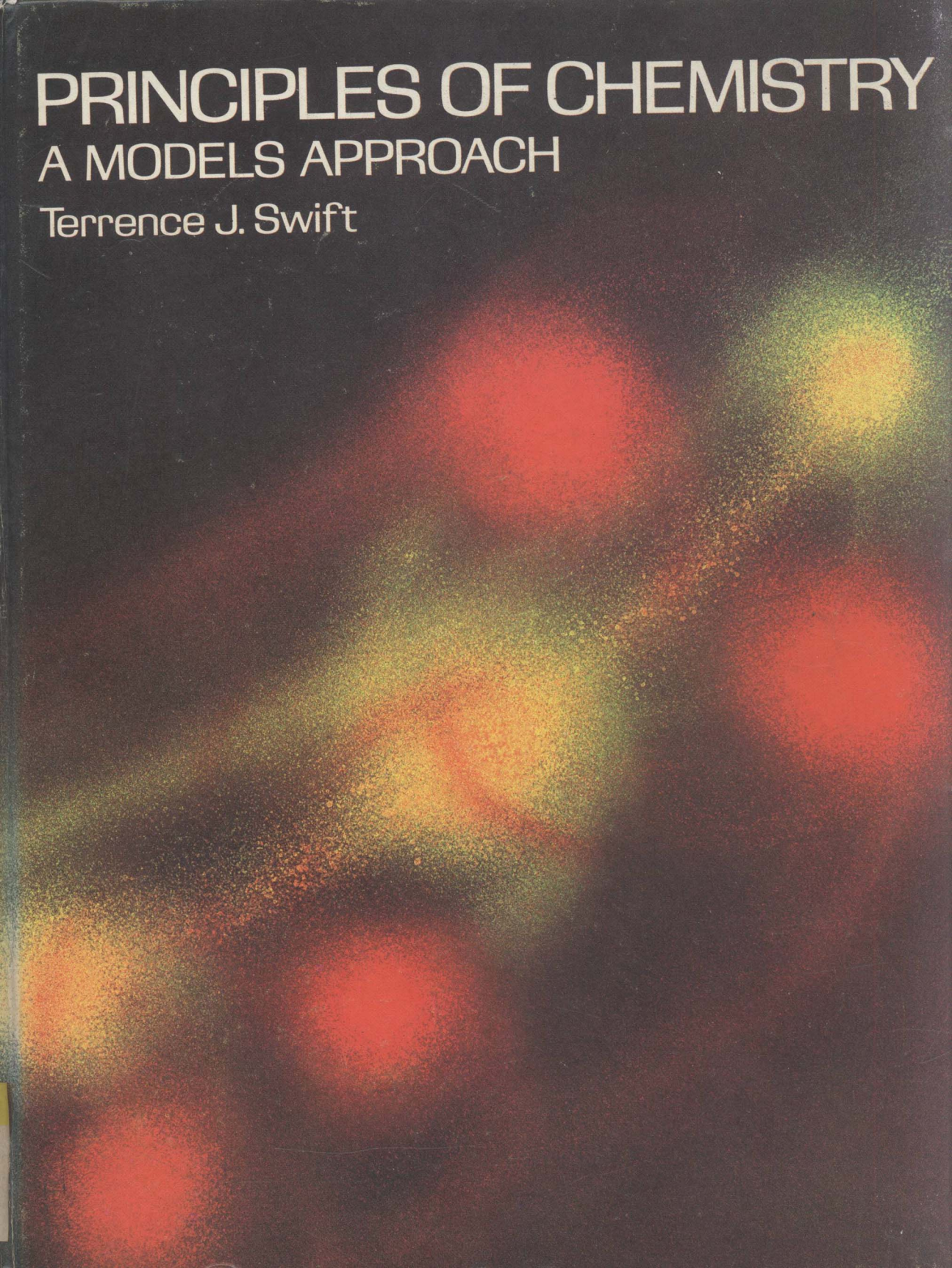


PRINCIPLES OF CHEMISTRY

A MODELS APPROACH

Terrence J. Swift



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Case Western Reserve University

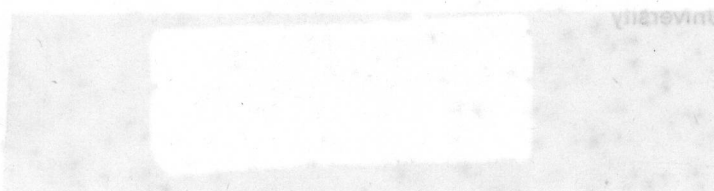


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TABLE OF ATOMIC WEIGHTS, 1971 (Based on Carbon-12)

Values in parentheses are estimated and denote, in most cases, isotopes of longest half-life. Digits given as subscripts are reliable to $\pm 3\%$; other values are reliable to $\pm 1\%$ in the last digit.

