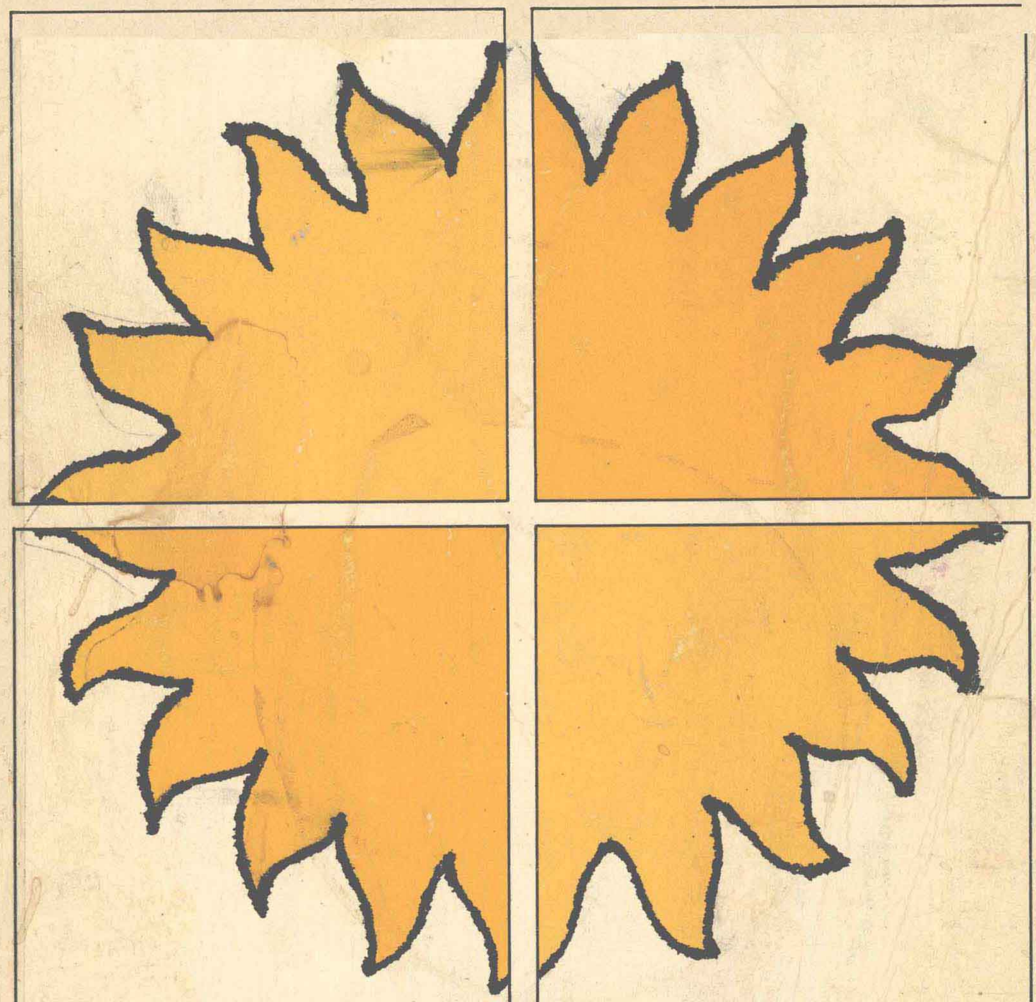
Energetics, Kinetics, and Life

An Ecological Approach



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Energetics, Kinetics, and Life: An Ecological Approach

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Preface

How can anyone justify writing another book on chemical thermodynamics and kinetics when the field is apparently so overpopulated? My answer to this very relevant question lies in the groups to which this book is addressed and in the philosophy of approach to the subject.

The purpose of this book is not to teach the details of chemical thermodynamics and kinetics—but to give the reader an "intuitive" and "qualitative" feel for these important subjects and to illustrate their wide applicability. Particular emphasis is placed on the relationships of these subjects to the environmental problems of pollution and overpopulation. It is hoped that this book will prove useful to several groups: nonscience majors taking introductory courses in science, science majors taking introductory courses in chemistry and biology, high school students in advanced science courses, and interested laymen.

As a chemist, I have been concerned for some time about the teaching of thermodynamics and kinetics to undergraduate chemistry majors. Although we appear to be exposing freshmen students to heavy doses of these subjects, I have the feeling that the students don't know why thermodynamics and kinetics are important or relevant. They respond to our force-feeding but, too frequently, they do not see the woods for the trees. It is the purpose of this book to provide such an overview, so that students may profit more from the excellent and more quantitative approaches of authors such as Mahan and Nash.

