CHEMISTRY, MATTER, AND THE UNIVERSE

Richard E. Dickerson · Irving Geis

Preface

In his *Voices of Silence*, André Malraux characterizes modern books of art reproductions as "Museums without Walls," lifting the observer out of the confines of any one museum and showing him the entire world of art. In the same spirit, this book attempts to combine text and illustrations to remove chemistry from the laboratory and present "Chemistry without Walls." The proper setting for the study of chemistry is the entire material universe, living and nonliving, and this is the motivation behind the writing of this book.

Chemistry sometimes is taught as a laboratory-oriented science, in which a practitioner at the bench adds one substance to another, and precipitates a third substance that subsequently is analyzed or used. Chemistry then becomes narrowed down to an intellectual exercise carried out by human beings. This is one aspect of the subject, it is true, but it bears the same relationship to the chemistry of this book as an exercise machine does to bicycle touring. Everything is chemistry. There is no change that occurs in our material universe that does not involve chemical processes. At one extreme, nuclear reactions can be described in chemical terms if proper account is taken of the conversion of mass to energy. At the other extreme, the activities of living organisms have their foundations in chemical processes. One of the most exciting future areas for study will be that of discovering in more detail how chemical reactions lead to the observed behavior of living organisms, and how these complex, living chemical systems evolved on our planet (and perhaps others).

Modern chemistry is essentially pictorial. Most of our success in explaining how chemical reactions take place has come from a knowledge of the structures of molecules in three dimensions, and the arrangements of electrons in molecules. Although the calculations of modern theoretical chemistry can be complicated, they are based firmly on models of molecules and reactions. The chemist combines information from many sources, and uses his imagination to "see" molecules that are below the resolving power of the finest microscope.

A one-line chemical equation can conjure up images of moving and colliding molecules in the mind of an experienced chemist, but to a beginner it can conceal as much as it reveals. An introductory chemistry textbook should illustrate in clear detail exactly what these shorthand equations really symbolize. At the beginning level, the guiding principle should be, "When in doubt, draw it out." An ideal combination of authors would be a chemist who understands the art of graphic presentation, and an illustrator who understands chemistry. This is the combination that we have tried to put together in this book.

The format of *Chemistry, Matter, and the Universe* is unusual. Every important chemical concept is illustrated, with an average of more than a figure per page, yet the book is not "illustrated" at all in the traditional sense. The writer and artist planned this book together as coauthors from the very first stages, discussing each two-page layout extensively from a chapter outline before either text or drawings existed. What were the key ideas of each chapter, and how could they be expressed pictorially? Every illustration performs some pedagogical function, even the outrageous cartoons. Drawings and narrative were planned together to form an organic whole, which is why no figure numbers are used. When the words describe an idea, the graphic realization of that idea is in front of the reader as reinforcement. This has made the book more laborious to produce, but has made the finished product a better teaching device.

Chemistry, Matter, and the Universe is intended primarily for a two-semester course, although it has been designed so it can be used for several shorter courses if desired. Each chapter in this book builds on what has come before. Although it is not easy to skip from one chapter to another, it is easy to progress steadily through the book but to stop at any one of several points. The first ten chapters are devoted to a qualitative and descriptive look at the chemical elements, the periodic table, molecular structure and bonding, and the chemical nature of our world. These chapters provide suitable material for a ten- or twelve-week course in chemistry for liberal arts or humanities students, and should leave the reader with at least an appreciation of the chemical nature of our universe. Chapters 11 through 17 introduce chemistry as a quantitative science, with discussions of mass, energy, entropy, chemical equilibrium, and the rates and mechanisms of reaction. Together, these seventeen chapters can be used in a half-year or two-term chemistry course for nonmajors.