SYMBOL	NO.	WEIGHT	SYMBOL	NO.	WEIGHT
Actinium	Ac	89 (227)	Mercury	Hg	80 200.5 ₉
Aluminum	Al	13 26.98154 ^a	Molybdenum	Mo	42 95.9 ₄
Americium	Am	95 (243)	Neodymium	Nd	60 144.2 ₄
Antimony	Sb	51 121.7 ₅	Neon	Ne	10 20.17 ₉ ^c
Argon	Ar	18 39.94 ₈ ^{b,c,d,g}	Neptunium	Np	93 237.0482 ^{b,f}
Arsenic	As	33 74.9216 ^a	Nickel	Ni	28 58.7 ₁
Astatine	At	85 (210)	Niobium	Nb	41 92.9064 ^a
Barium	Ba	56 137.3 ₄	Nitrogen	N	7 14.0067 ^{b,c}
Berkelium	Bk	97 (249)	Nobelium	No	102 (254)
Beryllium	Be	4 9.01218 ^a	Osmium	Os	76 190.2
Bismuth	Bi	83 208.9804 ^a	Oxygen	O	8 15.999 ₄ ^{b,c,d}
Boron	B	5 10.81 ^{c,d,e}	Palladium	Pd	46 106.4
Bromine	Br	35 79.904 ^c	Phosphorus	P	15 30.97376 ^a
Cadmium	Cd	48 112.40	Platinum	Pt	78 195.0 ₉
Calcium	Ca	20 40.08	Plutonium	Pu	94 (242)
Californium	Cf	98 (249)	Polonium	Po	84 (210)
Carbon	C	6 12.011 ^{b,d}	Potassium	K	19 39.09 ₈
Cerium	Ce	58 140.12	Praseodymium	Pr	59 140.9077 ^a
Cesium	Cs	55 132.9054 ^a	Promethium	Pm	61 (145)
Chlorine	Cl	17 35.453 ^c	Protactinium	Pa	91 231.0359 ^{a,f}
Chromium	Cr	24 51.996 ^c	Radium	Ra	88 226.0254 ^{a,f,g}
Cobalt	Co	27 58.9332 ^a	Radon	Rn	86 (222)
Copper	Cu	29 63.54 ₆ ^{c,d}	Rhenium	Re	75 186.2
Curium	Cm	96 (245)	Rhodium	Rh	45 102.9055 ^a
Dysprosium	Dy	66 162.5 ₀	Rubidium	Rb	37 85.467 ₈ ^c
Einsteinium	Es	99 (253)	Ruthenium	Ru	44 101.0 ₇
Erbium	Er	68 167.2 ₆	Rutherfordium	Rf	104 (257)
Europium	Eu	63 151.96	Samarium	Sm	62 150.4
Fermium	Fm	100 (254)	Scandium	Sc	21 44.9559 ^a
Fluorine	F	9 18.99840 ^a	Selenium	Se	34 78.9 ₆
Francium	Fr	87 (223)	Silicon	Si	14 28.08 ₅ ^d
Gadolinium	Gd	64 157.2 ₅	Silver	Ag	47 107.868 ^c
Gallium	Ga	31 69.72	Sodium	Na	11 22.98977 ^a
Germanium	Ge	32 72.5 ₉	Strontium	Sr	38 87.62 ₈ ^e
Gold	Au	79 196.9665 ^a	Sulfur	S	16 32.06 ^d
Hafnium	Hf	72 178.4 ₉	Tantalum	Ta	73 180.947 ₉ ^b
Hahnium	Ha	105 (260)	Technetium	Tc	43 98.9062 ^f
Helium	He	2 4.00260 ^{b,c}	Tellurium	Te	52 127.6 ₀
Holmium	Ho	67 164.9304 ^a	Terbium	Tb	65 158.9254 ^a
Hydrogen	H	1 1.0080 ^{b,d}	Thallium	Tl	81 204.3 ₇
Indium	In	49 114.82	Thorium	Th	90 232.0381 ^{a,f}
Iodine	I	53 126.9045 ^a	Thulium	Tm	69 168.9342 ^a
Iridium	Ir	77 192.2 ₂	Tin	Sn	50 118.6 ₉
Iron	Fe	26 55.84 ₇	Titanium	Ti	22 47.9 ₀
Krypton	Kr	36 83.80	Tungsten	W	74 183.8 ₅
Lanthanum	La	57 138.905 ₅ ^b	Uranium	U	92 238.029 ^{b,c,e}
Lawrencium	Lr	103 (257)	Vanadium	V	23 50.941 ₄ ^{b,c}
Lead	Pb	82 207.2 ^{d,g}	Xenon	Xe	54 131.30
Lithium	Li	3 6.94 ₁ ^{c,d,e}	Ytterbium	Yb	70 173.0 ₄
Lutetium	Lu	71 174.97 ₁	Yttrium	Y	39 88.9059 ^a
Magnesium	Mg	12 24.305 ^c	Zinc	Zn	30 65.38
Manganese	Mn	25 54.9380 ^a	Zirconium	Zr	40 91.22
Mendelevium	Md	101 (256)			

