2

The Atomic and Molecular
Structure of Matter

The properties of any kind of matter are most easily and clearly learned and understood when they are correlated with its structure, in terms of the molecules, atoms, and still smaller particles that compose it. This subject, the atomic structure of matter, will be taken up in this chapter.

2-1. Hypotheses, Theories, and Laws

When it is first found that an idea explains or correlates a number of facts, the idea is called a *hypothesis*. A hypothesis may be subjected to further tests and to experimental checking of deductions that may be made from it. If it continues to agree with the results of experiment the hypothesis is called a *theory* or *law*.

A theory, such as the atomic theory, usually involves some idea about the nature of some part of the universe, whereas a law may represent a summarizing statement about observed experimental facts. For example, there is a law of the constancy of the angles between the faces of crystals. This law states that whenever the angles between corresponding faces of

various crystals of a pure substance are measured they are found to have the same value, whether the crystal is a small one or a large one. It does not explain this fact. An explanation of the fact is given by the atomic theory of crystals, the theory that in crystals the atoms are arranged in a regular order (as described later in this chapter.)

Chemists and other scientists use the word theory in two somewhat different senses. The first meaning of the word is that described above— namely, a hypothesis that has been verified. The second use of the word theory is to represent a systematic body of knowledge, compounded of facts, laws, theories in the limited sense described above, deductive arguments, and so on. Thus by the atomic theory we mean not only the idea that substances are composed of atoms, but also all the facts about substances that can be explained and interpreted in terms of atoms and the arguments that have been developed to explain the properties of substances in terms of their atomic structure.

2-2.   The Atomic Theory

In 1805 the English chemist and physicist John Dalton (1766–1844) stated the hypothesis that all substances consist of small particles of matter, of several different kinds, corresponding to the different elements. He called these particles atoms, from the Greek word *atomos*, meaning indivisible. This hypothesis gave a simple explanation or picture of previously observed but unsatisfactorily explained relations among the weights of substances taking part in chemical reactions with one another. As it was verified by further work in chemistry and physics, Dalton's atomic hypothesis became the atomic theory.

The rapid progress of our science during the current century is well illustrated by the increase in our knowledge about atoms. In a popular textbook of chemistry written in the early years of the twentieth century atoms were defined as the "imaginary units of which bodies are aggregates." The article on "Atom" in the 11th edition of the *Encyclopaedia Britannica*, published in 1910, ends with the words "The atomic theory has been of priceless value to chemists, but it has more than once happened in the history of science that a hypothesis, after having been useful in the discovery and the coordination of knowledge, has been abandoned and replaced by one more in harmony with later discoveries. Some distinguished chemists have thought that this fate may be awaiting the atomic theory. . . . But modern discoveries in radioactivity are in favor of the existence of the atom, although they lead to the belief that the atom is not so eternal and unchangeable a thing as Dalton and his predecessors had imagined." Now, only half a century later, we have precise knowledge of the structure and properties of atoms and molecules. Atoms and molecules can no longer be considered "imaginary."

Dalton's Arguments in Support of the Atomic Theory

The Greek philosopher Democritus (about 460–370 B.C.), who had adopted some of his ideas from earlier philosophers, stated that the universe is composed of void (vacuum) and atoms. The atoms were considered to be everlasting and indivisible—absolutely small, so small that their size could not be diminished. He considered the atoms of different substances, such as water and iron, to be fundamentally the same, but to differ in some superficial way; atoms of water, being smooth and round, could roll over one another, whereas atoms of iron, being rough and jagged, would cling together to form a solid body.

The atomic theory of Democritus was pure speculation, and was much too general to be useful. Dalton's atomic theory, however, was a hypothesis that explained many facts in a simple and reasonable way.

In 1785 the French chemist Antoine Laurent Lavoisier (1743–1794) showed clearly that there is no measurable change in mass during a chemical reaction: the mass of the products is equal to the mass of the reacting substances.

In 1799 another general law, the *law of constant proportions*, was enunciated by the French chemist Joseph Louis Proust (1754–1826). The law of constant proportions states that different samples of a substance contain its elementary constituents (elements) in the same proportions. For example, it was found by analysis that the two elements hydrogen and oxygen are present in any sample of water in the proportion by weight 1:8.

Dalton stated the hypothesis that elements consist of atoms, all of the atoms of one element being identical, and that compounds result from the combination of atoms of two or more elements, each in definite number. In this way he could give a simple explanation of the law of conservation of mass and of the law of constant proportions.

A *molecule* is a group of atoms bonded to one another. If a molecule of water is formed by the combination of two atoms of hydrogen with one atom of oxygen, the mass of the molecule should be the sum of the masses of two atoms of hydrogen and an atom of oxygen, in accordance with the law of conservation of mass. The definite composition of a compound is then explained by the definite ratio of atoms of different elements in the molecules of the compound.

Dalton also formulated another law, the *law of simple multiple proportions*.* This law states that when two elements combine to form more than one compound, the weights of one element that combine with the same weight of the other are in the ratios of small integers.

It is found by experiment that, whereas one oxide of carbon consists of

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*The discovery of the law of simple multiple proportions was the first great success of Dalton's atomic theory. This law was not induced from experimental results, but was derived from the theory, and then tested by experiments.

carbon and oxygen in the weight ratio 3:4, another consists of carbon and oxygen in the ratio 3:8. The weights of oxygen combined with the same weight of carbon, 3 g, in the two substances are 4 g and 8 g; that is, they are in the ratio of the small integers 1 and 2. This ratio can be explained by assuming that twice as many atoms of oxygen combine with the same number of atoms of carbon in the second substance as in the first.

Dalton had no way of determining the correct formulas of compounds, and he arbitrarily chose formulas to be as simple as possible; for example, he assumed that the molecule of water consisted of one atom of hydrogen and one atom of oxygen, whereas in fact it consists of two atoms of hydrogen and one of oxygen.

2-3. Modern Methods of Studying Atoms and Molecules

During the second half of the nineteenth century chemists began to discuss the properties of substances in terms of assumed structures of the molecules. Precise information about the atomic structure of molecules and crystals of many substances was finally obtained during the recent period, beginning in 1912. Physicists have developed many powerful methods of investigating the structure of matter. One of these methods is the interpretation of the spectra of substances (see Figure 21-1). A flame containing water vapor, for example, emits light that is characteristic of the water molecule. The spectrum of water vapor may be observed when this light passes through a spectroscope. Measurements of the lines in the water spectrum have been made and interpreted, and it has been found that the two hydrogen atoms in the molecule are about 97 pm (that is, 97×10^{-12} m) from the oxygen atom. Moreover, it has been shown that the two hydrogen atoms are not on opposite sides of the oxygen atom, but that the molecule is bent, the angle formed by the three atoms being 104.5°. The distances between atoms and the angles formed by the atoms in many simple molecules have been determined by spectroscopic methods.