After a shift in perspective in Chapter 18, the final eight chapters lead the reader into the world of carbon compounds, macromolecules, and living organisms. Blaise Pascal described the universe as extending between two infinities, the infinitely large and the infinitely small; or in the language of science, from galaxies to nuclei. To these limits Teilhard de Chardin added a third: the infinitely complex. Life would be impossible without complex networks of reactions involving macromolecules, and of all the elements known, only carbon appears to be capable of building such molecules. Chemical systems complicated enough to show the properties of life must be organized both in space and in time; they must possess both a structure and a metabolism. The study of carbon-based life, and the question of whether it is the only possible form of life, are subjects that our recent advances in space exploration have transformed from philosophy into experimental chemistry. *Chemistry, Matter, and the Universe* ends with what the authors believe to be the most exciting great challenge facing chemistry: the problem of *life.*

In the traditional nomenclature, Chapters 1–10 would be described as inorganic chemistry, Chapters 11–17 as physical chemistry, Chapters 18–21 as organic chemistry, and Chapters 22–26 as biochemistry. Although this is true in principle, we try to show that these categories overlap, and are more pedagogical than real. Chemistry should be thought of as a unified whole, and in the most general terms as a framework for explaining the world in which we live, and from which we have evolved.

January 1976

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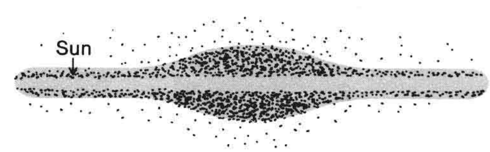
◀ *The Whirlpool Galaxy (Messier 51), one of billions of galaxies in the universe. Courtesy of The Hale Observatories*

CHAPTER 1

The View From a Distant Universe

Many reasons can be given for studying chemistry, ranging from, "It is an intellectual adventure," to "I can make a good living at it," or even "It is required for graduation." But the most valid response is simple. Chemistry is the study of how matter behaves. We have only one world in which to live. If we want to know how we can change it and what we cannot alter, or even simply to appreciate what we already have, then we must know how it works. Chemistry is the subject that tells us this. Physics may teach us fundamental facts about elementary particles, matter, and energy, but it stops short of drawing conclusions about how the different kinds of matter around us change and react. Biology describes the large-scale behavior of organisms, which at their core are elaborate chemical systems. Some of the most fruitful advances in biology in the past two decades have come from a thoroughly chemical approach. If we can expand the concept of chemistry beyond our present limited and inadequate knowledge, then biology fundamentally is the highest form of applied chemistry. If chemistry is the study of how matter behaves, we must not forget that we, ourselves, are an integral part of this material world.

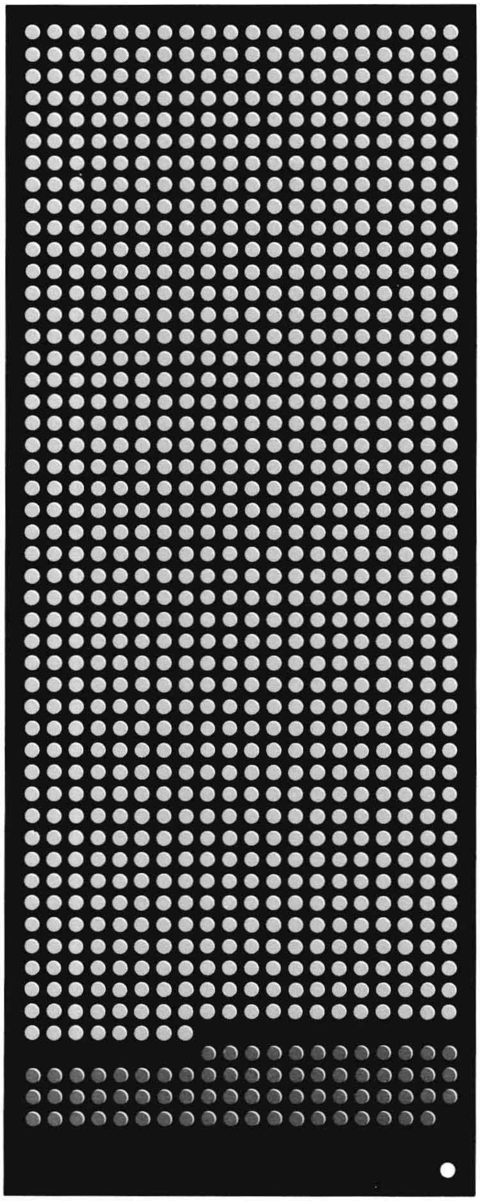
If we look at the world around us with a beginner's eye, it seems terrifyingly complex. Everything material is chemical, and everything is reacting, on one time scale or another. How can we possibly keep track of what is going on around us, let alone understand the principles involved? The chemical reactions that go on in our world are more tightly interlocked than was realized only a few years ago. How can we manipulate these reactions to our own advantage, and how can we be sure that if we change things at one place, this will not create unforeseen troubles somewhere else? These are real problems, and as the population of this planet has increased and the resources available recognized as finite, a great many people have come to ponder such problems. Chemistry, considered as a technique for managing a small planet,



