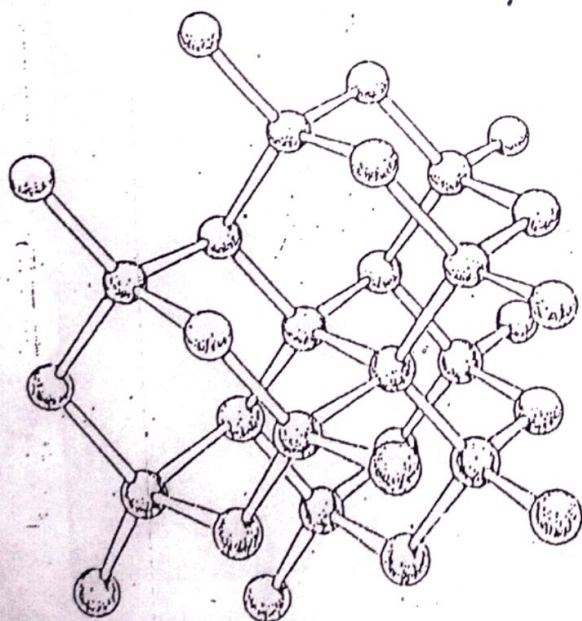


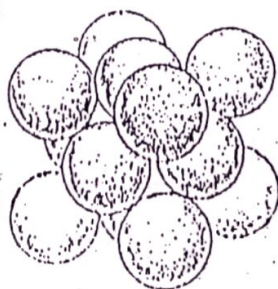
15 Solids

In Chapter 4, we characterized the gaseous state as the state of matter that shows almost complete *disorder* (or very high entropy). At the other extreme, the solid state is characterized by almost complete order (or very low entropy). Solids are orderly because almost all the atoms, molecules, or ions that make up solids are confined to small regions in the solid. They cannot move very far away from their positions without disrupting the whole structure of the solid. The atoms, molecules, or ions can be present in several different three-dimensional arrangements in space, and, as we shall see, these different three-dimensional arrangements of atoms, molecules, or ions result in the variety of geometrical structures we find in solids. It is their different structures, their compositions, as well as the different kinds of bonding found that are responsible for the way solids behave. For example, diamond has a melting point that is higher than 3550°C . It is composed of a single element, carbon, arranged in a three-dimensional network, where each carbon atom is connected to four other carbon atoms by covalent bonds (Figure 15-1a). In contrast, solid argon melts at -189°C . It has a cubic close-packed structure (Figure 15-1b) and the atoms are held together by weak van der Waals attractive forces.

Figure 15-1 (a) The three-dimensional network of diamond. (b) Cubic close-packed structure of solid argon.



(a)



(b)

X-ray Crystallography

Hundreds of years ago it was noticed that many crystals have regular shapes—hexagonal, cubic, etc. (Figure 15-2). In the eighteenth century a number of scientists proposed that these regular shapes were the result of a regular internal arrangement of particles. It was not easy to prove this idea, and science had to wait almost 200 years for the birth of a new experimental tool which allows us to "observe" the internal structure of solids. In this method, called **x-ray crystallography**, x rays are allowed to come into contact with a sample of solid matter. The x rays bounce off the atoms, molecules, or ions at certain angles. From measurements of these angles, and of the intensities of the x rays coming off, x-ray crystallographers gain information about the internal structure of the crystals. X-ray crystallography was developed in a truly serendipitous manner. A scientific conference was held in Munich in 1912. Among the many topics on the program, there were separate discussions of both crystallography and of x rays. One of the participants, Max von Laue (1879-1960), a German physicist, suggested that the interatomic spacings in crystals were of the same order of magnitude as the wavelengths of x rays. If this were so, then if x rays were passed through a crystal, a diffraction pattern would result (Figure 15-3). In the same year, Friedrich and Knipping performed the experiment on a crystal of zinc sulfide and it worked perfectly. Additional important