I am also concerned about the biology major and premedical student. It is now essential that they have an understanding of thermodynamic and kinetic ideas and their application to life processes. Hopefully, this introductory approach can allow and encourage them to study more advanced treatments.

The science education of the nonscience major is of equal importance. My experience indicates that the most fruitful approach for nonscience majors (and for science majors) is to deal in depth with a small number of scientific concepts that are applicable to a number of disciplines and problems—as opposed to bewildering the student with an array of scientific facts and ideas. We are slowly beginning to realize that "less may be more." The concepts of energy and entropy provide two of the most interesting and widely applicable themes for illustrating the nature and scope of science.

My second argument has to do with the approach to teaching these subjects—in particular, the area of chemical thermodynamics. There is considerable debate as to whether chemical thermodynamics should be presented *classically* or *statistically*. The approach used in this book is neither classical nor statistical, but rather, a blend of both. Since both approaches lead essentially to the same ideas, a careful blend of the parts of each that lend themselves to an "intuitive" understanding seems to be a legitimate and useful pedagogical approach.

The approach to thermodynamics in this book is to go directly to Gibbs Free Energy (ΔG), rather than building up to it via heat work, Carnot cycles, and the like. In effect this approach is an attempt to "get to the promised land without going through the desert." A true appreciation of thermodynamics requires a disciplined trek "through the desert," but, before one undertakes such a journey, it helps to have not only a general sense of direction but an understanding that the trip is worthwhile.

Finally, there is a need for more books that discuss chemical dynamics (energetics and kinetics) as a unified way of studying chemical reactions. The student should understand that a reaction will occur only if it is both thermodynamically and kinetically feasible.

This book is a "popular" approach and necessarily I have used a minimum of mathematics. No calculus whatsoever is used. The only mathematics needed includes simple arithmetic, solving of very simple equations ($y=ax$), and some appreciation of exponential numbers.

I am deeply indebted to the many scientists who have provided information and inspiration upon which much of this book is based. It is impossible to acknowledge all of these, but those listed in the bibliography at the end of the book were particularly helpful.

I also wish to thank all those students, professors, and reviewers who have taken the time to point out errors and suggest improvements. The errors and faults remaining are mine, not theirs. I am particularly indebted to Professor Donald H. Andrews, Professor Emeritus, Johns Hopkins University, and now Distinguished Professor of Biophysics, Florida-Atlantic University, Edward Kormondy, Director of the Commission on Undergraduate Education in the Biological Sciences, Professors Frank L. Lambert, Occidental College, P. P. Feeny, Cornell University, Jay M. Anderson, Bryn-Mawr College, David and Joyce Roderick of Foothill College and San Jose City College, and two of my colleagues at St. Andrews Presbyterian College, Donald G. Barnes and David E. Wetmore. Finally, my sincere thanks go to Mrs. Ruth Y. Wetmore for her patience and skill in converting my hieroglyphics into the final manuscript and to Mr. Jack C. Carey of Wadsworth Publishing Company for his encouragement and help in preparing this book.

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Chapter 1

Introduction

1-1 Why Study Energetics and Kinetics?

Why is your room normally in a chaotic state?

Why is it absurd to speak of a pollution-free environment, car, or product?

Can you cool a hot kitchen by opening the refrigerator door?

Why is it essentially impossible for most people in the world to eat steak?

Hydrogen and oxygen gases are mixed in a bottle and nothing happens. A match is lit near the mouth of the bottle and an explosion occurs. Why?

Why should you thank a green plant and an alligator today and every day?

How did our present atmosphere of nitrogen and oxygen evolve?

Which language contains more information per word—English, German, Latin, or Greek?

Why will the production of more food not solve the overpopulation problem?

A lump of sugar held in your hand at body temperature will not decompose, but if swallowed it is "burned" readily. Why?

How can you improve your study habits?

Is there a technological solution to pollution?

Hydrogen and bromine gases mixed in a brown bottle do not react, but when mixed in a clear bottle they can explode. Why?

How can we tell the direction of flow of time?

Which fuel provides more energy per pound—gasoline or coal?

How might we reduce air pollution from the deadly chemicals, sulfur dioxide and the oxides of nitrogen?