Also, the structures of many substances have been determined by the methods of diffraction of electrons and diffraction of x-rays. In the following pages we shall describe many atomic structures that have been determined by these methods. The x-ray diffraction method of determining the structure of crystals is discussed in Appendix IV.

It is stated above that in the water molecule the two hydrogen atoms are 97 pm from the oxygen atom. This usage is in accordance with the International System. In the past, however, it has been customary to describe interatomic distances with use of the Ångström* as the unit of

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*The Ångström was named in honor of a Swedish physicist, Anders Jonas Ångström (1814–1874), who in 1868 had published his measured values, to six significant figures, of the wavelengths of 1000 lines in the solar spectrum.
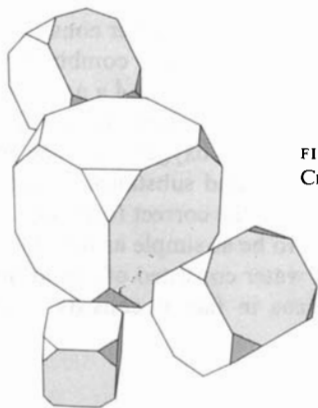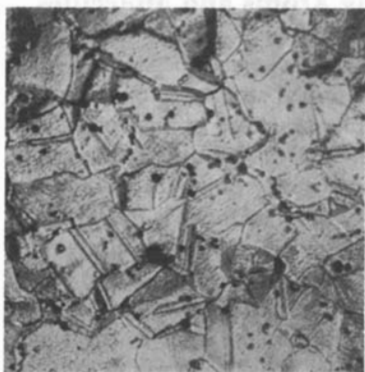
FIGURE 2-1
Crystals of native copper.

FIGURE 2-2
A polished and etched surface of a
piece of cold-drawn copper bar,
showing the small crystal grains that
compose the ordinary metal.
Magnification 200X (200-fold linearly).
The small round spots are gas bubbles.

length; 1 Å $= 10^{-8}$ cm $= 10^{-10}$ m $= 100$ pm. Because of the convenience
of the Ångström in the discussion of interatomic distances and because of
its use in reference books, we shall use it in this book. The hydrogen-
oxygen distance in the water molecule is 0.97 Å, and most bond lengths in
molecules and crystals lie between 1 Å and 4 Å.

2-4.   The Arrangement of Atoms in a Crystal

Most solid substances are crystalline in nature. Sometimes the particles of
a sample of solid substance are themselves single crystals, such as the cubic
crystals of sodium chloride in table salt. Sometimes these single crystals
are very large; occasionally crystals of minerals several meters in diameter
are found in nature.

   In our discussion we shall use *copper* as an example. Crystals of copper
as large as a centimeter on edge, as shown in Figure 2-1, are found in

deposits of copper ore. An ordinary piece of the metal copper does not consist of a single crystal of copper, but of an aggregate of crystals. The crystal grains of a specimen of a metal can be made clearly visible by polishing the surface of the metal, and then etching the metal slightly with an acid. Often the grains are small, and can be seen only with the aid of a microscope (Figure 2-2), but sometimes they are large, and can be easily seen with the naked eye, as in some brass doorknobs.

It has been found by experiment (Section 2-5) that *every crystal consists of atoms arranged in a three-dimensional pattern that repeats itself regularly.* In a crystal of copper all of the atoms are alike, and they are arranged in the way shown in Figures 2-3 and 2-4. This is a way in which spheres of uniform size may be packed together to occupy the smallest volume. This structure, called the *cubic closest-packed structure*, was assigned to the copper crystal by W. L. Bragg in 1913.

It is the regularity of arrangement of the atoms in a crystal that gives to the crystal its characteristic properties, in particular the property of growing in the form of polyhedra. (A polyhedron is a solid figure bounded by plane faces.) The faces of crystals are defined by surface layers of atoms, as shown in Figures 2-3 and 2-4. These faces lie at angles to one another that have definite characteristic values, the same for all specimens of the same substance. The principal surface layers for copper correspond to the six faces of a cube (cubic faces or cube faces); these faces are always ortho-gonal to (at right angles with) one another. The eight smaller surface layers, obtained by cutting off the corners of the cube, are called "octa-hedral faces." Native copper, found in deposits of copper ore, often is in the form of crystals with cubic and octahedral faces (Figure 2-1).

Atoms are not hard spheres, but are soft, so that by increased force they may be pushed more closely together (be compressed). This compres-sion occurs, for example, when a copper crystal becomes somewhat smaller in volume under increased pressure. The sizes that are assigned to atoms correspond to the distances between the center of one atom and the center of a neighboring atom of the same kind in a crystal under ordinary circumstances. The distance from a copper atom to each of its twelve nearest neighbors in a copper crystal at room temperature and atmospheric pressure is 2.55 Å; this is called the diameter of the copper atom in metallic copper. The radius of the copper atom is half this value.