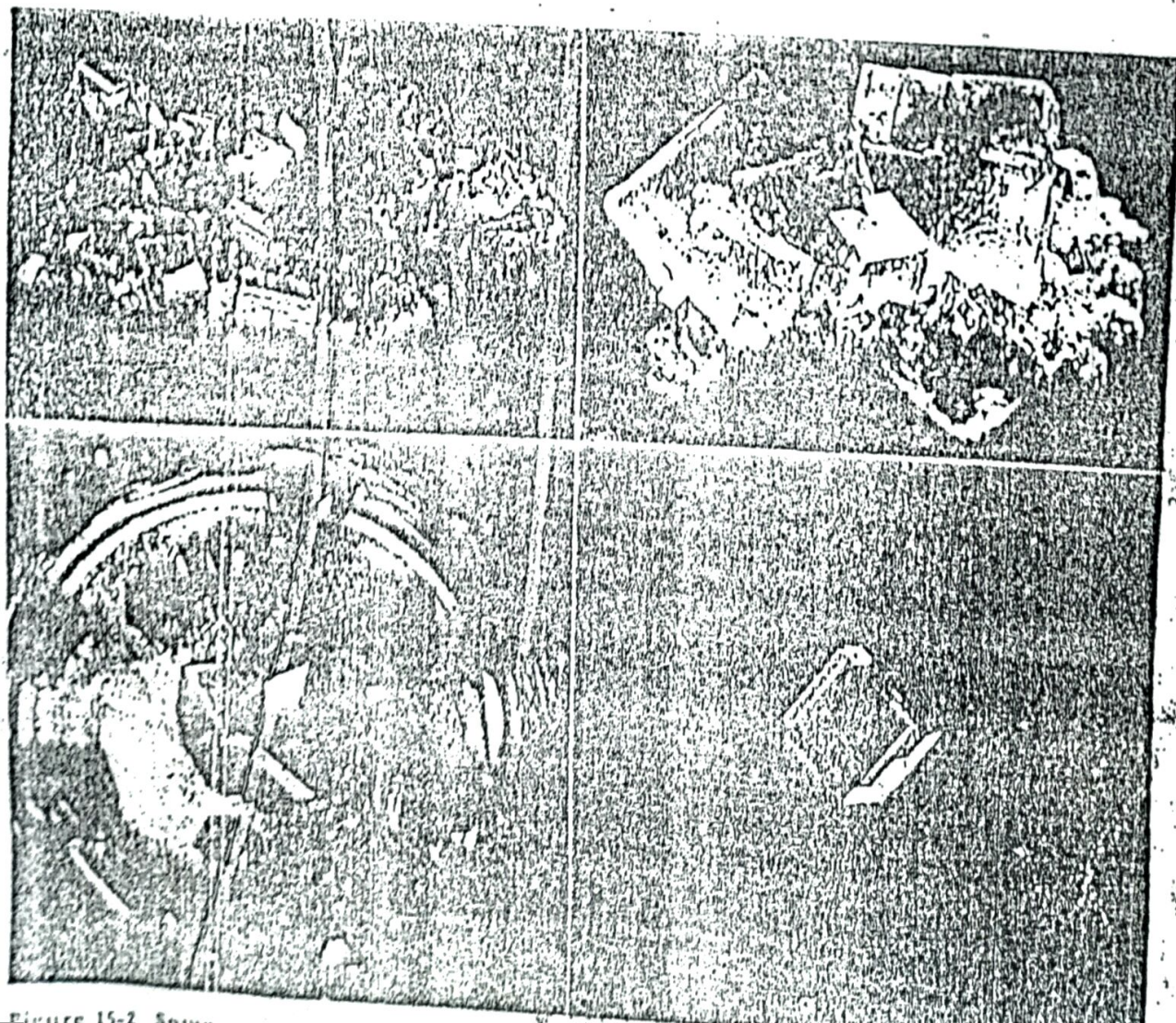


Figure 15-2 Some

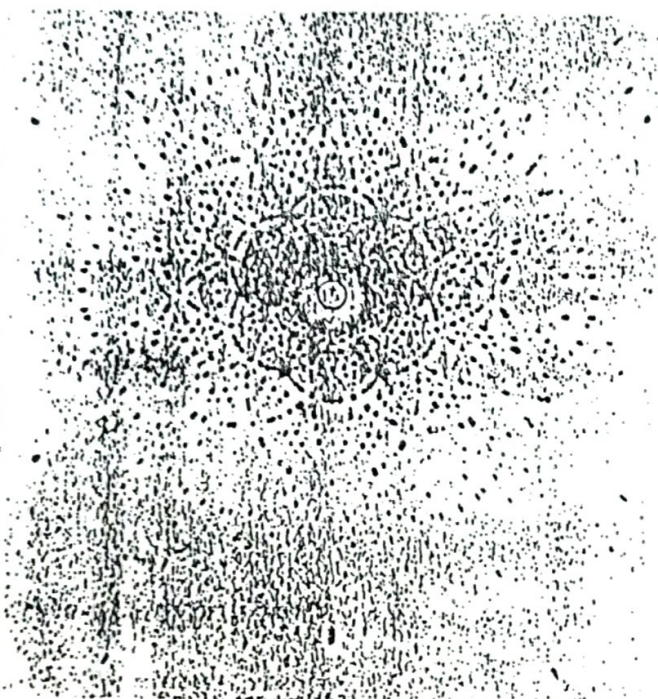


Figure 15-3 X-ray diffraction pattern produced by shining x rays on a crystal of beryl. [Courtesy of Eastman Kodak Research Laboratories]