How would you organize a company or a production line for greater efficiency?

How do poisons like cyanide kill and how do sulfa drugs heal?

Can the underdeveloped countries become developed?

How were the chemicals necessary for life on this planet originally formed?

Will carbon monoxide poisoning from automobiles on a busy downtown street be more severe on a hot day or a cold day?

Why can the United States be considered as the most overpopulated country in the world?

Can science provide us with any ethical rules?

Answers or at least insights to these and many other questions can be obtained by an understanding of chemical energetics and kinetics or chemical dynamics. This book is designed to provide you with an "intuitive" and "qualitative" feel for the kinetics of chemical processes and for two great laws of science—the first and second laws of thermodynamics—and to show their relationships to life processes.

Fortunately, the basic ideas of energetics and kinetics are surprisingly simple, and they require no specialized knowledge of chemistry, biology, physics, or mathematics to see many of their applications. Only the simplest mathematics will be used throughout this text, and if you can add, multiply, divide, subtract, and solve the problem below, you will have no problem with the mathematics in this book.

Study Question 1-1[1] How many cubic feet of dirt are in a hole that is 6 feet deep, 4 feet wide, and 10 feet long?

If your answer to Study Question 1-1 was 240 cubic feet, any difficulties you may have will be verbal, not mathematical, because a more careful analysis of the problem will reveal that the correct answer is *not* 240 cubic feet.

1-2 How Can We Describe the Universe?

Many people have the vague feeling that science is just a meaningless assortment of data and information. Scientists do gather data, but their primary concern is with organizing these data into meaningful patterns. Facts are merely stepping-stones to theories and scientific laws. We can begin our study by asking how the data and concepts of energetics and kinetics fit into our overall scheme of the physical universe.

In beginning any study of the physical universe, we can get our bearings by asking, "Am I studying something that is very small, very large, or of ordinary size?" The physical universe is, then, divided into three domains: the *micro world* of the very small (atoms, molecules, and subatomic particles), the *macro world* of everyday objects and events (baseballs, grains of sand, people, and so forth) and the *supermacro*, or *cosmic*, *world* of the very large (planets and galaxies), as summarized in Figure 1-1. The "normal" macro world is experienced directly with our senses, while the micro and supermacro worlds are for the most part experienced indirectly.

Consider the concept of length, or distance. What does it mean to say that the length of a book is 10 inches, or 25.4 centimeters? In effect, it means that we take a ruler that has been marked off in internationally-agreed-upon units of macro distance

[1] Throughout each chapter is a series of study questions designed to help you think about the material—to use it just after you have read it. In a sense they form a sort of programmed learning sequence that can be used to test your understanding of the material. These study questions will be of greater value if you answer them while proceeding through each chapter. Answers to most of these questions can be found at the end of the book.

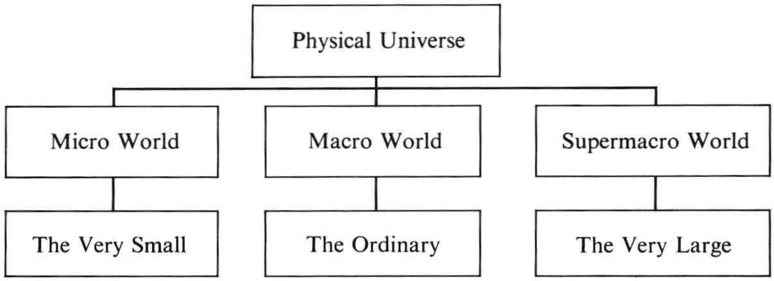

Figure 1-1 Classification of the Universe According to Relative Size.

(inches or centimeters) and determine that the book represents 10 or 25.4 of these units.

But what does it mean to say that the diameter of an atom is 10^{-8} cm (0.00000001 cm) or that the distance to the sun is 93 million miles? These micro and supermacro ideas of length, or distance, are quite different from our everyday distance concepts. To say that the diameter of an atom is 10^{-8} cm does not mean that someone took a very tiny ruler and measured the distance across the atom. Instead we measure this "distance" by indirect methods—for example, by analyzing what happens to matter when it is exposed to X-rays. Obviously no one has measured the distance to the sun using a yardstick. Again, indirect methods, such as using the velocity of light, enable us to measure very long distances.