Edge view of our own galaxy, the Milky Way, which has approximately 200 billion stars. One of these stars, 30,000 light years from the center, is our Sun.

seems much more formidable now than a few years ago when it was regarded only as a method of making new plastics and fuels. If you want to learn something about chemistry today, where do you begin?

The easiest way to begin is to step back a few million light years, and take a more detached view of the material universe. Some of the complexities then smooth out and the scene becomes simpler. What we see are many glowing bodies—stars—organized into star clusters, galaxies, and clusters of galaxies, extending to the outermost reaches of the universe. In our field of view, 999 out of 1000 atoms are either of the two lightest chemical elements—hydrogen or helium—with only a lone one-in-a-thousand being a heavier atom (left). All of the elements, compounds, and substances that loom so large on our planet are nothing more than "minor impurities" in the universe as a whole. The dust clouds between stars are predominately hydrogen, although careful examination will show a few other simple molecules. The heavier elements are found scattered in these dust clouds, in the centers of stars, and in the cold satellites such as Earth, which travel virtually undetected around some of the stars. On this scale, the material universe mainly is a world of hydrogen and helium.



Out of 1000 atoms in the universe, 999 are either hydrogen (light dots) or helium (color dots). Only one atom out of a thousand is one of the heavier elements (white dot).

A SIMPLE WORLD

Things are simpler in such a world. The same pieces that make up all atoms—protons, neutrons, and electrons—also make up hydrogen and helium, but in an especially simple way. In the following chapter, we will begin the study of atomic structure with a detailed discussion of hydrogen and helium. The reactions that these elements by themselves can undergo are simple and few. Four hydrogen atoms can fuse to make a helium atom, and the stars are fueled by the energy from this reaction. If the temperature at the center of a star is high enough, hydrogen fusion can be followed by helium fusion, and successive reactions, to produce the heavier elements. The heaviest of these elements have a tendency to break down again spontaneously, in the process of atomic fission.

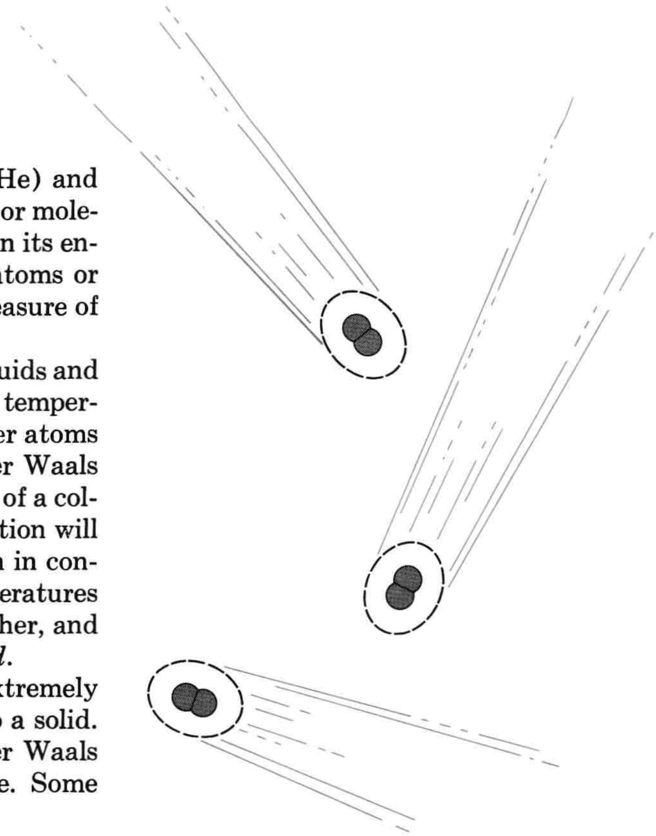
These examples all are *nuclear reactions,* in which one element is changed into another element by altering the structure of its nucleus. Nuclear reactions ordinarily are considered as part of the realm of physics, not chemistry. At far lower temperatures, closer to those of our own planet, the first true chemical reactions can take place, in which atoms come together, separate, and associate with other atoms, without altering their nuclear structures and their own identities. If two hydrogen atoms are brought together at a moderate temperature, they will bind to one another to form an H—H or H_2 molecule. Helium atoms do not behave in this way. When they collide, they bounce away unchanged and show little tendency to associate. The concept of the *chemical bond* that holds H atoms together, but not those of He, is the most important single idea in chemistry. When do bonds form between atoms, and why, and in what directions? How do these bonds determine how the resulting chemical substances behave?