contributions were made by William H. Bragg (1862-1942) and William L. Bragg (1890-1971) (father and son). A new and very powerful experimental tool was created.

Since that period, x-ray crystallographers have examined thousands of crystals and have been successful in elucidating the structure of a wide variety of solids, ranging from simple inorganic salts to complex proteins. In Chapter 21 we will discuss the structure of proteins and nucleic acids and the contributions made by x-ray crystallography. Figure 15-4 shows a typical modern x-ray diffraction device.

By the use of x-ray crystallography we know that almost all true solids consist of atoms, ions, or molecules arranged in a regular three-dimensional array. This regular array continues throughout the entire piece of solid, and shows up in the shape of the crystal itself. That is, the shape of the crystal is dependent on which particles are present and how they are arranged. Nearly all true solids are crystalline (that is, made up of crystals). Often the crystals are too tiny to be visible without a microscope or are so imperfect that it is difficult to make out their shapes, but the crystals are nearly always there. A few solids, called amorphous solids, are not made up of crystals at all. Some materials seem to be solids, but actually are not. An important example is glass. In spite of its appearance, glass is not a true solid, but actually a very viscous liquid! It has no regular array of atoms, ions, or molecules, and no melting point. You can demonstrate the liquid nature of glass by placing a glass plate onto two supports (Figure 15-5). After some weeks you will notice that the glass has sagged.

The perfect three-dimensional arrangement of atoms, ions, or molecules very seldom continues throughout an entire crystal (nearly all crystals contain some imperfections), but for the most part the stacking of atoms, ions, or molecules in a crystal is very regular.



Figure 15-4 A Modern Automatic X-ray Diffractometer. From left to right: the generator and diffractometer, the computer console, and the disc storage unit. [Courtesy of Syntex Analytical Instruments, Inc.]

Types of Unit Cells

15-2

The primary information obtained from an analysis of x-ray data concerns the unit cell of the crystal. A unit cell is the fundamental building block of the crystal. It is the smallest part of the crystal which if repeated by translation (movement) in three-dimensional space would reproduce the entire crystal.

To understand what a unit cell is, we will first look at a piece of wallpaper (Figure 15-6). Like most wallpaper, Figure 15-6 contains a repeating pattern. We can draw a parallelogram on one portion of the wallpaper and reproduce the entire pattern by translation of this parallelogram over the entire surface of the paper, provided that we have made our parallelogram large enough to include one complete unit of the pattern. We can use the word motif to refer to that part of the pattern that lies within a single parallelogram. The entire wallpaper is made up of this single motif, repeated as many times as is necessary to cover the whole wall.

We can look at a crystal in the same way, except that here the motif is repeated in three dimensions rather than two. In a crystal, the motif may consist of a single atom, ion, or molecule, or two, or three, or many, but it must be large enough to contain a complete unit of the pattern.

In order to picture the structure of crystals, it is helpful to imagine an array of points in space called a space lattice. Two such lattices, where the points (called lattice points) are connected by straight lines, are shown in Figure 15-7. As



Figure 15-5 A glass plate placed over two supports will slowly sink.

Unit cell is the smallest part of the crystal which if repeated in three-dimensional space would reproduce the entire crystal.