2-5. The Description of a Crystal Structure

Chemists often make use of the observed shapes of crystals to help in the identification of substances. The description of the shapes of crystals is the subject of the science of *crystallography*. The method of studying the structure of crystals by the diffraction of x-rays, which was discovered by
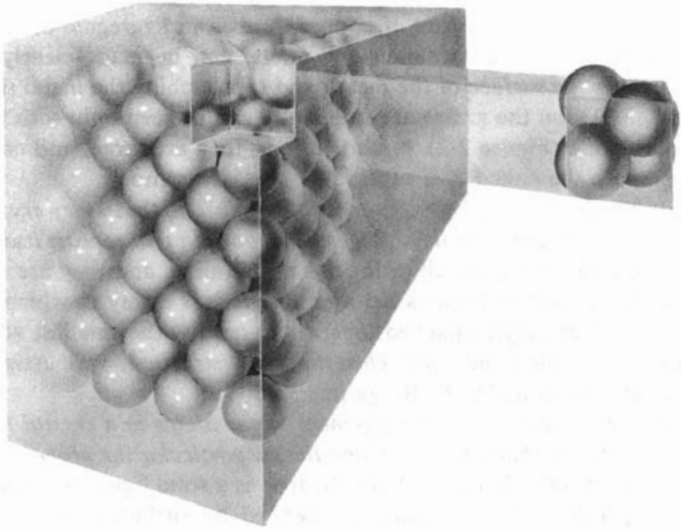
FIGURE 2-3
The arrangement of atoms in a crystal of copper. The small cube, containing
four copper atoms, is the unit of structure; by repeating it the entire
crystal is obtained.
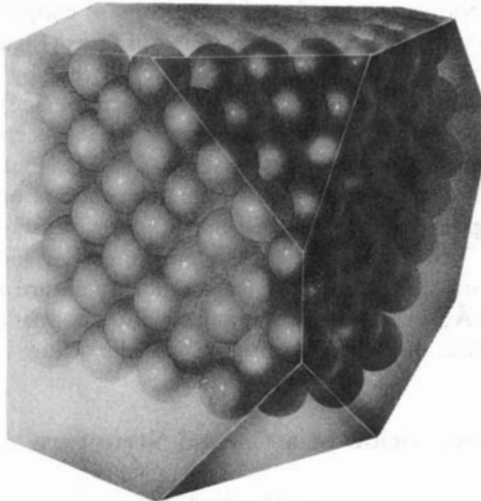
FIGURE 2-4
Another atomic view of a copper crystal, showing
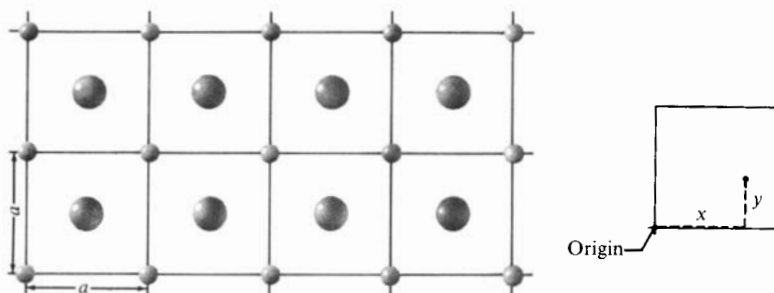small octahedral faces and large cube faces.

FIGURE 2-5
Arrangement of atoms in a plane. The unit of structure is a square. Small atoms
have the coordinates 0, 0 and large atoms the coordinates $\frac{1}{2}$, $\frac{1}{2}$.

the German physicist Max von Laue (1879–1960) in 1912 and developed
by the British physicists W. H. Bragg (1862–1942) and W. L. Bragg
(born 1890), has become especially valuable in recent decades. Much of
the information about molecular structure that is given in this book has
been obtained by the x-ray diffraction technique.

The basis of the description of the structure of a crystal is the unit of
structure, often called the *unit cell*. For cubic crystals the unit cell is a
small cube, which, when repeated parallel to itself in such a way as to fill
space, reproduces the entire crystal.

The way in which this is done can be seen from a two-dimensional ex-
ample. In Figure 2-5 there is shown a portion of a structure based on a
square lattice. The unit of structure of this square lattice is a square; when
this square is repeated parallel to itself in such a way as to fill the plane,
we obtain a sort of two-dimensional crystal. In this case there are present
a lattice of atoms of one sort, represented by small spheres at the inter-
sections of the lattice lines, and a lattice of atoms of another sort, repre-
sented by larger spheres at the centers of the unit squares. It is customary
to describe the structure by the use of coordinates x and y, giving the
position of the atoms relative to an origin at the corner of the unit cell,
with x and y taken as fractions of the edges of the unit of structure, as
indicated in the figure. The atom represented by the small sphere has the
coordinates $x = 0$, $y = 0$, and the atom at the center of the square has the
coordinates $x = \frac{1}{2}$, $y = \frac{1}{2}$.

Similarly, the unit cell of a cubic crystal is a cube which when repro-
duced in parallel orientation would fill space to produce a cubic lattice,
as shown in Figure 2-6. The unit cell of a given cubic crystal could be de-
scribed by giving the value of the edge of the unit, a, and the values of the
coordinates x, y, and z for each atom, as fractions of the edge of the
unit. Thus, for metallic copper, a cubic structure, the unit of structure is
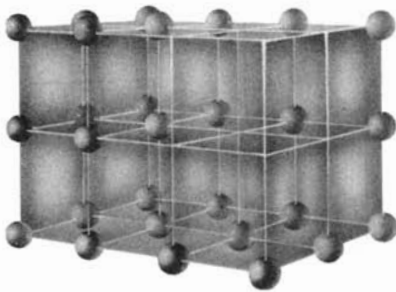
FIGURE 2-6
The simple cubic arrangement of atoms. The unit of structure is a cube, with one atom per unit, its coordinates being 0, 0, 0.
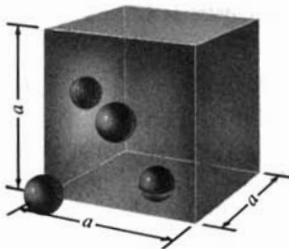

FIGURE 2-7
The cubic unit of structure for the face-centered cubic arrangement, corresponding to cubic closest packing of spheres. There are four atoms in the unit, with coordinates 0, 0, 0; 0, $\frac{1}{2}$, $\frac{1}{2}$; $\frac{1}{2}$, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, 0.
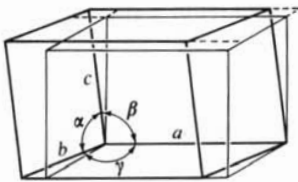

FIGURE 2-8
The parallelepiped representing a general unit of structure. It is determined by the lengths of its three edges, and by the three angles between the edges. A rectangular parallelepiped with its *ab* face in the same plane is also shown, light lines.
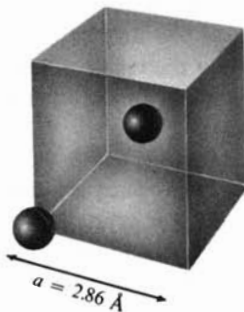

FIGURE 2-9
The unit of structure corresponding to the cubic body-centered arrangement. There are two atoms in the unit, with coordinates 0, 0, 0 and $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$.
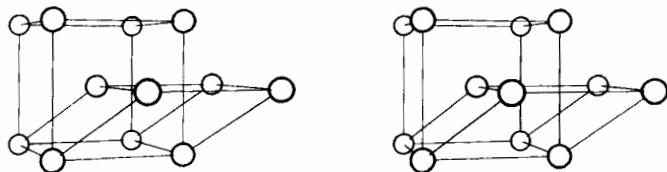
FIGURE 2-10

