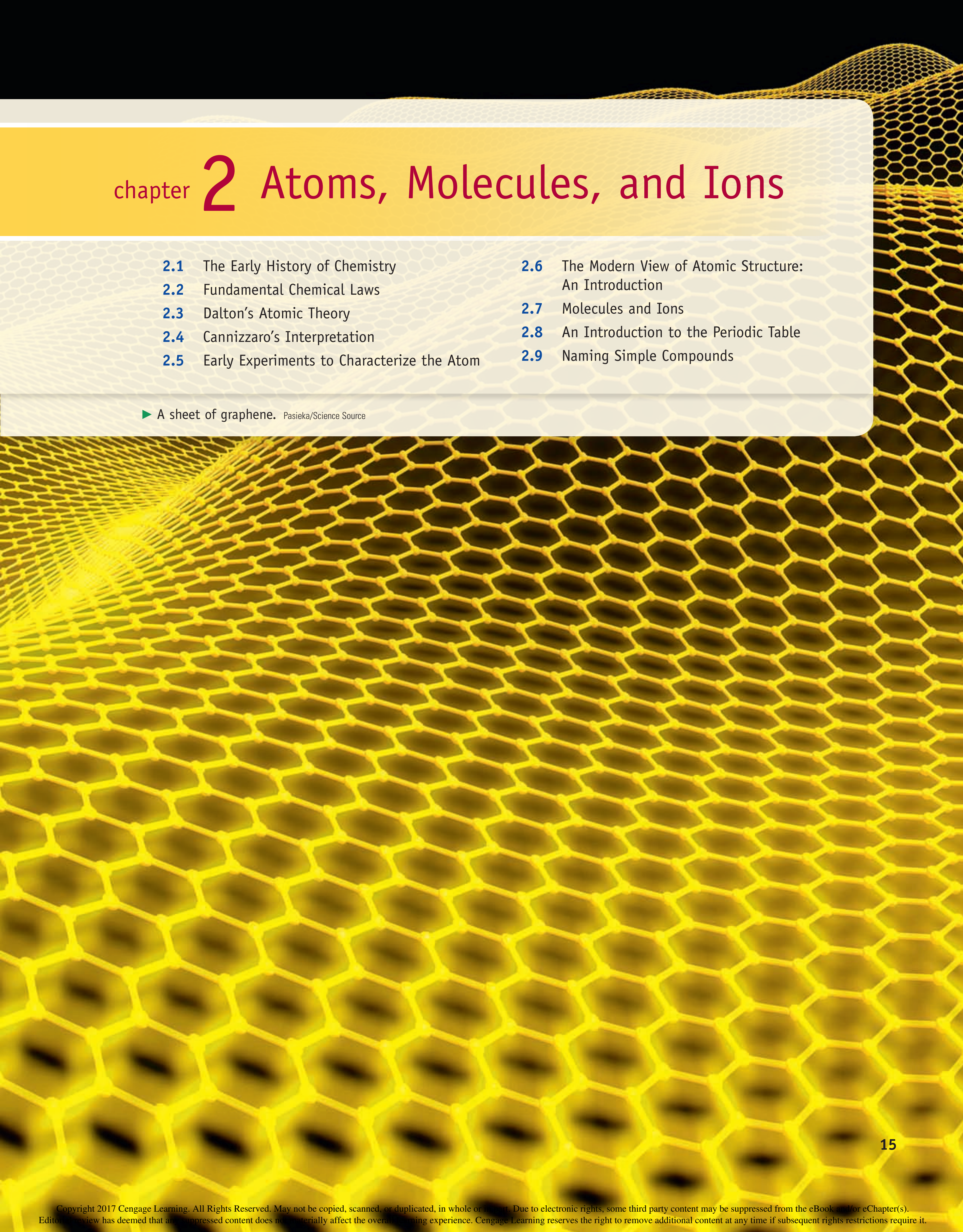
Difference between a law and a theory

- A law summarizes what happens; it comes from generally observed behavior.
- A theory is an attempt at an explanation of why nature behaves in a particular way; it is subject to modifications over time and sometimes fails.

Three general types of activities in industrial chemistry

- Isolating naturally occurring substances for use as raw materials
- Processing raw materials into commercial products via chemical reactions
- Using chemicals to provide services

chapter 2 Atoms, Molecules, and Ions



▶ A sheet of graphene. Pasieka/Science Source

In this chapter we present very briefly many of the fundamental concepts and some of the vocabulary of chemistry plus something about how the science developed. Depending on your specific background in chemistry, much of this material may be review. However, whatever your background, read this chapter carefully to be sure this material is fresh in your mind as we pursue the study of reaction chemistry in Chapters 3 and 4.

2.1 The Early History of Chemistry

Chemistry has been important since ancient times. The processing of natural ores to produce metals for ornaments and weapons and the use of embalming fluids are two applications of chemical phenomena that were used before 1000 B.C.

The Greeks were the first to try to explain why chemical changes occur. By about 400 B.C. they had proposed that all matter was composed of four fundamental substances: fire, earth, water, and air. The Greeks also considered the question of whether matter is continuous, and thus infinitely divisible into smaller pieces, or composed of small indivisible particles. One supporter of the latter position was Democritus, who used the term *atomos* (which later became *atoms*) to describe these ultimate particles. However, because the Greeks had no experiments to test their ideas, no definitive conclusion about the divisibility of matter was reached.

The next 2000 years of chemical history were dominated by a pseudoscience called alchemy. Alchemists were often mystics and fakes who were obsessed with the idea of turning cheap metals into gold. However, this period also saw important discoveries: Elements such as mercury, sulfur, and antimony were discovered, and alchemists learned how to prepare the mineral acids.