We eat, live, and breathe in the macro world. What we call common sense[2] or logical usually means logical on a macro scale. One problem in studying the micro world of the very small or the supermacro world of the very large is that we tend to superimpose our macro world logic on them. Sometimes the answers we get thus seem "strange" or "illogical."

Study Question 1-2 Could you recall or "design" instruments and other devices used to enable us to obtain indirect evidence of phenomena in the micro and supermacro worlds?

It is more useful to break these three domains into sublevels. One approach is to classify matter in the universe according to *levels of organization.* Matter in the universe is found in various levels of organization, with each level an aggregate, or group, of the units of matter at the preceding level, as shown in Figure 1-2. Another classification describes various levels of organization of matter as either *living* or *nonliving.* Although some things can obviously be classified as either living or nonliving, scientists are still trying to define what is meant by life, and there is a borderline of uncertainty, as shown in Figure 1-2.

[2] Common sense is sometimes described as the good sense that horses have not to bet on people.

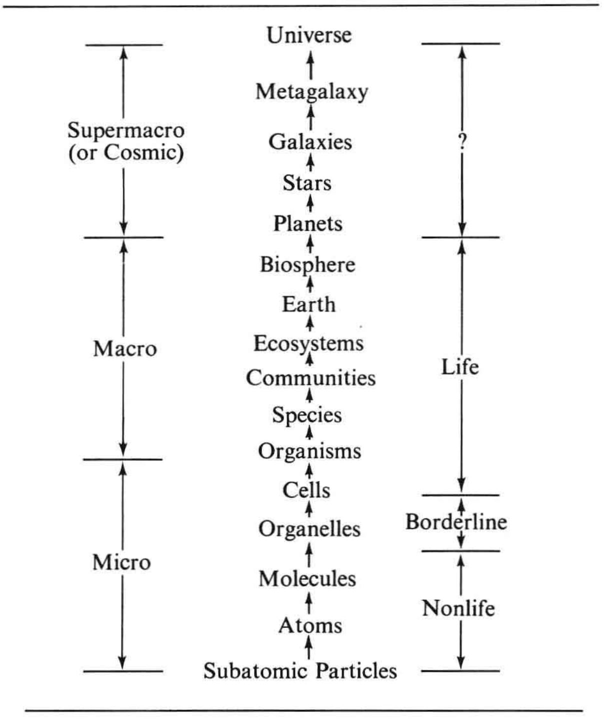

Figure 1-2 Levels of Organization of Matter.

Study Question 1-3 What is your definition of life? List carefully the qualities or criteria you would use to determine whether something is living or nonliving. Try to define some borderline cases. What is your definition of death?

The span of size and time from the extremely small world of subatomic particles and events to the very large domain of galaxies and cosmic time is summarized in Figure 1-3.

Using exponential numbers (powers of ten) to express quantities is convenient but deceptive. We tend to underestimate the vast differences between such numbers. Some implications of these differences are indicated in Figure 1-4.

Study Question 1-4 Exponential numbers sometimes represent people. It is estimated that from 1×10^7 to 2×10^7, or 10 to 20 million, people[3] now die each year

[3] P. R. Ehrlich and A. H. Ehrlich, *Population, Resources, Environment*, W. H. Freeman & Co., 1970. A lower but still horrifying estimate of the starvation rate is 4.5×10^6, or 4.5 million people per year. People speak of massive famines that may occur in the 1970's, 1980's, or 1990's. Yet a case can be made for the fact that we already have the greatest famine in the world's history, even using this lower estimate. Apparently we conveniently classify starvation as a famine only if it occurs in a particular country rather than on a global basis.