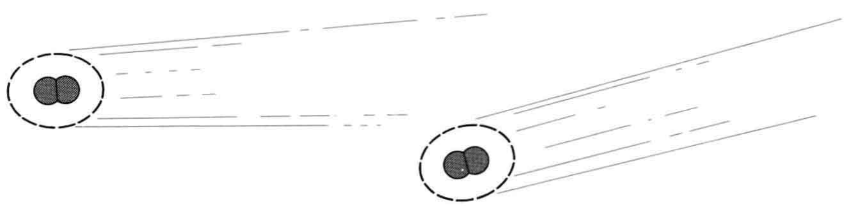
THE STATES OF MATTER

At temperatures similar to those on our planet, helium atoms (He) and hydrogen molecules (H_2) move about individually. Each atom or molecule in a *gas* moves independently with a speed that depends on its energy of motion. The higher the temperature, the faster the atoms or molecules of a gas move; and temperature in fact is a direct measure of the average energy of the molecules of a gas.

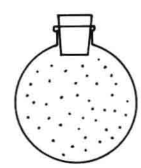
Gases are not the only form of matter in the universe. Liquids and solids also exist, especially with larger molecules and at lower temperatures. Every atom or molecule has a weak attraction for other atoms and molecules, or a "stickiness" on contact, known as van der Waals attraction. If the temperature is low and the energy of motion of a collection of molecules is small enough, this van der Waals attraction will hold the molecules together in a *liquid*. The molecules remain in contact but are free to slide past one another. At even lower temperatures and molecular energies, this freedom of motion is reduced further, and the molecules become locked into the frozen geometry of a *solid*.

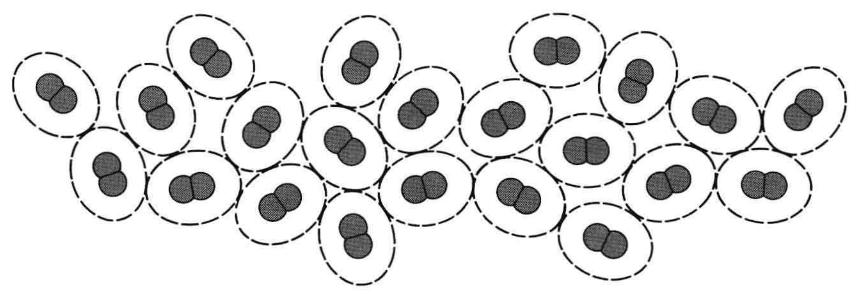
Tiny particles such as He and H_2 must be cooled to extremely low temperatures before they condense to a liquid or freeze to a solid. Larger molecules with more surface area have greater van der Waals "stickiness," and occur as liquids or solids at room temperature. Some