The foundations of modern chemistry were laid in the sixteenth century with the development of systematic metallurgy (extraction of metals from ores) by a German, Georg Bauer, and the medicinal application of minerals by the Swiss alchemist Paracelsus.

The first "chemist" to perform truly quantitative experiments was Robert Boyle (1627–1691), an Irish scientist, who carefully measured the relationship between the pressure and volume of gases. When Boyle published his book *The Sceptical Chemist* in 1661, the quantitative sciences of physics and chemistry were born. In addition to his results on the quantitative behavior of gases, Boyle's other major contribution to chemistry consisted of his ideas about the chemical elements. Boyle held no preconceived notion about the number of elements. In his view a substance was an element unless it could be broken down into two or more simpler substances. As Boyle's experimental definition of an element became generally accepted, the list of known elements began to grow, and the Greek system of four elements finally died. Although Boyle was an excellent scientist, he was not always right. For example, he clung to the alchemist's views that metals were not true elements and that a way would eventually be found to change one metal to another.

The phenomenon of combustion evoked intense interest in the seventeenth and eighteenth centuries. The German chemist Georg Stahl (1660–1734) suggested that a substance he called phlogiston flowed out of the burning material. Stahl postulated that a substance burning in a closed container eventually stopped burning because the air in the container became saturated with phlogiston. Oxygen gas, discovered by Joseph Priestley (1733–1804), an English clergyman and scientist, was found to support vigorous combustion and was thus supposed to be low in phlogiston. In fact, oxygen was originally called

Roald Hoffman/Cornell University

The Priestley Medal is the highest honor given by the American Chemical Society. It is named for **Joseph Priestley,** who was born in England on March 13, 1733. He performed many important scientific experiments, one of which led to the discovery that a gas later identified as carbon dioxide could be dissolved in water to produce *seltzer.* Also, as a result of meeting Benjamin Franklin in London in 1766, Priestley became interested in electricity and was the first to observe that graphite was an electrical conductor. However, his greatest discovery occurred in 1774, when he isolated oxygen by heating mercuric oxide.

Because of his nonconformist political views, he was forced to leave England. He died in the United States in 1804.

"dephlogisticated air." It is important to note that the observations made by Joseph Priestley did not contradict those made by Georg Stahl. However, Priestley's theory to explain what he saw was vastly different. As we stated in Chapter 1, *what* happens doesn't change, but our ideas about *why* a phenomenon occurs can change. Such is the nature of science.

2.2 Fundamental Chemical Laws

By the late eighteenth century, combustion had been studied extensively; the gases carbon dioxide, nitrogen, hydrogen, and oxygen had been discovered; and the list of elements continued to grow. However, it was Antoine Lavoisier (1743–1794), a French chemist (▼ Fig. 2.1), who finally explained the true nature of combustion, thus clearing the way for the tremendous progress that was made near the end of the eighteenth century. Lavoisier, like Boyle, regarded measurement as the essential operation of chemistry. His experiments, in which he carefully weighed the reactants and products of various reactions, suggested that *mass is neither created nor destroyed*. Lavoisier's discovery of this **law of conservation of mass** was the basis for the developments in chemistry in the nineteenth century.

Lavoisier's quantitative experiments showed that combustion involved oxygen (which Lavoisier named), not phlogiston. He also discovered that life was supported by a process that also involved oxygen and was similar in many ways to combustion. In 1789 Lavoisier published the first modern chemistry textbook, *Elementary Treatise on Chemistry,* in which he presented a unified picture of the chemical knowledge assembled up to that time. Unfortunately, in the same year the text was published, the French Revolution began. Lavoisier, who had been associated with collecting taxes for the government, was executed on the guillotine as an enemy of the people in 1794.

After 1800, chemistry was dominated by scientists who, following Lavoisier's lead, performed careful weighing experiments to study the course of chemical reactions and to determine the composition of various chemical compounds. One of these chemists, a Frenchman, Joseph Proust (1754–1826), showed that *a given compound always contains exactly the same proportion*

(Detail) *Antoine Laurent Lavoisier & His Wife* by Jacques Louis David, 1788. Image copyright © The Metropolitan Museum of Art/Art Resource, NY

Figure 2.1

Antoine Lavoisier with his wife. Lavoisier was born in Paris on August 26, 1743. From the beginning of his scientific career, Lavoisier recognized the importance of accurate measurements. His careful weighings showed that mass is conserved in chemical reactions and that combustion involves reaction with oxygen. Also, he wrote the first modern chemistry textbook. He is often called the father of modern chemistry.

Because of his connection to a private tax-collecting firm, radical French revolutionaries demanded his execution, which occurred on the guillotine on May 8, 1794.

of elements by mass. For example, Proust found that the substance copper carbonate is always 5.3 parts copper to 4 parts oxygen to 1 part carbon (by mass). The principle of the constant composition of compounds, originally called Proust's law, is now known as the **law of definite proportion.**

Proust's discovery stimulated John Dalton (1766–1844), an English schoolteacher (◀ Fig. 2.2), to think about atoms. Dalton reasoned that if elements were composed of tiny individual particles, a given compound should always contain the same combination of these atoms. This concept explained why the same relative masses of elements were always found in a given compound.

Manchester Literary & Philosophical Society

Figure 2.2
John Dalton (1766–1844), an Englishman, began teaching at a Quaker school when he was 12. His fascination with science included an intense interest in meteorology (he kept careful daily weather records for 46 years), which led to an interest in the gases of the air and their ultimate components, atoms. Dalton is best known for his atomic theory, in which he postulated that the fundamental differences among atoms are their masses. He was the first to prepare a table of relative atomic weights.

Dalton was a humble man with several apparent handicaps: He was poor; he was not articulate; he was not a skilled experimentalist; and he was color-blind, a terrible problem for a chemist. Despite these disadvantages, he helped revolutionize the science of chemistry.