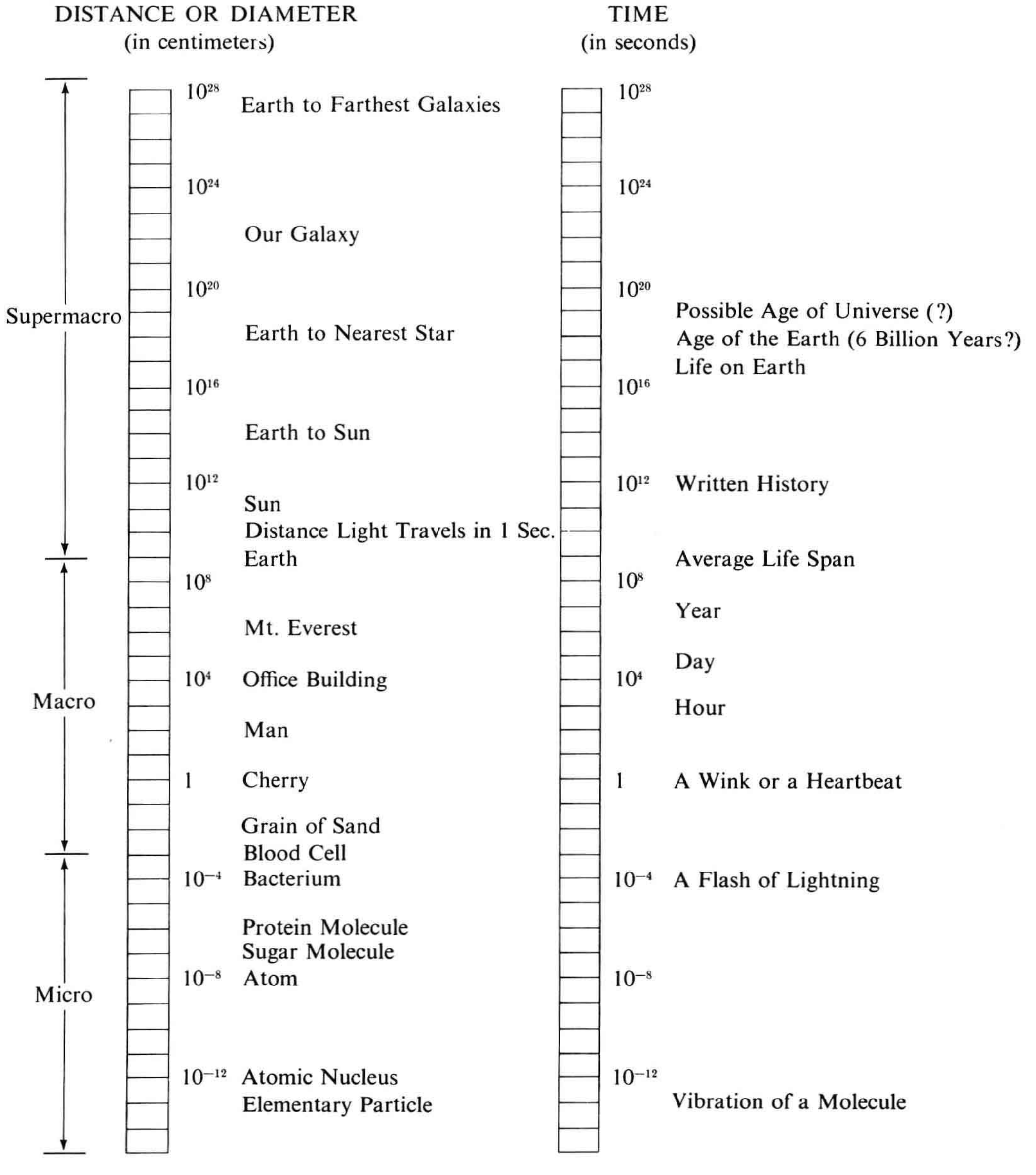

Figure 1-3 Scale of Distance and Time in the Universe.

10^6	One million —Number of distinct types of animals known to have evolved
10^9	One billion
3.5×10^9	Three and one-half billion —Number of people on earth —Number of heart beats in a lifetime —Number of cells in a man's brain
10^{11}	One-hundred billion —Number of stars in our galaxy (About 30 stars for each person on the earth) —Number of galaxies in the universe
10^{12}	One trillion —Number of dollars spent in U.S. in 1970 (Gross National Product)
10^{13}	Ten trillion —Number of cells in the human body
10^{14}	One-hundred trillion —Every dollar spent in U.S. for everything between 1829–1970 (our Gross National Product for the past 140 years)
10^{15}	One quadrillion
10^{21}	Mass of the Earth's atmosphere in grams
10^{23}	—Number of molecules in a teaspoon of water —Number of red corpuscles on earth —Number of stars and other heavenly bodies in the observable universe
10^{80}	—Number of atoms in the universe

Figure 1-4 Implications of Some Exponential Numbers (all values are approximate).

from starvation, malnutrition, or diseases resulting from malnutrition. Half of these people are children under five.

a. Taking the average casualty rate due to overpopulation as 15 million (1.5×10^7), calculate the number of human beings who died of starvation during your lunch hour today.
b. Calculate the number dying each day. Each week.
c. During the past 500 years there have been over 250 wars (one every two years on the average) with battlefield deaths of approximately 35 million, or 3.5×10^7. How many years does it take for the present starvation rate to equal the total deaths from all wars fought during the past 500 years?
d. The number of Americans killed in *all* of our wars is approximately 570,000, or 5.7×10^5. How many weeks does it take to equal this figure as a result of overpopulation?