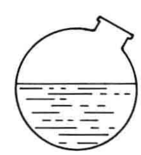


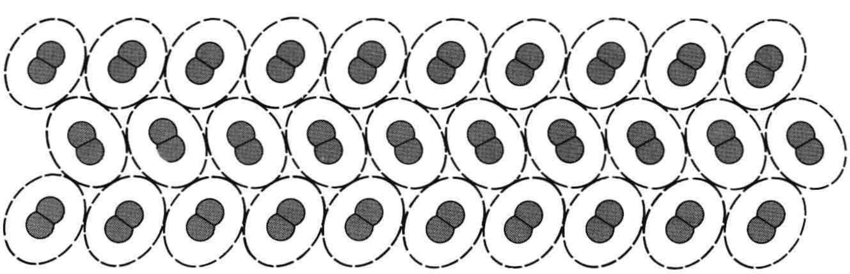
GAS: In a gas the individual molecules move freely through space, and do not touch except at the moments of collision, from which they rebound. A gas has neither a fixed shape nor a fixed volume; it adapts to the shape of its container and can be expanded or compressed.



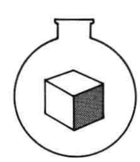


LIQUID: The molecules of a liquid are in contact with one another, but have enough energy to slip past one another and change their positions. Therefore, a liquid has a relatively fixed volume, but no definite shape.





SOLID: In a crystalline solid the molecules are packed against one another in a regular pattern, and do not have enough energy to break that pattern and slide from one place to another. Crystals have a definite volume and shape, and work must be done to deform or break them.



THE CONE NEBULA: The dark cone is a cloud of gas, mainly hydrogen, which obscures the light of the more luminous stars behind. New stars condense from such dark gas clouds. Courtesy of The Hale Observatories.

atoms can gain or lose electrons to become electrically charged *ions*. These ions are held together in solids known as salts by the electrostatic forces between ions of opposite charge. After the study of bond-making-and-breaking reactions that molecules can undergo, one of the most important areas of chemistry is to explain the behavior and properties of substances in terms of the interactions between the molecules of which they are made.

THE BIOGRAPHY OF A UNIVERSE

The universe is very far from being chemically uniform, which is a result of the way the universe developed. The earliest stars, perhaps thirteen billion years ago, condensed from a thin gas of hydrogen. As a star condensed, the heat generated in its center triggered the hydrogen fusion process, in which four hydrogen nuclei coalesce to a helium nucleus with the release of a large amount of energy. The star "switched on." In big stars with sufficient ability to retain heat, higher temperatures in the center led to the successive triggering of helium fusion and then to reactions producing the heavier elements. The stars were the "crucibles" in which the heavier elements were formed. Supernova explosions scattered these elements through the cosmos as debris from which, in time, the second-generation suns such as our own formed.

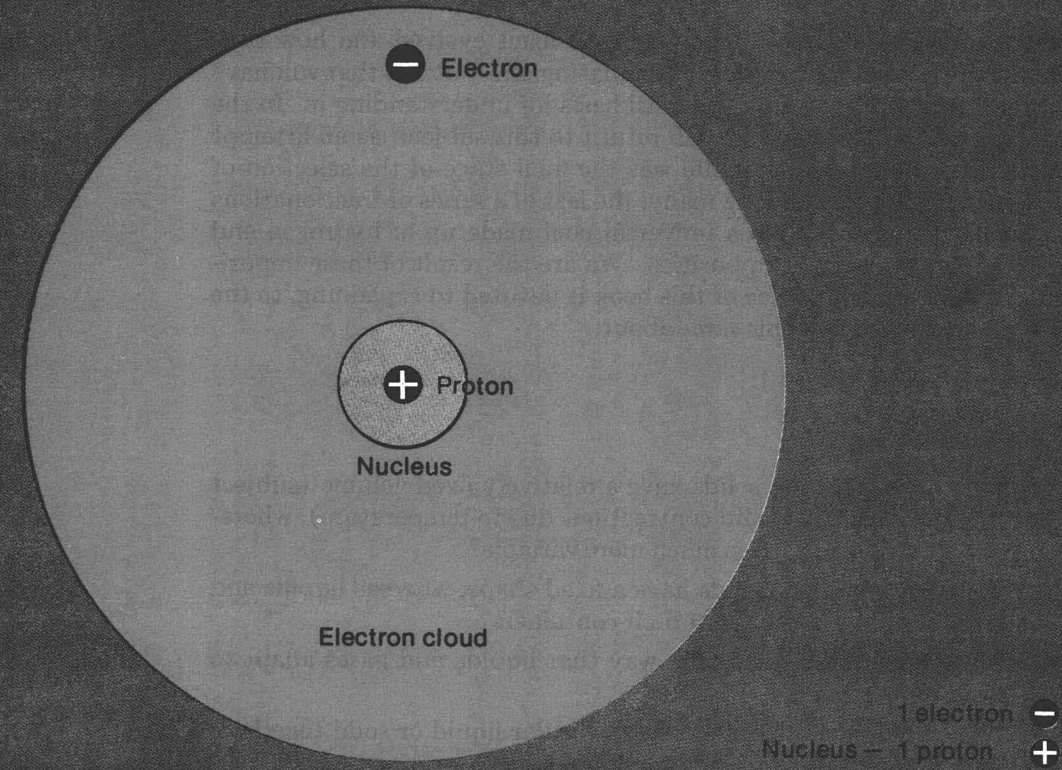
Our solar system thus was enriched in heavy elements from its very beginning. As the sun coalesced at the center of a cloud of diffused matter, so did the various planets farther out. The large planets with enough gravitational pull to retain all of their original material, such as Jupiter and Saturn, remained sunlike in overall composition. The Earth and the other small inner planets had their volatile elements driven away by the heat of the sun and by the weakness of their own attraction for them. The only substances left were the nonvolatiles; thus Earth became a denuded ball of rock. This is why our planet is so rich in silicon–oxygen minerals today; these were the substances that would not boil away.