Stereoscopic view of the body-centered cubic structure, found for iron and some other metals. [The stereo drawings in this book can be viewed by looking at the right drawing with the right eye and the left drawing with the left eye from a distance of a few inches. It may help to hold a stiff piece of paper upright between the drawings. A moment or two may be required before the viewer learns to integrate the two images.]

a cube with edge $a = \sqrt{2} \times 2.55$ Å and with four atoms per unit, with coordinates $x = 0$, $y = 0$, $z = 0$; $x = 0$, $y = \frac{1}{2}$, $z = \frac{1}{2}$; $x = \frac{1}{2}$, $y = 0$, $z = \frac{1}{2}$; and $x = \frac{1}{2}$, $y = \frac{1}{2}$, $z = 0$, as shown in Figure 2-7. Often these coordinates are written without giving the symbols x, y, and z; it is then said that there are four copper atoms in the unit, at 0, 0, 0; 0, $\frac{1}{2}$, $\frac{1}{2}$; $\frac{1}{2}$, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, 0.

In the unit cube shown in Figure 2-7 the coordinates place an atom at only one of the eight corners. Of course, when this unit cube is surrounded by other unit cubes, atoms are placed at the seven other corners, these atoms being formally associated with the adjacent unit cubes.

The unit of structure of the most general sort of crystal, a triclinic crystal (see Appendix III and Figure III-4), is a general parallelepiped, as shown in Figure 2-8. It can be described by giving the values a, b, and c, the lengths of the three edges, and the values of α, β, and γ, the angles between pairs of edges.

Example 2-1. The metal iron is cubic, with $a = 2.86$ Å, and with two iron atoms in the unit cube, at 0, 0, 0 and $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$. How many nearest neighbors does each iron atom have, and how far away are they?

Solution. We draw a cubic unit of structure, with edge 2.86 Å, as shown in Figure 2-9, and we indicate in it the positions 0, 0, 0 and $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$. When cubes of this sort are reproduced parallel to one another, we see that we obtain the structure shown in Figure 2-10; this is called the *body-centered arrangement*. It is seen that the atom at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ is surrounded by eight atoms, the atom at 0, 0, 0 and seven similar atoms. Also, the atom at 0, 0, 0 is surrounded by eight atoms. In each case the surrounding atoms are at the corners of a cube. This situation is described by saying that each atom in the body-centered arrangement has *ligancy* 8 (or *coordination number* 8).

To calculate the interatomic distance, we note that the square of this distance is equal to $(a/2)^2 + (a/2)^2 + (a/2)^2$, and hence the distance itself is equal to $\sqrt{3}a/2$. Thus the distance between each iron atom and its neighbors is found to be 1.732×2.86 Å$/2 = 2.48$ Å. The metallic radius of iron is hence 1.24 Å.

Example 2-2. The English mathematician and astronomer Thomas Harriot (1560–1621), who was tutor to Sir Walter Raleigh and who traveled to Virginia* in 1585, was interested in the atomic theory of substances. He believed that the hypothesis that substances consist of atoms was plausible, and capable of explaining some of the properties of matter. His writings contain the following propositions:

" 9. The more solid bodies have Atoms touching on all Sydes.
"10. Homogeneall bodies consist of Atoms of like figure, and quantitie.
"11. The waight may increase by interposition of lesse Atoms in the vacuities betwine the greater.
"12. By the differences of regular touches (in bodies more solid), we find that the lightest are such, where euery Atom is touched with six others about it, and greatest (if not intermingled) where twelve others do touch euery Atom."

Assuming that the atoms can be represented as hard spheres in contact with one another, what difference in density would there be between the two structures described in the above proposition 12?

Solution. The structure in which every atom is in contact with six others about it that Harriot had in mind is probably the simple cubic arrangement, shown in Figure 2-11. In this arrangement of atoms the unit of structure is a cube that contains one atom, which can be assigned the coordinates 0, 0, 0. Each atom is then in contact with six other atoms, which are at the distance d from it. The volume of the unit cube is accordingly d^3. If the mass of the atom is M, the density for this arangement is Md^{-3}.

The denser structure referred to by Harriot, where twelve atoms are in contact with each atom, is the cubic closest-packed arrangement described in the preceding section. (Harriot had apparently discovered that there is no way of packing equal hard spheres in space that gives a greater density than is given by this arrangement.) The cubic unit of structure for this arrangement contains four atoms. Its edge, a, is equal to $2^{1/2}d$, and its volume to $2^{3/2}d^3$. The mass contained in the unit cube is $4M$, and the density is accordingly $4M/2^{3/2}d^3$, or $2^{1/2}M/d^3$. We have thus found that the dense structure described by Harriot has density $2^{1/2} = 1.414$ times that of the less dense structure; it is accordingly 41.4% denser than the less dense structure.

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*He took the potato and tobacco back to Europe, and was perhaps the first smoker known to have died of lung cancer. (R. Taton (ed.), *The Beginnings of Modern Science*.)
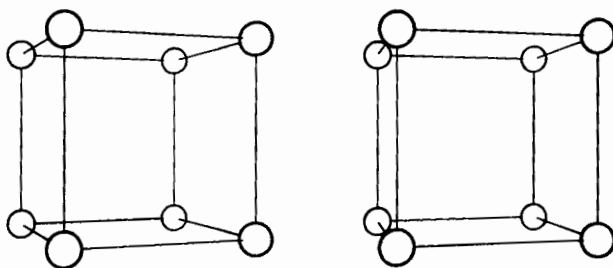
FIGURE 2-11
Simple cubic packing of spheres (stereo).

2-6.   Crystal Symmetry; the Crystal Systems

The principal classification of crystals is on the basis of their symmetry. An object has symmetry if some operation can be carried out on it such that, when the operation is completed, the object appears unchanged. For example, a three-bladed propeller can be rotated about its axis through $120°$ ($\frac{1}{3}$ of a revolution), and it is then indistinguishable from its original condition, provided that the three blades are exactly identical with one another. Similarly, it can be rotated through $240°$ ($\frac{2}{3}$ of a revolution), again becoming indistinguishable from its original condition. These operations of rotation by $\frac{1}{3}$ of a revolution and rotation by $\frac{2}{3}$ of a revolution, together with the original operation involving no change, constitute the symmetry of a threefold axis of symmetry. Other examples of symmetry are given in Appendix III.

Only a few symmetry elements are shown by crystals. They can be combined in 32 different ways, called *point groups*, corresponding to the 32 crystal classes. These crystal classes are divided into six crystal systems, as described in Appendix III.