But Dalton discovered another principle that convinced him even more of the existence of atoms. He noted, for example, that carbon and oxygen form two different compounds that contain different relative amounts of carbon and oxygen, as shown by the following data:

	Mass of Oxygen That Combines with 1 g of Carbon
Compound I	1.33 g
Compound II	2.66 g

Dalton noted that compound II contained twice as much oxygen per gram of carbon as compound I, a fact that could be easily explained in terms of atoms. Compound I might be CO, and compound II might be CO_2. This principle, which was found to apply to compounds of other elements as well, became known as the **law of multiple proportions:** *When two elements form a series of compounds, the ratios of the masses of the second element that combine with 1 gram of the first element can always be reduced to small whole numbers.*

These ideas are also illustrated by the compounds of nitrogen and oxygen, as shown by the following data:

	Mass of Nitrogen That Combines with 1 g of Oxygen
Compound I	1.750 g
Compound II	0.8750 g
Compound III	0.4375 g

which yield the following ratios:

$$\frac{\text{I}}{\text{II}} = \frac{1.750}{0.8750} = \frac{2}{1}$$

$$\frac{\text{II}}{\text{III}} = \frac{0.8750}{0.4375} = \frac{2}{1}$$

$$\frac{\text{I}}{\text{III}} = \frac{1.750}{0.4375} = \frac{4}{1}$$

The significance of these data is that compound I contains twice as much nitrogen (N) per gram of oxygen (O) as does compound II and that compound II contains twice as much nitrogen per gram of oxygen as does compound III. In terms of the numbers of atoms combining, these data can be explained by any of the following sets of formulas:

Compound I	N_2O		NO		N_4O_2
Compound II	NO	or	NO_2	or	N_2O_2
Compound III	NO_2		NO_4		N_2O_4

In fact, an infinite number of other possibilities exists. Dalton could not deduce absolute formulas from the available data on relative masses. However, the data on the composition of compounds in terms of the relative masses of the elements supported his hypothesis that each element consisted of a certain type of atom and that compounds were formed from specific combinations of atoms.

2.3 Dalton's Atomic Theory

In 1808 Dalton published *A New System of Chemical Philosophy*, in which he presented his theory of atoms.

Dalton's Model ▶

1. Each element is made up of tiny particles called atoms.
2. The atoms of a given element are identical; the atoms of different elements are different in some fundamental way or ways.
3. Chemical compounds are formed when atoms combine with one another. A given compound always has the same relative numbers and types of atoms.
4. Chemical reactions involve reorganization of the atoms—changes in the way they are bound together. The atoms themselves are not changed in a chemical reaction.

These statements are a modern paraphrase of Dalton's ideas.

It is instructive to consider Dalton's reasoning on the relative masses of the atoms of the various elements. ▶ In Dalton's time, water was known to be composed of the elements hydrogen and oxygen, with 8 grams of oxygen present for every 1 gram of hydrogen. If the formula for water were OH, an oxygen atom would have to have eight times the mass of a hydrogen atom. However, if the formula for water were H_2O (two atoms of hydrogen for every oxygen atom), this would mean that each atom of oxygen is 16 times as heavy as *each* atom of hydrogen (since the ratio of the mass of one oxygen to that of *two* hydrogens is 8 to 1). Because the formula for water was not then known, Dalton could not specify the relative masses of oxygen and hydrogen unambiguously. To solve the problem, Dalton made a fundamental assumption: He decided that nature would be as simple as possible. This assumption led him to conclude that the formula for water should be OH. He thus assigned hydrogen a mass of 1 and oxygen a mass of 8.

mass (m): the quantity of matter in a body

Using similar reasoning for other compounds, Dalton prepared the first table of **atomic masses** (formerly called atomic weights by chemists, since mass is usually determined by comparison to a standard mass—a process called *weighing**). ▶ Many of the masses were later proved to be wrong because of Dalton's incorrect assumptions about the formulas of certain compounds, but the construction of a table of masses was an important step forward.

weight: $m \times g$

Although not recognized as such for many years, the keys to determining absolute formulas for compounds were provided in the experimental work of the French chemist Joseph Gay-Lussac (1778–1850) and by the hypothesis of an Italian chemist named Amedeo Avogadro (1776–1856). In 1809 Gay-Lussac performed experiments in which he measured (under the same conditions of temperature and pressure) the volumes of gases that reacted with one another. For example, Gay-Lussac found that 2 volumes of hydrogen react

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*Technically, weight is the force exerted on an object by gravitational attraction to a body such as the earth (weight = mass × acceleration due to gravity). It is mass (the quantity of matter in a body), not weight, that chemists use in their measurements, although the two terms are sometimes used interchangeably.

Universal Images Group/Superstock

Joseph Louis Gay-Lussac (1778–1850), a French physicist and chemist, was remarkably versatile. Although he is now primarily known for his studies on the combining of volumes of gases, Gay-Lussac was instrumental in the studies of many of the other properties of gases. Some of Gay-Lussac's motivation to learn about gases arose from his passion for ballooning. In fact, he made ascents to heights of over 4 miles to collect air samples, setting altitude records that stood for approximately 50 years. Gay-Lussac also was the codiscoverer of boron and the developer of a process for manufacturing sulfuric acid. As chief assayer of the French mint, Gay-Lussac developed many techniques for chemical analysis and invented many types of glassware now used routinely in labs. Gay-Lussac spent his last 20 years as a lawmaker in the French government.

with 1 volume of oxygen to form 2 volumes of gaseous water and that 1 volume of hydrogen reacts with 1 volume of chlorine to form 2 volumes of hydrogen chloride.

In 1811 Avogadro interpreted these results by proposing that, *at the same temperature and pressure, equal volumes of different gases contain the same number of particles*. This assumption (called **Avogadro's hypothesis**) makes sense if the distances between the particles in a gas are very great compared with the sizes of the particles. Under these conditions the volume of a gas is determined by the number of molecules present, not by the size of the individual particles.