Our Earth has an atmosphere today only because of outgassing of the planetary interior, mainly through volcanic action after surface temperatures had fallen. The gases that were emitted were not those that were most common in the original material of the solar system, but those that could be trapped in chemical combination with minerals: water vapor, ammonia, hydrogen sulfide, carbon dioxide, and other small carbon and nitrogen molecules. The helium that was present initially was lost because it did not react chemically and could not be retained in a nonvolatile form.

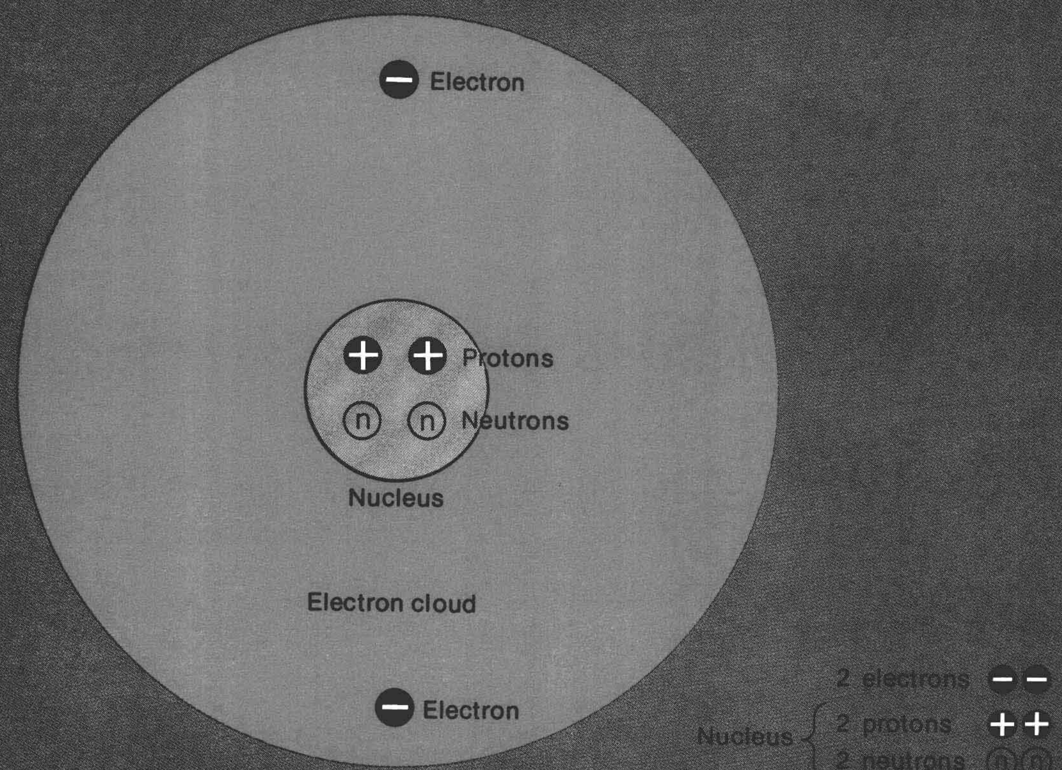
Our present atmosphere, which essentially is 80% nitrogen and 20% oxygen, is quite different even from the original outgassed atmosphere. That primal atmosphere contained many components that would combine readily with oxygen, but did not contain free oxygen itself. Today's oxygen-rich atmosphere is the result of the slow action by one of the most remarkable phenomena to arise in the universe: Life. Out of this pool of carbon, oxygen, nitrogen, and hydrogen compounds, on the surface of a ball of silicate rock, there evolved the most complex and most subtle chemical systems that the universe has known: living organisms. The story of how living organisms evolved and how they have transformed our planet is a fascinating one, but one that will have to wait until we have laid a chemical basis for understanding it. In the last chapters of this book we will return to this subject, as an attempt to tie everything together. Life was the final stage of the selection of certain elements from among many, the last of a series of fractionations of chemical elements from a universal pool made up of hydrogen and helium, plus a few trace impurities. We are the result of these impurities, and one central theme of this book is devoted to explaining, to the best of our ability, how this came about.