An infinite crystal also has translations and other operations involving translations as identity operations. There are 230 possible combinations of these identity operations, which are called *space groups*. A discussion of the 230 space groups is given in Appendix III.

2-7.   The Molecular Structure of Matter

Molecular Crystals

The only building stone of a copper crystal is the copper atom; in this crystal there do not exist any discrete groups of atoms smaller than the crystal specimen itself. On the other hand, crystals of many other substances contain discrete groups of atoms, which are called molecules. An example of a molecular crystal is shown in the upper left part of Figure
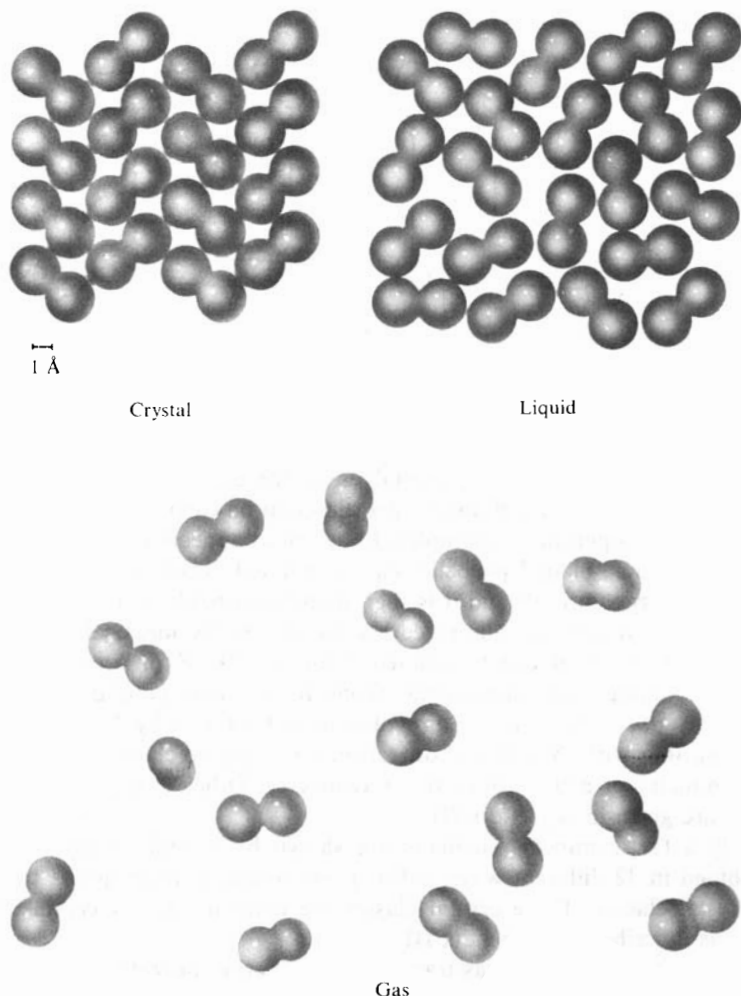
Crystal   Liquid

Gas

FIGURE 2-12
Crystalline, liquid, and gaseous iodine, showing diatomic molecules I_2.

2-12, which is a drawing representing the structure of a crystal of the blackish-gray solid substance iodine, as determined by the x-ray diffraction method. The iodine atoms are grouped together in pairs, to form diatomic molecules (molecules containing two atoms each).

The distance between the two atoms in the same molecule of a molecular crystal is smaller than the distances between atoms in different molecules. In the iodine crystal the two iodine atoms in each molecule are only 2.68 Å apart, whereas the small distances between iodine atoms in different molecules range from 3.56 to 4.40 Å.

Moreover, the forces acting between atoms within a molecule are much stronger than those acting between molecules. As a result, it is much harder to cause the molecule to change its shape than to change the positions of the molecules relative to one another. For example, when a crystal of iodine is put under pressure it decreases in size: the molecules can be pushed together until the intermolecular distances have decreased by several percent; but the molecules themselves retain their original size, with no comparable change in interatomic distance within the molecule. Also, when a crystal of iodine at low temperature is heated it expands, so that each of the molecules occupies a larger space in the crystal; but the iodine–iodine distance within the molecule stays very close to the normal 2.68 Å.

The molecules of different chemical substances contain varying numbers of atoms, bonded together. An example of a molecule more complicated than iodine is shown in Figure 2-13; this molecule, of the substance cyanuric triazide, contains three carbon atoms and twelve nitrogen atoms. Within the molecule the small interatomic distances have values between 1.11 Å and 1.38 Å. The smallest interatomic distances between molecules are 3.12 Å and 3.16 Å. It is found that in most molecular crystals the intermolecular distances between atoms are about 1.60 Å greater than the intramolecular distances (bond lengths) for the same kinds of atoms.

Crystals Containing Giant Molecules

Immense numbers of molecules of different kinds are found in the complicated structures of plants and animals. Many of these molecules are very large, containing tens of thousands of atoms. Scientists are beginning to gather detailed information about the structure of these giant organic molecules.

The *viruses* are aggregates of giant molecules with very interesting properties. Some diseases, such as measles, smallpox, infantile paralysis (poliomyelitis), and the common cold, are caused by viruses. Virus particles have the power of self-duplication—that is, the power of causing other particles identical with themselves to be formed when they are in the right environment. A disease such as measles results from the formation of a great many measles-virus particles in a human body that has been infected by a few of these particles.

Another property that virus particles have, in common with ordinary small molecules, is the ability to form crystals. The particles of a virus are all essentially alike in size and shape and can order themselves in the regular arrangement that constitutes a crystal.