If Avogadro's hypothesis is correct, Gay-Lussac's result,

$$\text{2 volumes of hydrogen react with 1 volume of oxygen} \longrightarrow \text{2 volumes of water vapor}$$

can be expressed as follows:

$$\text{2 molecules of hydrogen react with 1 molecule of oxygen} \longrightarrow \text{2 molecules of water}$$

These observations can be explained best by assuming that gaseous hydrogen, oxygen, and chlorine are all composed of diatomic (two-atom) molecules: H_2, O_2, and Cl_2, respectively. Gay-Lussac's results can then be represented as shown in Fig. 2.3 ▼. (Note that this reasoning suggests that the formula for water is H_2O, not OH as Dalton believed.)

Unfortunately, Avogadro's interpretations were not accepted by most chemists. The main stumbling block seems to have been the prevailing belief that only atoms of different elements could attract each other to form molecules. Dalton and the other prominent chemists of the time assumed that identical atoms had no "affinity" for each other and thus would not form diatomic molecules.

Because no general agreement existed concerning the formulas for elements such as hydrogen, oxygen, and chlorine or for the compounds formed from these elements, chaos reigned in the first half of the nineteenth century. Although during this period chemists, such as the Swedish chemist Jöns Jakob Berzelius (1779–1848), made painstaking measurements of the masses of various elements that combined to form compounds, these results were interpreted in many different ways, depending on the assumptions about the formulas of the elements and compounds, and this led to many different tables of atomic masses. The situation was so confused that 19 different formulas for the

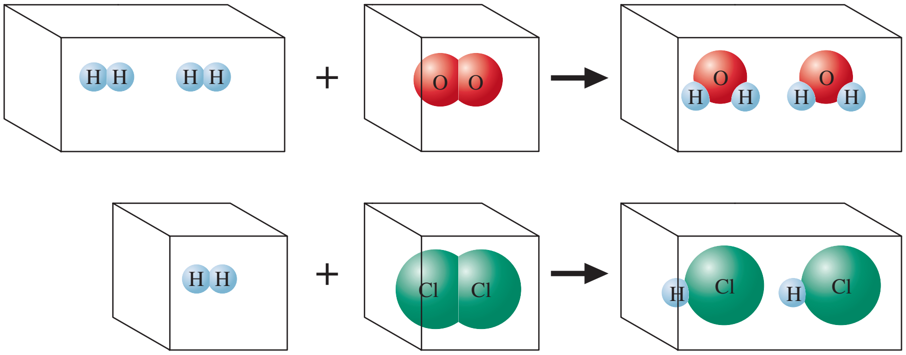


Figure 2.3
A representation of combining gases at the molecular level. The spheres represent atoms in the molecules, and the boxes represent the relative volumes of the gases.

compound acetic acid were given in a textbook written in 1861 by F. August Kekulé (1829–1896). In the next section we will see how this mess was finally cleaned up, primarily because of the leadership of the Italian chemist Stanislao Cannizzaro (1826–1910).

2.4 | Cannizzaro's Interpretation

Convinced that chemists had to find a way to agree on a common set of atomic masses, the German chemist F. August Kekulé organized the First International Chemical Congress held in 1860 at Karlsruhe, Germany. At this meeting the young Italian chemist Stanislao Cannizzaro presented his ideas so clearly and forcefully, both in formal and informal talks, that a consensus about atomic masses began to develop in the chemical community. Cannizzaro was guided by two main beliefs:

1. Compounds contained whole numbers of atoms as Dalton postulated.
2. Avogadro's hypothesis was correct—equal volumes of gases under the same conditions contain the same number of molecules.

Applications of Avogadro's hypothesis to Gay-Lussac's results of combining volumes of gas convinced Cannizzaro that hydrogen gas consisted of H_2 molecules. Thus he arbitrarily assigned the relative molecular mass of hydrogen (H_2) to be 2. He then set out to measure the relative molecular masses for other gaseous substances. He did so by comparing the mass of 1 liter of a given gas with the mass of 1 liter of hydrogen gas (both gases at the same conditions of temperature and pressure). For example, the ratio of the masses of 1-liter samples of oxygen and hydrogen gas is 16:

$$\frac{\text{Mass of 1.0 L oxygen gas}}{\text{Mass of 1.0 L hydrogen gas}} = \frac{16}{1} = \frac{32}{2} \blacktriangleright$$

Both gases are at the same temperature and pressure.

Since by Avogadro's hypothesis both samples of gas contain the same number of molecules, the mass of an oxygen molecule (which he assumed to be O_2) must be 32 relative to a mass of 2 for the H_2 molecule. Since each molecule contains two atoms, the relative atomic masses for oxygen and hydrogen are then 16 and 1, respectively. Using this same method, Cannizzaro found the relative molecular mass of carbon dioxide to be 44 (relative to 2 for H_2). Chemical analysis of carbon dioxide had shown it to contain 27% carbon (by mass). This percentage corresponds to (0.27)(44 g), or 12 g, of carbon in 44 g of carbon dioxide, and $44\text{ g} - 12\text{ g} = 32\text{ g}$ of oxygen. Recall that the oxygen atom has a relative mass of 16. Thus if the formula of carbon dioxide is assumed to be CO_2, then the relative mass of carbon is 12 because $12 + 2(16) = 44$. However, if the formula of carbon dioxide is C_2O_2, then 12 represents the relative mass of two carbon atoms, giving carbon a relative mass of 6. Similarly, the formula C_3O_2 for carbon dioxide gives a relative mass of 4 for carbon. Thus the relative mass of the carbon atom cannot be determined from these data without knowing the formula for carbon dioxide. This is exactly the type of problem that had plagued chemists all along and was the reason for so many different mass tables.