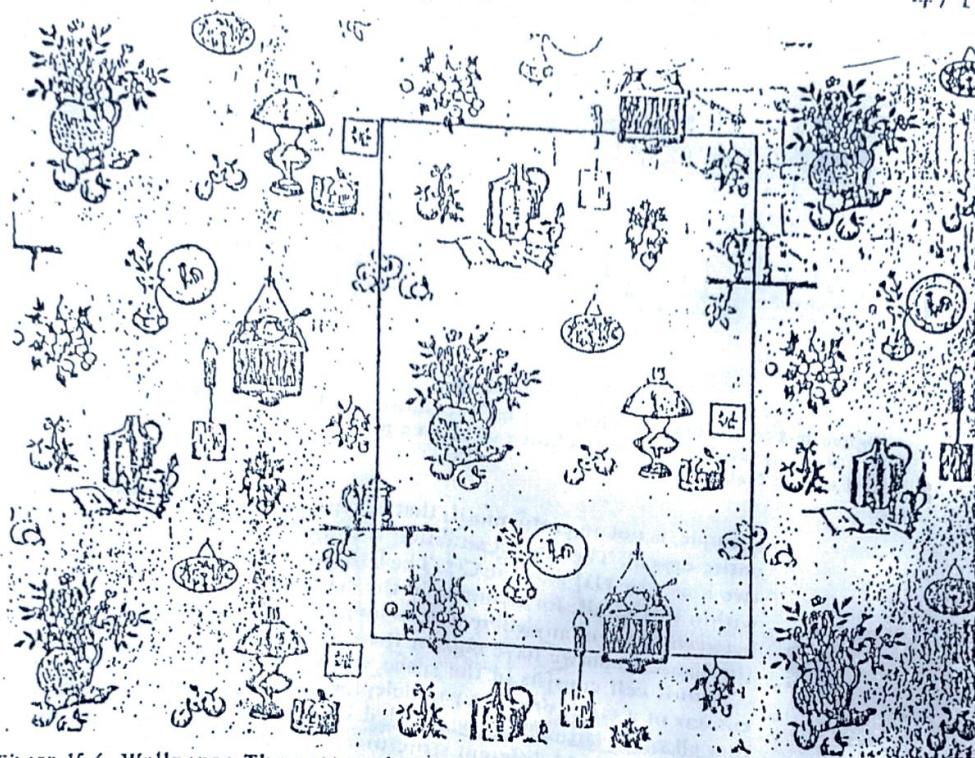
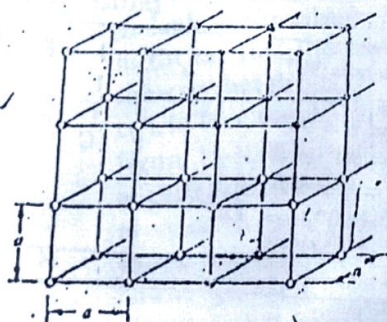


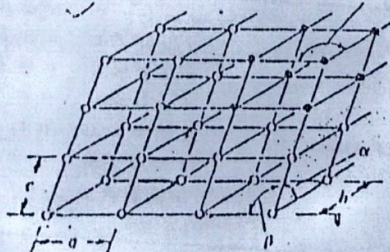
Figure 15-6 Wallpaper. The pattern is repeated by translation of the motif (outlined in color).

shown in the figure, the lattice points are arranged in a regular repeating order. We set up a different space lattice for each kind of crystal, choosing the distances and angles between the lattice points so as to suit the particular crystal involved. There is one lattice point for each motif. We may choose to put a lattice point anywhere we like within a motif, but then we must put all the other lattice points at the same relative place in every motif. The lattice points themselves are geometric points that occupy no volume.

When choosing a lattice we must be careful that there is one and only one lattice point for each motif. For example, consider the NaCl crystal, which has the structure shown in Figure 15-8. It might appear that we could choose single ions of Na^+ and Cl^- to be our lattice points (Figure 15-8a). This is not correct, because Na^+ , for



All distances equal,
All angles = 90°



Distances unequal
No angle = 90°

Figure 15-7 Two three-dimensional space lattices. The unit cells are shown in color.

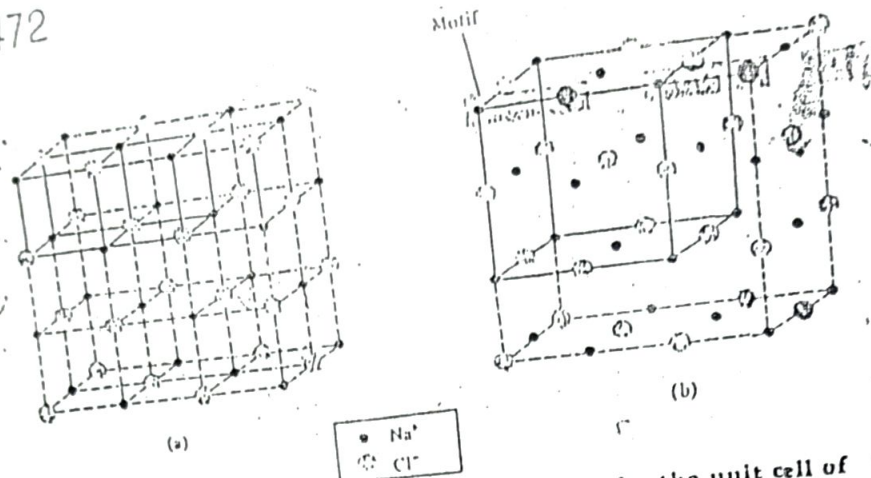


Figure 15-8 (a) Incorrect choice of lattice points for the unit cell of the NaCl crystal. (b) Correct choice of lattice points for the unit cell of the NaCl crystal.