In recent years it has become possible to photograph virus particles. They are too small to be seen with a microscope using ordinary visible light, which cannot permit objects much smaller in diameter than the
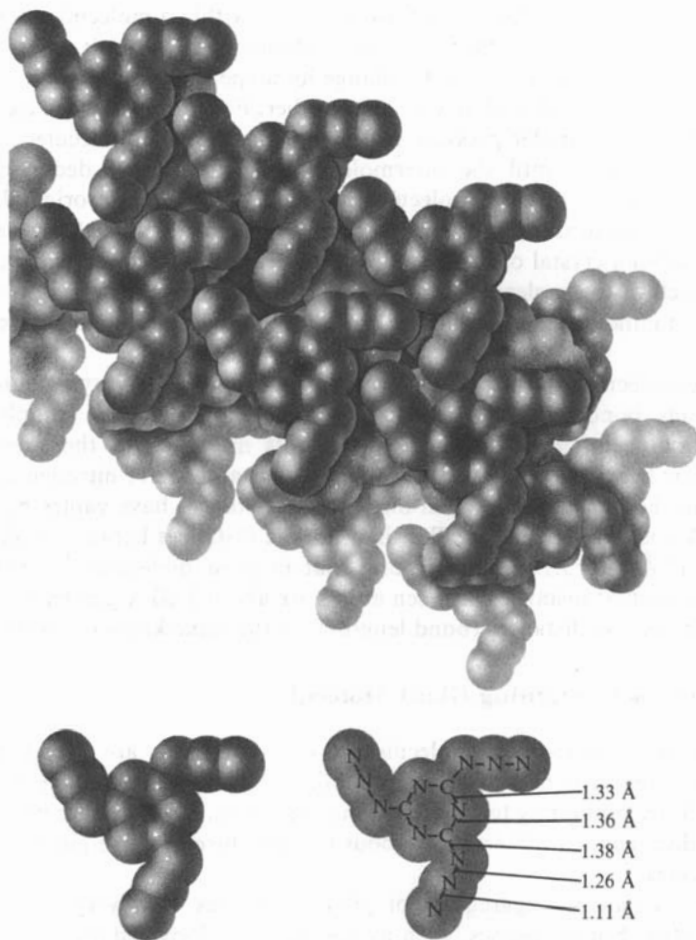
FIGURE 2-13
Above, portion of crystal of cyanuric triazide, C_3N_{12}, showing how the molecules pack together. Below, separate molecules.

wavelength of light, about 5000 Å, to be seen. However, electron micro-scopes, which use beams of electrons in place of beams of light, permit objects as small as 5 Å in diameter to be seen.

A photograph made with the electron microscope, reproduced here as Figure 2-14, shows the virus that causes a disease in tomato plants. Each virus particle is about 200 Å in diameter. It is made of about 450,000 atoms. In the photograph the individual particles can be clearly seen, and the regular way in which they arrange themselves in the crystal is evident.

FIGURE 2-14
Electron micrograph of crystals of necrosis virus protein, showing particles in ordered arrangement. Linear magnification 65,000. (From R. W. G. Wyckoff.)

The Evaporation of a Molecular Crystal

At a low temperature the molecules in a crystal of iodine lie rather quietly in their places in the crystal. As the temperature increases, the molecules become more and more agitated; each one bounds back and forth more and more vigorously in the little space left for it by its neighbors, and each one strikes its neighbors more and more strongly as it rebounds from them. This increase in molecular motion with increase in temperature causes the crystal to expand somewhat, giving each molecule a larger space in which to carry out its thermal oscillation.

A molecule on the surface of the crystal is held to the crystal by the forces of attraction that its neighboring molecules exert on it. Attractive forces of this kind, which are operative between all molecules when they are close together, are called *van der Waals attractive forces*, this name being used because it was the Dutch physicist J. D. van der Waals (1837–1923) who first gave a thorough discussion of intermolecular forces in relation to the nature of gases and liquids.

These attractive forces are quite weak. Hence occasionally a molecule will become so agitated as to break loose from its neighbors, and to fly off into the surrounding space. If the crystal is in a vessel, there will soon be present in the space within the vessel, through this process of evaporation, a large number of these free molecules, each moving in a straight-line path, and occasionally colliding with another molecule or with the walls of the vessel to change the direction of its motion. These free molecules constitute iodine vapor, or iodine gas (Figure 2-12). The gas molecules are very much like the molecules in the crystal, their interatomic distance being practically the same; it is the distances between molecules that are much larger in a gas than in a crystal.

Iodine vapor is violet in color and has a characteristic odor. The odor of tincture of iodine (a solution of iodine in alcohol, used as an antiseptic) is a combination of the odor of iodine vapor and the odor of ethyl alcohol.

It may seem surprising that molecules on the surface of a crystal should evaporate directly into a gas, but in fact the process of slow evaporation of a crystalline substance is not uncommon. Solid pieces of camphor or of naphthalene (as used in moth balls, for example) left out in the air slowly decrease in size because of the evaporation of molecules from the surface of the solid. In the same manner, snow may disappear from the ground without melting if the ice crystals evaporate at a temperature below that of their melting point. Evaporation is accelerated if a wind is blowing, to take the water vapor away from the immediate neighborhood of the snow crystals and to prevent the vapor from condensing again on the crystals.

The Nature of a Gas

The characteristic feature of a gas is that its molecules are not held together, but are moving about freely in a volume rather large compared with the volume of the molecules themselves. The van der Waals attractive forces between the molecules still operate whenever two molecules come close together, but usually these forces are negligibly small because the molecules are far apart. Because of this freedom of molecular motion, a specimen of gas does not have either definite shape or definite size. A gas shapes itself to its container. A quantitative study of the properties of gases will be taken up later (Chapter 9).

Gases at ordinary pressure are very dilute: the molecules themselves constitute only about one one-thousandth of the total volume of the gas, the rest being empty space. Thus 1 g of solid iodine has a volume of about 0.2 cm³ (its density is 4.93 g cm⁻³), whereas 1 g of iodine gas at 1 atm pressure and at the temperature 184°C (its boiling point) has a volume of 148 cm³, over 700 times greater. The volume of all the molecules in a gas

at ordinary pressure is accordingly small compared with the volume of the gas itself. On the other hand, the diameter of a gas molecule is not extremely small compared with the distance between molecules; in a gas at room temperature and 1 atm pressure the average distance from a molecule to its nearest neighbors is about ten times its molecular diameter, as indicated in Figure 2-12.

The Vapor Pressure of a Crystal

A crystal of iodine in an evacuated vessel will gradually change into iodine gas by the evaporation of molecules from its surface. Occasionally one of these free gas molecules will again strike the surface of the crystal, and it may stick to the surface, held by the van der Waals attraction of the other crystal molecules. This is called *condensation* of the gas molecules.

The rate at which molecules evaporate from a crystal surface is proportional to the area of the surface, but is essentially independent of the pressure of the surrounding gas, whereas the rate at which gas molecules strike the crystal surface is proportional to the area of the surface and also is proportional to the concentration of the molecules in the gas phase (the number of gas molecules in a unit of volume).