Cannizzaro addressed this problem by obtaining the relative molecular masses of many other compounds containing carbon. For example, consider the data shown in Table 2.1 ▼. Notice from these data that the relative mass of carbon present in the compounds is always a multiple of 12. This observation strongly suggests that the relative mass of carbon is 12, which in turn would mean that the formula for carbon dioxide is CO_2.

CHEMICAL INSIGHTS

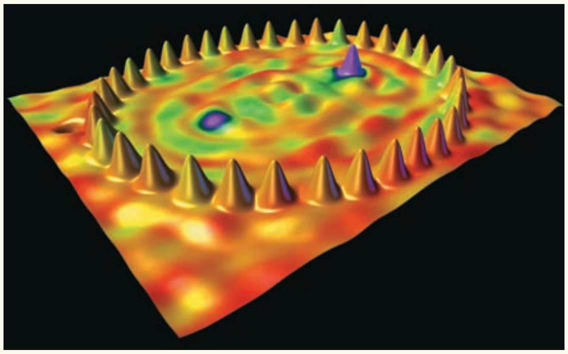
Seeing Atoms

There are many pieces of evidence that convince us that matter is made up of atoms. Some of the most compelling evidence comes from scanning probe microscopy. This technique employs a microscopic tip, which responds to a surface to reveal its architecture. The principal methods of scanning probe microscopy are scanning tunneling microscopy (STM) and atomic force microscopy (AFM).

The scanning tunneling microscope was invented at IBM's Zurich Research Laboratory in Switzerland in the early 1980s by Gerd K. Binning and Heinrich Rohrer, who subsequently won the Nobel Prize in Physics for their work. STM uses an ultrasharp metal tip that is brought to within about 1 nm of the surface. A small voltage is applied to the tip, which produces current flow between the surface and the tip. This tunneling* current is strongly dependent on the distance of the tip from the surface. A feedback circuit, which senses the current flow, keeps the tip at a constant distance from the surface. The tip can also be used to move atoms around on the surface, as illustrated by the elliptical arrangement of cobalt atoms shown in Fig. 2.4 ▶.

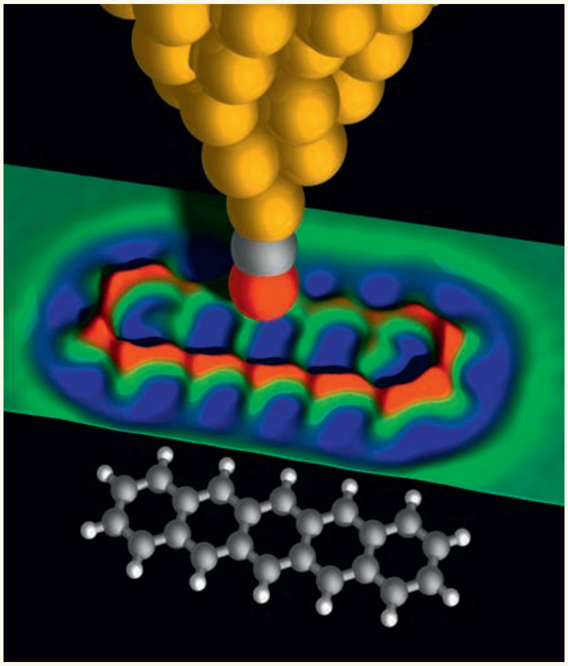
AFM is similar in many ways to STM. In AFM, the attractive and repulsive forces acting on a tiny arm near the surface are measured, and a relief map is produced from the results.

Recently, IBM researcher Leo Gross and his coworkers have found that the image produced by AFM can be greatly improved by inserting a carbon monoxide (CO) molecule at the end of the gold AFM tip. This technique enables the AFM probe to produce a detailed image of an entire molecule such as pentacene ($C_{22}H_{14}$) as depicted in Fig. 2.5 ▶.



IBM Almaden Research Center

Figure 2.4
Image of a ring of cobalt atoms placed on a copper surface.



IBM Research GmbH

Figure 2.5
Top, A depiction of the EMF tip in which a CO molecule has been added to the tip (consisting of gold atoms). The image of the pentacene molecule is shown in blue, green, and red.
Bottom, A ball and stick model of the pentacene ($C_{22}H_{14}$) molecule (carbon atoms are black, hydrogen atoms are white)

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*The term *tunneling* refers to the ability of electrons from the surface to escape even though they do not apparently possess enough energy to overcome the large potential energy holding them there. This quantum mechanical phenomenon is known as tunneling (the electron "tunnels through" the potential barrier).

Table 2.1

Relative Mass Data for Several Gases Containing Carbon

Compound	Relative Molecular Mass	Percent Carbon (by Mass)	Relative Mass of Carbon Present
Methane	16	75	12
Ethane	30	80	24
Propane	44	82	36
Butane	58	83	48
Carbon dioxide	44	27	12

EXAMPLE 2.1

Predicting the Formulas for Compounds Containing Carbon

The first four compounds listed in Table 2.1 contain only carbon and hydrogen. Predict the formulas for these compounds.