example, is not an entire motif; that is, repetition of thision will not reproduce the entire crystal. The correct situation is shown in Figure 15-8b. The motif contains two ions: one Na^+ and one Cl^- . The lattice point may be chosen anywhere we wish within this motif; for example, in the center of the Na^+ , or of the Cl^- , or halfway between them, or anywhere else, as long as we choose the same place in each motif (in Figure 15-8b we have chosen the center of the Na^+ ion).

A unit cell consists of the space within eight lattice points which occupy the corners of a cube, or other parallelepiped (Figure 15-7). A. Bravais (1848) showed that all space lattices can be divided into 14 types. Table 15-1 lists the 14 Bravais lattices, and the 14 different structures are depicted in Figure 15-9. From Table 15-1 we see that there are seven basic crystal systems which are identifiable by these unit-cell axes and angles. The most regular is the cubic lattice, with all axes and angles equal, while the triclinic system is the least regular, with in axes or angles equal. As shown in the figure and table, there are three kinds of cubic lattice. In the simplest, called **primitive**, (designated *P*), the unit cell consists only of the volume defined by the eight lattice points at the corners of the cube. In the other two types the unit cell contains additional lattice points. The **body-centered cubic** lattice (designated *I*) has a ninth lattice point at the center of the cube, while the **face-centered cubic** lattice (*F*) has 14 lattice points in the unit cell: eight at the corners and one more at the center of each face of the cube. The monoclinic system occurs in two types: the primitive system, and the **end-centered** (*C*) system, with an additional lattice point at each end of the unit cell. Similarly, the

Table 15-1 The 14 Bravais Lattices^a

System	Unit-cell axes and angles		Lattice symbol
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	<i>P</i> <i>I</i> <i>F</i>
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	<i>P</i> <i>I</i>
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	<i>P</i> <i>I</i> <i>F</i> <i>C</i>
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	<i>P</i> <i>C</i>
Rhombohedral (trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	<i>P</i>
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ; \gamma = 120^\circ$	<i>P</i>
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	<i>P</i>
			14

^aThe meaning of the letters *a*, *b*, *c*, α , β , and γ is shown in Figure 15-7.