If some iodine crystals are put into a flask, which is then stoppered and allowed to stand at room temperature, it will soon be evident that a quantity of iodine has evaporated, because the gas phase in the flask will become violet in color. After a while the intensity of coloration of the gas phase will no longer increase, but will remain constant. This steady state is reached when the concentration of gas molecules becomes so great that the rate at which gas molecules strike the crystal surface and stay there is just equal to the rate at which molecules leave the crystal surface. The gas pressure at this steady state is called the *vapor pressure* of the crystal.

A steady state of this sort is an example of *equilibrium*. The study of physical equilibrium, such as this equilibrium between the crystal and its vapor, and of chemical equilibrium, representing a steady state among various substances that are reacting chemically with one another, constitutes an important part of general chemistry. It must be recognized that equilibrium is not a situation in which nothing is happening, but rather a situation in which opposing reactions are taking place at the same rate, so as to result in no over-all change.

The vapor pressure of every crystal increases as temperature increases. The vapor pressure of iodine has the value 0.26×10^{-3} atm at 20°C and 0.118 atm at 114°C, the melting point of a crystal. The crystals of iodine that are heated to a temperature only a little below the melting point evaporate rapidly, and the vapor may condense into crystals in a cooler

part of the vessel. The complete process of evaporation of a crystal and recondensation of a gas directly as crystals, without apparently passing through the liquid state, is called *sublimation*. Sublimation is often a valuable method of purifying a substance.

Units of Pressure

In the preceding paragraph the vapor pressure of iodine is given in atmospheres. *One atmosphere* (standard atmospheric pressure) is equal to $101.325 \text{ kN m}^{-2}$. It is not an approved IS unit of pressure, but it is especially important in chemistry because many properties of substances have been measured and recorded at 1 atm pressure.

Another unit of pressure that has been much used in the past is the *torr*, which is the height in millimeters of a column of mercury that balances the pressure. The symbol mm Hg is sometimes used for torr. The name of the unit is taken from the name of the inventor of the mercury barometer, the Italian physicist Evangelista Torricelli (1608–1647). One atmosphere is equal to 760 torr.

The Nature of a Liquid

When iodine crystals are heated to 114°C they melt, forming liquid iodine. The temperature at which the crystals and the liquid are in equilibrium—that is, at which there is no tendency for the crystals to melt or for the liquid to freeze—is called the *melting point* of the crystals, and the *freezing point* of the liquid. This temperature is 114°C for iodine.

Liquid iodine differs from solid iodine (crystals) mainly in its fluidity. Like the solid, and unlike the gas, it has a definite volume, 1 g occupying about 0.2 cm^3, but it does not have a definite shape; instead, it fits itself to the shape of the bottom part of its container.

From the molecular viewpoint the process of melting can be described in the following way. As a crystal is heated, its molecules are increasingly agitated, and move about more and more vigorously; but at lower temperatures this thermal agitation does not carry any one molecule any significant distance away from the position fixed for it by the arrangement of its neighbors in the crystal. At the melting point the agitation finally becomes so great as to cause the molecules to slip by one another and to change somewhat their location relative to one another. They continue to stay close together, but do not continue to retain a regular fixed arrangement; instead, the grouping of molecules around a given molecule changes continually, sometimes being much like the close packing of the crystal, in which each iodine molecule has twelve near neighbors, and sometimes considerably different, the molecule having only ten or nine or eight near neighbors, as shown in Figure 2-12. Thus a liquid, like a crystal, is a

condensed phase, as contrasted with a gas, the molecules being piled rather closely together; but whereas a crystal is characterized by regularity of atomic or molecular arrangement, a liquid is characterized by randomness of structure. The randomness of structure usually causes the density of a liquid to be somewhat less than that of the corresponding crystal.

The Vapor Pressure and Boiling Point of a Liquid

A liquid, like a crystal, is, at any temperature, in equilibrium with its own vapor when the vapor molecules are present in a certain concentration. The pressure corresponding to this concentration of gas molecules is called the *vapor pressure of the liquid* at the given temperature.

The vapor pressure of every liquid increases with increasing temperature. The temperature at which it reaches a standard value (usually 1 atm) is called the *boiling point* (standard boiling point) of the liquid. At this temperature it is possible for bubbles of the vapor to appear in the liquid and to escape to the surface.

The vapor pressure of liquid iodine at its freezing point, 114°C, is 0.118 atm. This is exactly the same as the vapor pressure of iodine crystals at this temperature, as described in the section before the preceding one. That is, iodine gas at a pressure of 0.118 atm is in equilibrium with liquid iodine at 114°C, the freezing point of the liquid, and this gas is also in equilibrium with iodine crystals at this temperature, their melting point. The crystals and the liquid are in equilibrium at the freezing point (melting point), and they then have exactly the same vapor pressure. If the two phases had different vapor pressures, the phase with the larger pressure would continue to evaporate, and the vapor would continue to condense as the other phase, until the first phase had disappeared.

The vapor pressure of liquid iodine reaches 1 atm at 184°C, which is the boiling point of iodine.

Other substances undergo similar changes in phase when they are heated. When copper melts, at 1083°C, it forms liquid copper, in which the arrangement of the copper atoms shows the same sort of randomness as that of the molecules in liquid iodine. Under 1 atm pressure copper boils at 2310°C to form copper gas; the gas molecules are single copper atoms. The vapor pressure of a substance can be measured by various techniques, such as that illustrated in Figure 2-15. In this experiment the barometric pressure is measured by measuring the height of a column of mercury in an evacuated tube. If the barometric pressure happened to be exactly normal, the height of the column would be 760.0 mm. The column of mercury is supported by the pressure of the air on the exposed surface of the mercury. Now if a substance, such as a drop of water, were to be introduced into the space in the tube above the column of mercury, by slipping it underneath the open bottom end of the tube and releasing it to permit it to rise
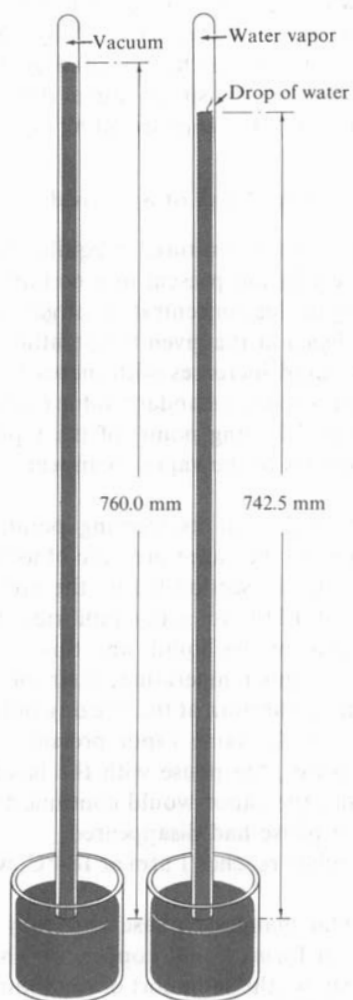
FIGURE 2-15
A simple method of measuring the vapor pressure of a liquid.

to the top of the column, molecules of this substance would evaporate into the space above the column of mercury, until equilibrium between the vapor and the condensed phase was reached. The top of the column of mercury would then be subjected to the pressure of this vapor, equal to the vapor pressure of the substance, and the column of mercury would decrease in height. The results of measurements of this sort on iodine crystals and liquid iodine are shown in Figure 2-16.