^aMononuclidic element.

^bElement with one predominant isotope (about 99-100 per cent abundance).

^cElement for which the atomic weight is based on calibrated measurements.

^dElement for which variation in isotopic abundance in terrestrial samples limits the precision of the atomic weight given.

^eElement for which users are cautioned against the possibility of large variations in atomic weight due to inadvertent or undisclosed artificial isotopic separation in commercially available materials.

^fMost commonly available long-lived isotope.

^gIn some geological specimens this element has a highly anomalous isotopic composition corresponding to an atomic weight significantly different from that given.

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Preface

Instructors in college introductory chemistry courses are faced with an extremely formidable task. Their students have a wide variety of interests, ranging from those of the prospective health scientist to those of the future chemical researcher. Because the career interests of most of these students require them to take chemistry courses beyond the introductory level, basic chemistry courses must present the fundamental facts and concepts in such a way that students not only learn them but can use and retain them. When one considers the wealth of facts and concepts most chemists consider basic, it is easy to conclude that the instructor's task is almost impossible.

Added to the problem is the great diversity of preparation in chemistry with which students enter college. Some enter with excellent chemistry backgrounds and are fully prepared for a sophisticated treatment of the subject at the college level. Unfortunately, the number is usually relatively small. In fact, a larger number of students have had almost no preparation at all in chemistry and in instances where there has been preparation retention by the student is extremely poor. Thus, the diversity of background and the lack of retention on the part of students in the introductory chemistry course demand that the instructor begins at a very elementary level and proceeds in a very systematic fashion. The material must be presented in such a way that students—including the well-prepared—are interested and challenged.

How does one construct a chemistry course which is both highly structured for the poorly-prepared student and highly flexible for the well-prepared student? The author of *Principles of Chemistry: A Models Approach* believes that a solution lies in centering the course around the systematic development of the physical intuition of students. It is generally conceded that there are at least three factors involved in mastering a science. These are acquiring a knowledge of the basic facts of the science, acquisition of the quantitative techniques and developments associated with the concepts of the science, and understanding those concepts in physical terms. The latter factor must be considered the most important of the three, because it ties together the other two and serves as a guide for further pursuits in the science. Furthermore, without a good physical understanding, students soon forget the facts and concepts.

How can physical intuition be systematically developed? One way is by concentrating on the construction and application of models. Models in chemistry are mental pictures of matter which chemists formulate in order to understand the

properties of matter. They are useful approximations of material objects that can be developed systematically from very crude approximations to extremely sophisticated ones.

The process of model building is fundamental to the thinking of most chemists and is without doubt the best way yet devised to tie together chemical facts and concepts. Furthermore, model building can be done in such a way as to involve the student in every step of the process. It is an approach that all students will find interesting and challenging, including the well prepared ones.

Instructors have had considerable experience in constructing and using models of matter; students have not. As a consequence, there are two forewords to this text, one addressed to the instructor and the other to the student. However, before the forewords a brief discussion of the process of model building and some general comments on the philosophy of the models approach as reflected in the text are in order.

Model construction begins with experimental observations. The model is thus a collection of proposed features of the matter under investigation which are consistent with the experimental observations. One of the most useful characteristics of models is their predictive value. Once constructed, the model leads to predictions of additional facts. The appropriate experiments are then devised and performed and the predictions checked to provide corroboration for the model. If the experimental results are in disagreement with the predictions, the model is either discarded and a new one constructed or the original model is refined. Thus, the process of model building involves a never-ending interplay between experiment and theory.