QUESTIONS

1. Why do liquids and solids have a relatively fixed volume (subject to small expansions and contractions due to temperature), whereas the volume of a gas is much more variable?
2. Why do crystalline solids have a fixed shape, whereas liquids and gases adapt to the shape of their containers?
3. What is different about the way that liquids and gases adapt to their containers?
4. What holds the molecules of a molecular liquid or solid together? Why doesn't this same factor hold for gases?
5. What were the earliest two chemical elements?
6. Why are these two elements so much rarer on Earth than they are in the universe as a whole?



Atomic number 1
HYDROGEN ATOM



Atomic number 2
HELIUM ATOM

◀ *Elementary particles (electrons, protons, and neutrons) that make up the hydrogen and helium atoms*

CHAPTER 2

Atoms, Molecules, and Moles

Hydrogen and helium occupy a special place in the chemical world because they are the elements from which all other elements were made. They have another aspect that makes them useful to us now: They are the simplest of all atoms. All of the ideas about simple atomic structure that can be illustrated with hydrogen and helium will carry directly over to the study of the heavier atoms.

ELECTRONS, NUCLEI, AND ATOMIC NUMBER

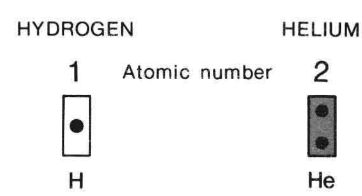
An atom is made up of a very small but heavy central nucleus with a positive charge, surrounded by a negatively charged cloud of electrons. Because atoms are so small, the familiar units of feet or centimeters are useless in measuring them. A more common unit of length is the angstrom, symbolized Å. There are 100,000,000 or 10^8 Å in one centimeter, or to express matters the other way around,

$$1\ \text{Å} = \frac{1}{10^8}\ \text{cm} = 10^{-8}\ \text{cm} = 0.00000001\ \text{cm}$$

Most atoms are of the order of 1.0 Å to 2.4 Å in diameter, which is why angstroms are so convenient.

The nucleus of an atom is much smaller yet, typically with a diameter of 10^{-13} cm or 10^{-5} Å. If an atom were as large as a football stadium, the nucleus would be the size of a small ladybug crawling across the 50-yard line. In spite of this size difference, virtually all of the mass of an atom is concentrated in its nucleus. One electron, which has a negative charge, weighs only 1/1836 as much as the lightest of all nuclei, that of the hydrogen atom (proton).

An atomic nucleus is built from two major kinds of particles: protons and neutrons. A proton carries one unit of positive charge, which



The electron shells of hydrogen and helium atoms will be symbolized by rectangles. When the shell is filled (as in helium), the rectangle will be colored.