Solution Since the compounds contain only carbon and hydrogen, the percent hydrogen in each compound (by mass) is 100 − % carbon. We can then find the relative mass of hydrogen present as follows:

$$\text{Relative mass of hydrogen} = \frac{\text{percent hydrogen}}{100} \times \text{relative molecular mass}$$

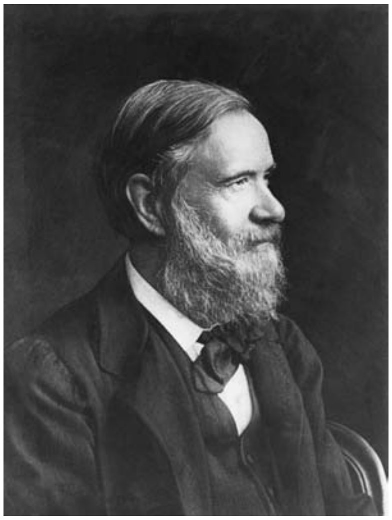
In tabular form the results are as follows:

Compound	Relative Molecular Mass	Percent Hydrogen	Relative Mass of Hydrogen
Methane	16	25	4
Ethane	30	20	6
Propane	44	18	8
Butane	58	17	10

Combining the preceding results with those from Table 2.1, we find that methane contains relative masses of carbon and hydrogen of 12 and 4, respectively. Using the relative atomic mass values of 12 and 1 for carbon and hydrogen gives a formula of CH_4 for methane. Similarly, the relative masses of carbon and hydrogen in ethane of 24 and 6, respectively, lead to a formula of C_2H_6 for ethane. Similar reasoning gives formulas for propane and butane of C_3H_8 and C_4H_{10}, respectively.

Cannizzaro's work was so convincing because he collected data on so many compounds. Although he couldn't absolutely prove that his atomic mass values were correct (because he had no way to verify absolutely the formulas of the compounds), the consistency of the large quantity of data he had collected eventually convinced virtually everyone that his interpretation made sense and that the relative values of atomic mass that he had determined were correct. The confusion was finally over. Chemistry had the universal (relative) mass standards that it needed.

It is worthwhile to note that Cannizzaro's work led to *approximate* values of the relative atomic masses. His goal was not to determine highly precise values for atomic masses but rather to pin down the approximate values (for example, to show that oxygen's relative mass was 16 rather than 8). The most



Bettmann/Corbis

Stanislao Cannizzaro (1826–1910). Cannizzaro's work ended the confusion of atomic mass values.

precise values for atomic masses were determined by quantitative experiments in which the combining masses of elements were carefully measured, such as in the work of Berzelius.

In the next chapter we will have much more to say about atomic masses, including the origin of the very precise values used by today's chemists.

2.5 | Early Experiments to Characterize the Atom

On the basis of the work of Dalton, Gay-Lussac, Avogadro, Cannizzaro, and others, chemistry was beginning to make sense. The concept of atoms was clearly a good idea. Inevitably, scientists began to wonder about the nature of the atom. What is an atom made of, and how do the atoms of the various elements differ?

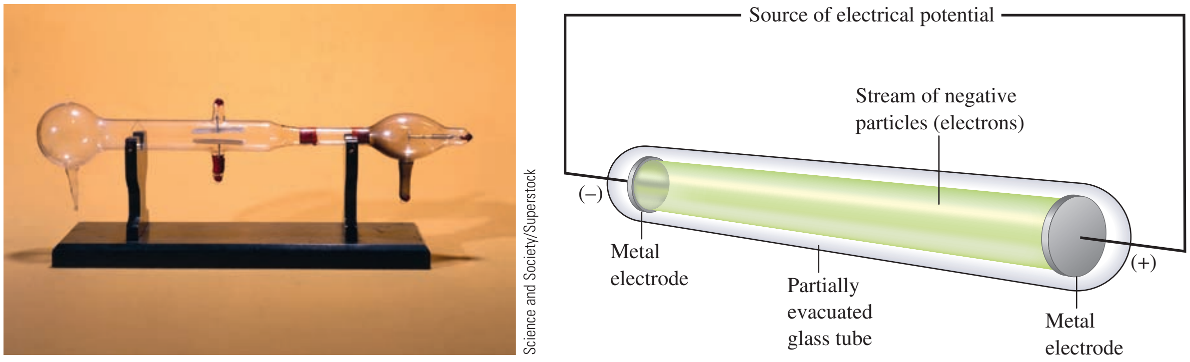
The Electron

The first important experiments that led to an understanding of the composition of the atom were done by the English physicist J. J. Thomson (1856–1940), who studied electrical discharges in partially evacuated tubes called *cathode-ray tubes* (▼ Fig. 2.6) during the period from 1898 to 1903. Thomson found that when high voltage was applied to the tube, a "ray" he called a **cathode ray** (because it emanated from the negative electrode, or cathode) was produced. Because this ray was produced at the negative electrode and was repelled by the negative pole of an applied electric field (▶ Fig. 2.7), Thomson postulated that the ray was a stream of negatively charged particles, now called **electrons.** From experiments in which he measured the deflection of the beam of electrons in a magnetic field, Thomson determined the *charge-to-mass ratio* of an electron:

$$\frac{e}{m} = -1.76 \times 10^{8}\ \mathrm{C/g}$$

where e represents the charge on the electron in coulombs (C) and m represents the electron mass in grams.

One of Thomson's primary goals in his cathode-ray tube experiments was to gain an understanding of the structure of the atom. He reasoned that since electrons could be produced from electrodes made of various types of metals, *all* atoms must contain electrons. Since atoms were known to be electrically neutral, Thomson further assumed that atoms also must contain some positive



Science and Society/Superstock

Figure 2.6
A cathode-ray tube. The fast-moving electrons excite the gas in the tube, causing a glow between the electrodes. The green color in the photo is due to the response of the screen (coated with zinc sulfide) to the electron beam.

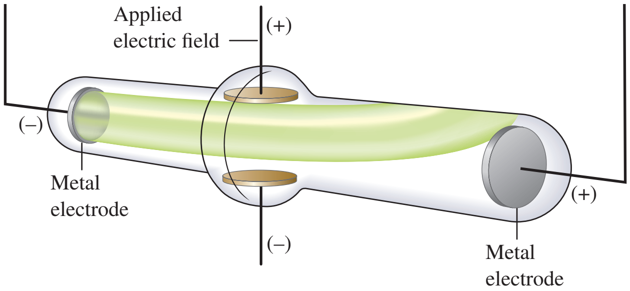


Figure 2.7
Deflection of cathode rays by an applied electric field.