Behind these appalling figures are unique individual human beings—not numbers —not things.

1-3 The Portion of the Universe to be Studied

How do energetics and kinetics fit into our overall classification of the physical universe according to relative size (Figure 1-1)? We will be concerned with chemical behavior in the *macro* world. Theoretical chemistry can be divided into three major categories: *chemical statics, chemical dynamics*, and *statistical mechanics.*

Look at a lump of sugar. The chemist is concerned with two questions: (1) what is its structure—that is, what are its basic units and how are they arranged? and (2) what holds these structural units together (chemical bonding)? These two questions of structure and bonding are the concern of chemical statics. It is a study of the micro world of individual atoms and molecules, and *quantum mechanics* is the branch of theoretical chemistry devoted to answering these questions.

The subject of this book is chemical dynamics, a study of chemical reactions at the macro level. It, in turn, is divided into two branches—chemical energetics and chemical kinetics.

Imagine mixing two colorless gases in a quart bottle. After several minutes a reddish color develops and the bottle has become warm. Why is heat given off ? How much heat is given off ? Why did it take several minutes for the reaction to occur? How did the two chemicals react to produce the red color?

Chemical energetics, or *chemical thermodynamics*,[4] is concerned with the energy (or heat) changes that occur. The branch dealing with the rate, or speed, of reaction and the stepwise mechanism, or path, by which a given reaction occurs is known as *chemical kinetics.* The general distinction between chemical thermodynamics and kinetics can be illustrated by the following analogy.

Imagine a person standing in the middle of the room with a stepladder beside him. You close your eyes and the person is now standing on the third rung of the ladder. Thermodynamics is concerned primarily with the difference in energy between the initial state (floor) and the final state (ladder), while chemical kinetics is concerned with the exact path, or mechanism, the person used to get from the initial state (floor) to the final state (ladder) and the speed, or rate, at which the change occurred.

A third branch of theoretical chemistry, called statistical mechanics, involves the calculation of the values of macroscopic properties by averaging the microscopic values. Statistical mechanics provides the bridge between the micro world of quantum mechanics and the macro world of chemical dynamics, as shown in Figure 1-5. These various branches of theoretical chemistry are summarized in Figure 1-6.

The thermodynamic properties of matter that are observed and measured are properties of aggregates, containing enormous numbers of atoms or molecules. These aggregates exist under dynamic conditions; atoms and molecules are moving at extremely high velocities, undergoing trillions of collisions each second, and they are subject to drastic "environmental" changes due to changes in temperature or pressure or to the addition or removal of vast "populations" of atoms and molecules.

[4] Historically, the term thermodynamics, as the prefix thermo implies, developed from a study of only one form of energy—heat. Since we are concerned with all forms of energy, the field is more aptly termed energetics, or chemical energetics. In this book these two names are used interchangeably.

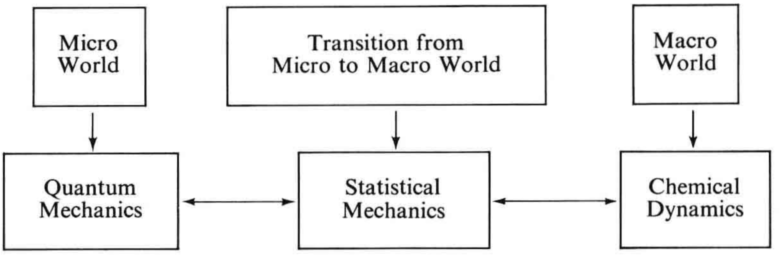

Figure 1-5 Classification According to Levels of Organization of Matter.

We would not expect to get an accurate view of American society by interviewing and thoroughly studying one American. By analogy the macro behavior and properties of aggregates of atoms or molecules cannot be adequately described and predicted from an understanding of the behavior of an individual atom or molecule. A quantum mechanical analysis of the microcosm will provide useful and necessary information but not sufficient information to describe macroscopic properties.