Generally, college students in introductory chemistry courses should not have to accept a concept on faith. Concepts must make sense to them in physical terms or they will neither be able to use the concepts nor retain them.

Because model building is a highly physical process (as contrasted with mathematical procedures) it is very desirable to minimize the mathematical level and the number of mathematical operations used in the process. Consequently, the calculus is not used in this text, and even the amount of algebra is kept to a minimum. Important equations are developed, but in general they follow from models rather than lead to them.

I wish to acknowledge my debt of gratitude to two former teachers who have served as great examples to me of what a scholar and teacher should be. They are Professor George Schulte of Loras College and Professor R. E. Connick of the University of California, Berkeley. I wish also to acknowledge with gratitude the assistance of a number of reviewers, whose contributions to the development of the manuscript were far above the ordinary. They are Professor Robert Brasted, University of Minnesota; Professor George Fleck, Smith College; Professor Michael Henchman, Brandeis University; and Professor Frank Rioux, St. John's University, Minnesota. I would be remiss if I did not express my appreciation to Professor G. R. McMillan of Case Western Reserve University for his many helpful discussions and suggestions, and also to Mr. T. S. Viswanathan for his meticulous efforts in correcting proofs.

It has been a great pleasure working with Mr. Jeff Holtmeier, Dr. Paul Bryant, and others of the staff at D. C. Heath and Company. They all have been completely dedicated to making this the best text possible. A textbook which has the development of visual images as its theme must contain outstanding artwork. Mr. Leonard Preston, the artist, is responsible for several key developments in the artwork. My thanks also go to Mrs. Eileen Green and Mrs. Frances Novak, who typed the manuscript on some

schedules that were often nearly impossible. Finally, I would like to acknowledge the patience and understanding of my wife, Therese, and my daughters, Mary Margaret and Elizabeth, for tolerating a preoccupied husband and father.

TERRENCE J. SWIFT

Foreword to the Instructor

This text has been successfully used in manuscript form by me in a large introductory chemistry course at Case Western Reserve University in the 1973-74 academic year, the manuscript having been organized from my lectures in the course in previous years. Each chapter as it appears in the book was put in final form only after it had been classroom tested. In this foreword I hope to explain the rationale for the approaches taken in key chapters and to indicate areas where I believe special emphasis should be placed. Both explanations are presented in more detail in an instructor's manual that is available from the publishers.

As a general comment I would point out that there is no such thing as a correct model. Students should be made aware that it is pointless for them to expect to be told the "truth," as far as explanation of chemical phenomena are concerned. The reason, of course, being that there is no such thing as absolute truth in any explanation. One of the virtues of the process of model building is that it shows the limitations of explanations. You can aid immensely in making this point by using alternative models to the ones developed in the text. Students thus can see that there is more than one valid way to view the same phenomenon.

The first six chapters are almost exclusively concerned with model building. I have put special emphasis on the process in Chapter 2. The gaseous state, of itself, does not merit the lengthy treatment given it. However, Chapter 2 is the chapter in which the discussions of model building begin in earnest and is the first place where the student is given examples of models and shown how they relate to actual observations.

I believe that to make sense out of chemistry in physical terms it is necessary to have an adequate grasp of such elementary physical quantities as momentum and kinetic energy. Hence, basic concepts in mechanics are developed briefly in Chapter 2, with other elementary physical concepts being presented as they are needed in succeeding chapters. In these developments no previous knowledge of physics on the part of the student is assumed.

The principal model developed in the first half of the text is the wave model of the atom (Chapter 4). The concepts of energy levels, quantum numbers, and orbitals seem like magic to students unless these concepts are developed. It is not necessary to go into Schrödinger wave mechanics for this development. Waves are easy to picture and energy levels, quantum numbers, and atomic orbitals can be derived in a nonmathematical fashion which is relatively easy to visualize.

Chapter 5 is concerned with chemical bonding. Students need to have, early in the course, a very clear picture of why any given chemical bond exists. In addition

they need to have a model with which to predict the numbers, kinds, and something of the strengths of bonds between most atoms. Such a model is that of molecular orbitals formed, in Chapter 5, by the pictorial overlap of atomic orbitals. Molecular orbitals are an anathema to many instructors and consequently are often de-emphasized in their teaching. However, I believe these instructors are overlooking an extremely useful model, which can be (but admittedly often is not) constructed in a way which is easy to visualize.

Chapter 6 contains a variation on the valence-shell, electron-pair repulsion method for predicting molecular geometry. The variation has proven to be very effective in improving students' predictive ability and it is used often in succeeding chapters.