The vapor pressure of liquids and crystals is discussed in greater detail in Sections 11-2 and 11-3.
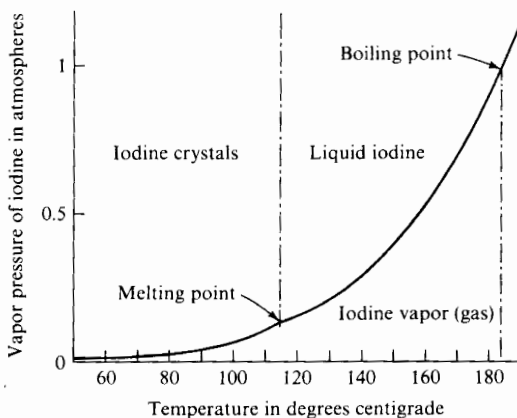
FIGURE 2-16
A graph showing the vapor-pressure curve of iodine crystal and the vapor-pressure curve of liquid iodine. The melting point of the crystal is the temperature at which the crystal and the liquid have the same vapor pressure, and the boiling point of the liquid (at 1 atm pressure) is the temperature at which the vapor pressure of the liquid equals 1 atm.

Exercises

2-1. What are the differences between a hypothesis, a theory, a law, and a fact? Classify the following statements as hypotheses, theories, laws, or facts:

   (a) The interior of the moon consists of granite and similar silicate rocks.

   (b) Hydrogen, nitrogen, oxygen, and neon are all gases under ordinary conditions.

   (c) The force f acting on a body with mass m causes it to be accelerated by the amount $f m^{-1}$.

   (d) The properties of gases can be explained by considering the motion of the molecules composing them.

   (e) All crystals contain atoms or molecules arranged in a regular way.

2-2. Discuss some of the evidence for the atomic nature of matter.

2-3. The metal indium forms tetragonal crystals. The unit of structure is a rectangular parallelepiped, with edges $a = 3.24$ Å, $b = 3.24$ Å, and $c = 4.94$ Å. There are two atoms in the unit of structure, with coordinates $0, 0, 0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

  (*a*) Calculate distances from each atom to its twelve nearest neighbors; note that four are at one distance, and eight at another distance.

  (*b*) Show that if the axial ratio c/a were equal to 1.414, the twelve distances would be equal.

  (*c*) What is the relation between the unit of structure with this axial ratio (1.414) and the cubic unit of structure described in the text for cubic closest packing?

2-4. Diamond has a cubic unit of structure, with $a = 3.56$ Å. There are eight atoms in the unit, with coordinates $0, 0, 0$; $0, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, 0, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; $\frac{1}{4}, \frac{3}{4}, \frac{3}{4}$; $\frac{3}{4}, \frac{1}{4}, \frac{3}{4}$; $\frac{3}{4}, \frac{3}{4}, \frac{1}{4}$. How many nearest neighbors does each atom have? What is the distance to each of these neighbors? (Answer: 4; 1.54 Å.)

2-5. The sodium chloride crystal has a cubic unit of structure, with $a = 5.628$ Å. There are four sodium atoms (sodium ions) in the unit of structure, with coordinates $0, 0, 0$; $0, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, 0, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, 0$; and also four chlorine atoms (chloride ions), with coordinates $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, 0, 0$; $0, \frac{1}{2}, 0$; $0, 0, \frac{1}{2}$. Make a drawing showing the cubic unit of structure and the positions of the atoms. How many nearest neighbors does each atom have? What is the interatomic distance for these neighbors? What polyhedron is formed by them (at the corners)? This arrangement of atoms, called the sodium chloride arrangement, is a common one for salts.

2-6. The cesium chloride crystal is cubic with $a = 4.11$ Å, Cs at $0\ 0\ 0$ and Cl at $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$. How many nearest neighbors does each atom have? At what distance are they? What polyhedron do they define?

2-7. The vapor pressure of solid carbon dioxide at its melting point, $-56.5°C$, is 5 atm. How do you explain the fact that solid carbon dioxide when used for packing ice cream does not melt to form liquid carbon dioxide? If you wanted to make some liquid carbon dioxide, what would you have to do?

2-8. Define vapor pressure of a crystal, and also vapor pressure of a liquid. Can you think of an argument showing that these two vapor pressures of a substance must be equal at the melting point?

2-9. What is the effect of increase in pressure on the boiling point of a liquid? Estimate the boiling point of liquid iodine at a pressure of 0.5 atm (see Figure 2-16).

2-10. Carbon dioxide (dry ice) consists of CO_2 molecules. These molecules are linear, with the carbon atom in the center. Make three drawings, representing your concepts of carbon dioxide gas, carbon dioxide liquid, and carbon dioxide crystal, and describe these structures.

GENERAL CHEMISTRY

Linus Pauling

"An excellent text, highly recommended."
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When it was first published, this first-year chemistry text revolutionized the teaching of chemistry by presenting it in terms of unifying principles instead of as a body of unrelated facts. Those principles included modern theories of atomic and molecular structure, quantum mechanics, statistical mechanics and thermodynamics. In addition, Dr. Pauling attempted to correlate the theories with descriptive chemistry, the observed properties of substances, to introduce the student to the multitude of chemical substances and their properties.

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The principles of quantum mechanics are discussed on the basis of the de Broglie wavelength of the electron. The quantized energy levels of a particle in a box are derived by means of a simple assumption about the relation of the de Broglie waves to the walls of the box. No attempt is made to solve the Schrödinger wave equation for other systems, but the wave functions of hydrogen-like electrons are presented and discussed in some detail, and the quantum states for other systems are also covered. Statistical mechanics is introduced before thermodynamics, and the discussion of thermodynamics is based on it. This arrangement reflects the author's belief that beginning students can understand statistical mechanics better than chemical thermodynamics.

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