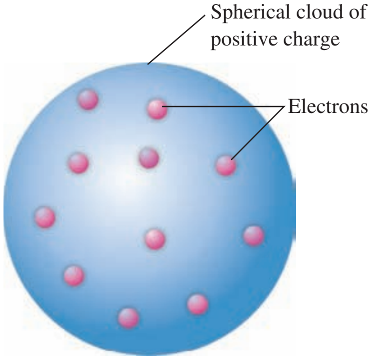


Figure 2.8
Thomson's plum pudding model.

charge. Thomson postulated that an atom consisted of a diffuse cloud of positive charge with the negative electrons embedded randomly in it. This model, shown in Fig. 2.8 ▶, is often called the *plum pudding model* because the electrons are like raisins dispersed in a pudding (the positive-charge cloud), as in plum pudding, a favorite English dessert.*

In 1909 Robert Millikan (1868–1953), working at the University of Chicago, performed very clever experiments involving charged oil drops. These experiments allowed him to determine the magnitude of the electron charge (▼ Fig. 2.9). With this value and the charge-to-mass ratio determined by Thomson, Millikan was able to calculate the mass of the electron as 9.11×10^{-31} kilogram.


C. Byatt-norman/Shutterstock.com #19116133

A classic English plum pudding.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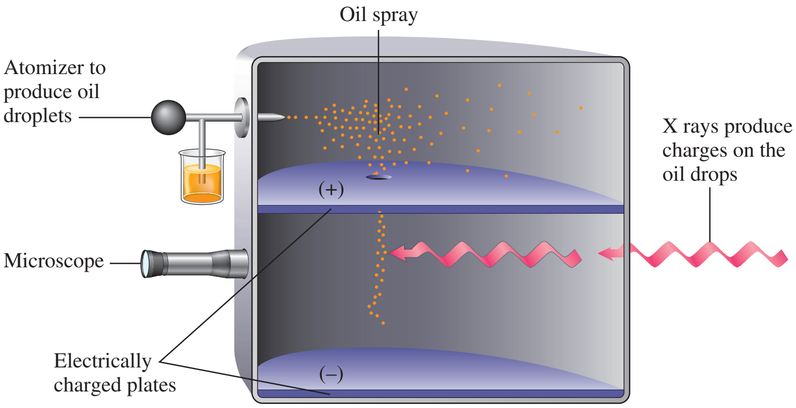

Figure 2.9
A schematic representation of the apparatus Millikan used to determine the charge on the electron. The fall of charged oil droplets due to gravity can be halted by adjusting the voltage across the two plates. The voltage and the mass of an oil drop can then be used to calculate the charge on the oil drop. Millikan's experiments showed that the charge on an oil drop is always a whole-number multiple of the electron charge.

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*Although J. J. Thomson is generally given credit for this model, the idea was apparently first suggested by the English mathematician and physicist William Thomson (better known as Lord Kelvin and not related to J. J. Thomson).

CHEMICAL INSIGHTS Marie Curie: Founder of Radioactivity

Marie Sklodowska Curie, one of the truly monumental figures of modern science, was born in Warsaw, Poland, on November 7, 1867. Marie developed an early interest in chemistry, and it is interesting that Dmitri Mendeleev, creator of the periodic table and friend of Marie's father (a high school mathematics and physics teacher), predicted great success for the young woman when he met her in Warsaw.

To escape political persecution in Poland by the Russians, Marie emigrated in 1891 at the age of 24 to Paris, where she decided to pursue a degree in science at the Sorbonne Institute. While studying there, Marie met Pierre Curie, a well-respected physicist who, among other things, had studied the temperature dependence of magnetism, which led to the formulation of Curie's law. Marie and Pierre were married in 1895, after which Marie decided to pursue a doctorate in physics. As the subject of her doctoral thesis, she decided to study the strange radiation emitted by uranium ore, which had been accidentally discovered by Henri Becquerel. Marie was recruited for the task by Becquerel himself. As she began her studies, Madame Curie noticed that pitchblende produced more radiation than uranium, and she became convinced that an as-yet-unknown element in pitchblende was responsible for this "radioactivity"—a term that she coined.

The next step was to identify and isolate the radioactive element or elements in pitchblende. Pierre interrupted his own research—he thought it would be for just a few weeks—to collaborate with his wife on the project. The Curies actually

Bettmann/Corbis

Marie Sklodowska Curie (1867–1934) in her laboratory.

Radioactivity

In the late nineteenth century, scientists discovered that certain elements produce high-energy radiation. For example, in 1896 the French scientist Antoine Henri Becquerel accidentally found that the image of a piece of mineral containing uranium could be produced on a photographic plate in the absence of light. He attributed this phenomenon to a spontaneous emission of radiation by the uranium, which his student, Marie Curie, called **radioactivity.** Studies in the early twentieth century demonstrated three types of radioactive emission: gamma (γ) rays, beta (β) particles, and alpha (α) particles. A γ ray is high-energy "light"; a β particle is a high-speed electron; and an α particle has a $2+$ charge—that is, a charge twice that of the electron and with the opposite sign. The mass of an α particle is 7300 times that of an electron. More modes of radioactivity are now known, and we will discuss them in Chapter 20. Here we will consider only α particles because they were used in some crucial early experiments.

borrowed money to support themselves and convinced the Austrian government to send them 1 ton of pitchblende from the mines at Joachimsthal. After receiving this 5 cubic foot pile of "sand" from Austria, the Curies worked to chemically digest the ore. In this process they worked with batches as large as 40 pounds at a time in an improvised laboratory with a leaky roof. Working through the bitter winter of 1896 and all through 1897 (in which they had their first daughter, Iréne, who also became a prominent scientist), in July 1898 the Curies finally isolated a previously unknown element they named polonium after Marie's homeland. Although most people would be satisfied by discovering a new element 400 times more radioactive than uranium, the Curies kept working. By this time, the 1 ton of pitchblende had been concentrated to an amount that would fit into an ordinary flask. Marie continued to extract and crystallize increasingly smaller amounts of material. Finally, in November 1898 she obtained crystals of the salt of another new element that the Curies named radium, which turned out to be 900 times more radioactive than uranium.