One approach to understanding American society would be to study and interview each American and then average the results statistically. Similarly, one could, in principle, determine the energy and position of all of the individual atoms and molecules in an aggregate of matter and then average the values to describe aggregate properties. This deterministic goal has been shown not to be feasible on experimental, theoretical, and practical grounds.

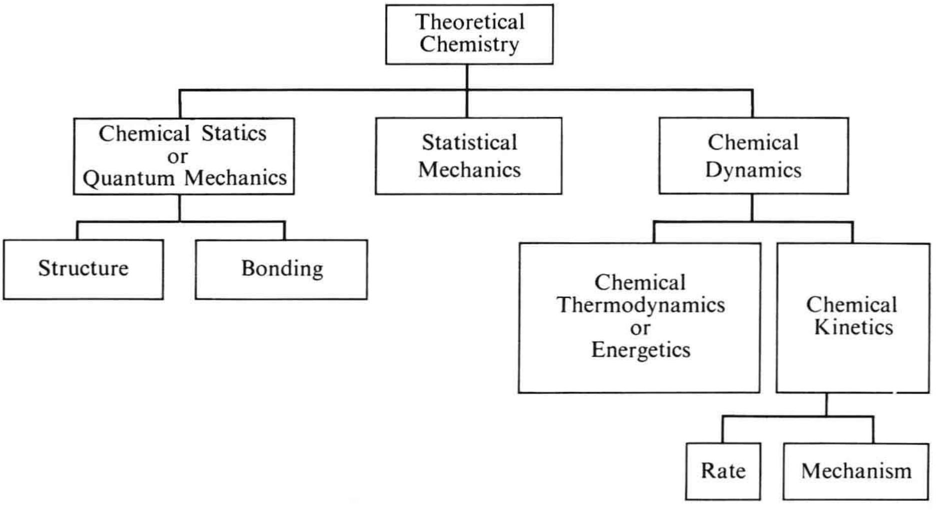

Figure 1-6 Major Branches of Theoretical Chemistry.

Experimentally and theoretically, according to interpretations of *Heisenberg's Uncertainty Principle*, we cannot obtain accurate and precise information simultaneously about both the position and velocity of very small particles such as electrons, atoms, and molecules. In other words, if we know the exact position of an electron, we have essentially no idea of its velocity; and if we determine its velocity very accurately, we do not know where it is located. One explanation for this is that in order to "look" at an atom or electron, we have to put so much energy into the system that we drastically change what we are trying to measure. In effect we are like an elephant trying to use his foot to pick up a particular marble from a pile of marbles. By putting his big foot into the system he scatters the marbles, so that the position of the particular marble has been changed radically.

Even if we could obtain complete and accurate information about atoms and molecules, the task of calculating macro properties from micro data could not be carried out on a practical basis. Suppose we try solving this problem for a tiny drop of water weighing approximately one thousandth of a gram. Such a drop would contain about 10^{20} molecules of water; by averaging the motions of this number of molecules, we could predict the properties of the water drop. A fast digital computer can carry out a simple mathematical operation (addition or subtraction) in one millionth of a second. Assuming (very optimistically) that the computer could calculate the motion of a single water molecule in this same time, then to calculate the motions of all 10^{20} molecules would take about 3 million years and would cost about 65 billion dollars in computer time—and this is for only one tiny drop of water.

The problem is really not so bad as this argument seems to suggest. At the macro level we do not make measurements on individual atoms or molecules, but on aggregates containing myriad atoms or molecules. For example, the pressure of the gas in an automobile tire depends on the average number of molecules hitting a particular area in a specified time and on the average energy of each collision. The temperature of a substance is a measure of the average energy of motion of its individual atoms, and the color of a substance depends on the average number of quanta or "energy lumps" of light of different wavelengths that it absorbs. Fortunately, chemical thermodynamics is concerned only with the difference in average energy values between the initial reactant chemicals and the final products. Because thermodynamic measurements of the initial and final stages can be made directly, it is probably the most successful branch of chemistry in providing the information we need to predict physical and chemical changes.

1-4 The Seven Fundamental Questions of Chemical Dynamics

Imagine that you have graduated from college and you are now a multimillionaire. You are actively concerned to use your wealth wisely to improve the lot of mankind rather than in buying gadgets and other trivia. In 1980, a young scientist approaches you with the idea of investing 20 million dollars in a plant for making a chemical substitute for food. If successful, this venture might enable you to solve the food problem in an overpopulated, starving world. What questions would you want to ask