A major part of the descriptive chemistry in the text appears in Chapters 7 through 11. This is rather unusual, in that it precedes the discussions of thermodynamics and equilibrium. My experience has been that descriptive chemistry is best approached on two different levels. The first is a qualitative level, based on the concepts of chemical bonding, and the second is a quantitative level based on thermodynamics. Most students experience great difficulties with chemical equilibria unless they are familiar with the molecular structures and reactions involved.

By placing the major part of descriptive chemistry in the text immediately following the development of atomic and molecular models we can demonstrate the predictive and correlative power of models. Large amounts of descriptive material are difficult to present successfully, because it is easy to lose the interest of the student confronted with a mass of detail. As a consequence, descriptive chemistry (particularly non-metallic inorganic chemistry) is often neglected, a situation approved of by some chemical educators but deplored by others. I believe that the models approach provides some solution to this problem. By pointing out (Chapters 7 through 11) just how successful they are in predicting and explaining molecular structures and reactions, models provide a theme for relating otherwise apparently unrelated facts.

While the predictive approach to descriptive chemistry has its advantages in maintaining student interest, it also has one potential drawback that must be recognized. Since the models precede the facts, students can easily conclude that the facts are subservient to the models, and that something is true because we predicted the something to be true. They, therefore, must be reminded in this game we are playing that a proper perspective must be kept. Models come and go, but facts remain facts.

In recent years, many high school chemistry courses have become very concept centered, at the expense of the consideration of chemical compounds and chemical reactions. Consequently, most of the compounds and chemical reactions discussed in Chapters 7 through 11 of this text may be unfamiliar to many of your students. I recommend emphasis on classroom demonstrations, particularly in connection with Chapters 8 and 9. These two chapters have been written so that the students can master them through their own reading. The challenge is to bring them to life, and this can be done through classroom demonstrations.

Chapter 12 is, for an introductory text, a rather thorough treatment of spectroscopy. We, as instructors, confidently state all sorts of detailed information about molecular structures, and students certainly wonder about the source of our information. With the judicious use of a few simple models spectroscopic methods can be

introduced which will allow the students themselves to deduce molecular structures.

The approach to thermodynamics in Chapter 15 is probably the most important feature of this text. It has been my experience that of all the areas of chemistry thermodynamics is the most difficult for students to grasp, use, and retain. This is particularly true of anything having to do with the second law. I believe that the problem exists because the student is not given any easily visualizable model which relates to the second law. To some extent this problem exists because, in a strict sense, thermodynamics is model independent. One can use the laws of thermodynamics without relating them to atoms and molecules in any way. As a chemist I have always found this way of using the laws self-defeating, and pedagogically the model-independent approach has been a failure in every instance that I have ever seen it used. As with other physical entities, entropy and Gibbs free energy must be made visualizable or students will have little feeling for them. The models of matter spreadedness and energy spreadedness developed in Chapter 15 permit the visualization of entropy and Gibbs free energy. The use of these two models has permitted my students to grasp, use, and retain the concepts of thermodynamics. In fact, it was the success in this area of the use of visualizable models that led to the development of the model approach in this text.

A mathematical analysis of a simple process involving matter spreading is presented in the text. The detailed analysis of energy spreading is more complicated and is not presented. Norman Craig has given such an analysis (N.C. Craig, *J. Chem. Educ.*, **47**, 342 (1970)) in a particularly lucid and concise treatment.

The models of matter spreadedness and energy spreadedness adequately introduce the concept of equilibrium, and the general concept of equilibrium is consequently developed in Chapter 16. Chapters 17, 18, 19, and 20 are a return to descriptive chemistry. The treatment in these chapters is quantitative in terms of specific equilibria. The student learns the standard procedures for handling equilibria quantitatively. However, the models of matter and energy spreadedness are woven throughout these four chapters, so that the student can visualize why specific equilibria are as they are.

Chapter 21 is devoted to chemical kinetics. The focus of this chapter is on the question of why some reactions are rapid and others are slow. In order to answer that question specific reaction mechanisms are proposed. There probably are no more debatable models in chemistry than specific reaction mechanisms. Except for a few cases, space limitations in the text prevent proposals of alternate mechanisms for reactions and discussing the pros and cons of each. It would help the student to think of reaction mechanisms in terms of the visualizable encounters of atoms and molecules, if you supply alternative mechanisms.