For their work the Curies were awarded the Nobel Prize in Physics in 1903, sharing the award with Henri Becquerel. In 1904, Pierre was awarded a chair in physics at the Sorbonne. He was killed tragically on the streets of Paris on April 19, 1906, when he was knocked down by a cab and the wheels of a heavy van passing in the opposite direction ran over his head. After mourning for just a few weeks, Marie Curie decided to proceed with the research on radium. In an unprecedented action, she was awarded her late husband's chair and became the first woman to teach at the Sorbonne.

Marie Curie worked tirelessly to develop radioactivity as a new discipline in physics. With the help of five assistants, she studied the effects of radioactivity and developed the atomic theory of its origin. In 1911, Marie was awarded her second Nobel Prize, this time in chemistry, for the chemical processes discovered in the identification of radium and polonium and for the subsequent characterization of those elements. During World War I, she trained doctors in the new methods of radiology and, after learning to drive, personally transported medical equipment to hospitals. After the war, Madame Curie assumed leadership of the newly built Radium Institute in Paris. In 1920, a campaign was mounted in the United States to produce 1 gram of radium for Marie to support her research. She traveled to the United States to receive the precious vial of radium at the White House in 1921.

Marie Curie continued her studies of radioactivity until just before her death of leukemia in 1934. She was truly one of the greatest scientists of the twentieth century.

The Nuclear Atom

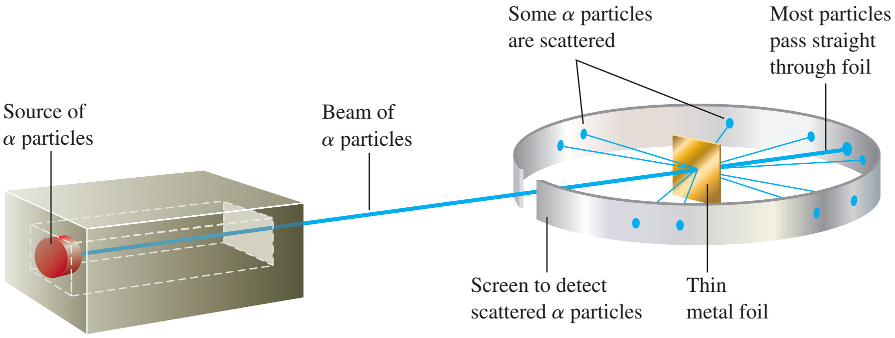
In 1911 Ernest Rutherford (▶ Fig. 2.10), who performed many of the pioneering experiments to explore radioactivity, carried out an experiment to test Thomson's plum pudding model. The experiment involved directing α particles at a thin sheet of metal foil, as illustrated in Fig. 2.11 ▼. Rutherford reasoned that if Thomson's model were accurate, the massive α particles should

Portrait of Ernest Rutherford, 1932 by Oswald Hornby Birley, Royal Society, London, UK/Bridgeman Art Library

Figure 2.10

Ernest Rutherford (1871–1937) was born on a farm in New Zealand. In 1895 he placed second in a scholarship competition to attend Cambridge University but was awarded the scholarship when the winner decided to stay home and get married. As a scientist in England, Rutherford did much of the early work on characterizing radioactivity. He named the α and β particles and the γ ray and coined the term *half-life* to describe an important attribute of radioactive elements. His experiments on the behavior of α particles striking thin metal foils led him to postulate the nuclear atom. He also invented the name *proton* for the nucleus of the hydrogen atom. He received the Nobel Prize in Chemistry in 1908.

Figure 2.11
Rutherford's experiment on α-particle bombardment of metal foil. (Gold foil was used in the original experiments because it can be hammered into extremely thin sheets.)



crash through the thin foil like cannonballs through gauze, as shown in Fig. 2.12(a) ▼. He expected the α particles to travel through the foil with, at the most, very minor deflections in their paths. The results of the experiment were very different from those Rutherford anticipated. Although most of the α particles passed straight through, many of the particles were deflected at large angles, as shown in Fig. 2.12(b) ▼, and some were reflected, never hitting the detector. This outcome was a great surprise to Rutherford. (He wrote that this result was comparable to shooting a howitzer at a piece of paper and having the shell reflected back.)

Rutherford knew from these results that the plum pudding model for the atom could not be correct. The large deflections of the α particles could be caused only by a center of concentrated positive charge that contains most of the atom's mass, as illustrated in Fig. 2.12(b). Most of the α particles pass directly through the foil because the atom is mostly open space. The deflected α particles are those that had a "close encounter" with the massive positive center of the atom, and the few reflected α particles are those that made a "direct hit" on the much more massive positive center.

In Rutherford's mind these results could be explained only in terms of a **nuclear atom**—an atom with a dense center of positive charge (the **nucleus**) and electrons moving around the nucleus at a distance that is large relative to the nuclear radius.

Critical Thinking

You have learned about three different models of the atom: Dalton's model, Thomson's model, and Rutherford's model. What if Dalton was correct? What would Rutherford have expected from his experiments with gold foil? What if Thomson was correct? What would Rutherford have expected from his experiments with gold foil?

Figure 2.12
(a) The expected results of the metal foil experiment if Thomson's model were correct. (b) Actual results.