Chapter 22 is a lengthy treatment of biochemistry, a topic that my students have usually voted the most interesting in the course. The chapter has far more detail than the student is expected to master. However, it contains several very important concepts, which should be presented in a framework of real structures and reactions, even though students will not learn and retain these structures and reactions. The chapter is unique among the others in that it contains sections that are identified as optional material. These sections include detailed analyses of some important life processes, the degree of detail exceeding that normally presented in an introductory text. It is my intention that students use these sections as they see fit to help them understand the processes discussed. As a minimum they will see the types of mo-

lecular structures and chemical reactions involved. As a maximum they can verify, detail for detail, important statements that are made about life processes.

The length of the text has been kept to one which can be completely covered in two semesters or three quarters. This is particularly important in a text that is as highly structured as this one. If students are to accept nothing on faith, chapters must build on each other and the last chapters are a culmination of the whole development.

The traditional drawback of the thematic approach, exemplified by this text, is the inflexibility of textual presentation. I have tried to minimize this problem by organizing the chapters in an order which I believe is most common in introductory courses.

The problems at the ends of chapters emphasize explanations and predictions rather than substitutions into equations, although some of the latter are included to acquaint students with units and their uses. Particularly challenging problems are indicated by asterisks. The problems are rarely repetitive and their numbering follows the order of topic development in each chapter. Numerical answers and other answers which are not lengthy are included after the text's appendices. Detailed solutions to all problems are included in the instructor's manual. It is my hope that those problems which are particularly illustrative of important concepts be discussed in class.

Foreword to the Student

The first question to be addressed in any course is, "What can you, the student, expect to obtain from this course?" The answer in the case of a course in which this text is used is that you may expect to be able to view the properties of matter in essentially the same way as the practicing chemist does. This, of course, raises a second question. "What is unique about the way in which the practicing chemist views the properties of matter?" When observing a steel bar, for example, a chemist might note that it is a solid at room temperature; it is shiny, hard, and a good conductor of heat and electricity; it undergoes chemical changes (e.g., it rusts when exposed to air and water). The practicing chemist can account for these properties, although it is by no means obvious to the nonchemist what it is about the steel that gives it such properties and makes it different from wood.

The ability of chemists to account for the properties of matter lies in their ability to construct **models** of any given substance. These models are mental images of the tiny units of which all matter is composed. Mentally, chemists visualize atoms and molecules, their structures and their motions, and picture these structures and motions giving rise to measurable properties.

I like to view models of matter as abstract paintings. Any given substance is incredibly complex in its structure, and if we are to understand even one facet of the substance's behavior we must focus on that one facet, almost to the exclusion of all others. This is what the abstract artist does, and it is also what the scientist does in constructing models. The result in both cases is a distorted view of the object as a whole but, hopefully, one that provides greater insight into the particular facet under study. Thus, in the case of the steel bar we would employ a different mental picture in considering rusting than we would in considering hardness. However, the two pictures would not be contradictory, any more than two artists' conceptions of the same object would be contradictory.

Because models are actually inexact views of matter, two different scientists will often employ different models in viewing the same phenomenon. There is no such thing as a correct model. There are only models with varying degrees of usefulness. In this text I have tried to introduce those models most commonly employed by chemists. Your instructor will undoubtedly wish to introduce his or her own models—views of certain objects and processes. It is most desirable that you also be an active participant in this process of model building. The process is one of the most stimulating activities of a scientist, and you can participate in it even as your scientific background is only beginning to develop. The problems at the ends of chap-

ters place a strong emphasis on model development, as well as on the explanation of phenomena in terms of those models.

The first six chapters of the text are devoted to building up pictures of atoms and molecules, their structures, and something of their motions. Chapters 7, 8, 9, 10, and 11 are largely concerned with the application of the models previously developed to the chemical behavior of matter in its myriad of forms. Our models allow us both to understand the behavior of matter and to predict that behavior in many cases. Predictive ability is one of the most desirable skills you can acquire.

Chapters 12, 13, and 14 are concerned with physical properties. These chapters contain a mixture of model development and application. Chapters 15 and 16 are devoted to the development of a general model for spontaneous change. In Chapters 17, 18, 19, and 20 this model is applied to a wide variety of physical and chemical changes. Chapter 21 deals with the rate at which chemical changes occur. We shall want to be able to see precisely why a given change occurs rapidly or slowly and to be able to devise ways to speed it up or slow it down. Chapter 22 is a lengthy application of many of our models to the chemistry of life processes.

If I may be permitted to rephrase the answer to the question which opened this foreword, the aim in this text is to have the subject of chemistry make sense to you in physical terms which you can visualize.

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