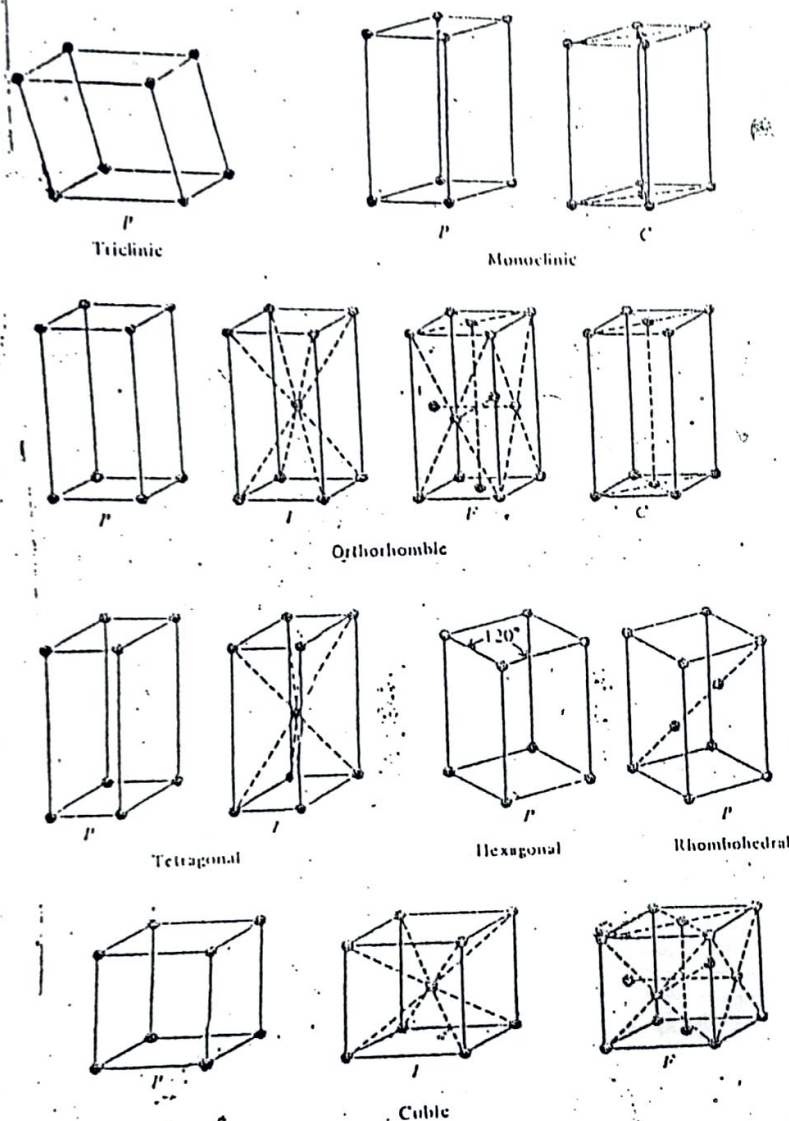


Figure 15-9 The 14 Bravais Lattices. The letters denote the kinds of lattice: P (primitive), I (body-centered), F (face-centered), C (end-centered).

orthorhombic and tetragonal systems each occur in more than one type (Figure 15-9). The other three systems, rhombohedral, hexagonal, and triclinic, each only occur as primitive types.

An x-ray study of a given crystal not only tells us which type of lattice is present, but also the dimensions and angles of the unit cell.

On the average, how many lattice points are associated with a given unit cell? Let us look at the simple primitive cubic system (Figure 15-10a). At first glance, we might say that there are eight lattice points in this cell, but a little thought will show us that this is not so. Each lattice point does not belong exclusively to one unit cell. In fact, every one of these lattice points is shared by eight unit cells, as shown in Figure 15-10d. Therefore, in a primitive cubic system, each unit cell "owns" only $\frac{1}{8}$ of each lattice point. The same is true for the corner points in all the systems. Every corner point belongs to each unit cell. Each lattice point on a face (see Figure 15-10e for the face-centered cubic system) is part of two unit cells (for each cell "owns" $\frac{1}{2}$), while each body-centered lattice point, of course, belongs only to one cell. Figure 15-10b shows a body-centered cubic lattice.

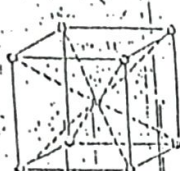
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Ch. 15 / Solids

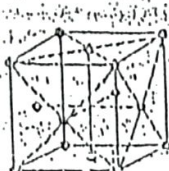
C. J. Allen



Simple cubic



Body-centered cubic



Face-centered cubic



(d)

A lattice point at a corner is shared by 8 unit cells.



(e)

A lattice point at a face is shared by 2 unit cells.

Figure 15-10 (a-c) The three cubic unit cells: primitive, body-centered, and face-centered. (d, e) Corner and edge lattice points are shared by adjacent unit cells.

We are now ready to calculate how many lattice points are associated with the three types of cubic-lattice unit cell.

	Simple cubic	Face-centered cubic	Body-centered cubic
Corner lattice points	8	8	8
Number belonging to each unit cell	$\times \frac{1}{8}$ 1	$\times \frac{1}{8}$ 1	$\times \frac{1}{8}$ 1
Face lattice points	0	6	0
Number belonging to each unit cell	0	$\times \frac{1}{2}$ 3	0
Body lattice points	0	0	1
Number belonging to each unit cell	0	0	$\times 1$ 1
Total lattice points belonging to each unit cell	1	4	2

Example: X-ray analysis shows that nickel crystallizes in a face-centered cubic unit cell with an edge of 3.63 Å. Each motif consists of a single nickel atom, and the lattice point is at the center of each atom.

Calculate: (a) The number of atoms in the unit cell.

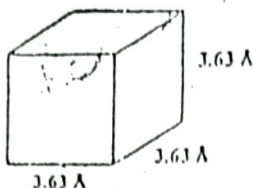
(b) The volume of the unit cell, cm^3 .

(c) The density of the solid.

We have already calculated that the number of atoms in a face-centered cubic unit cell is four atoms/unit cell.

(b) Using Figure 17-10c, we can calculate the volume of the cell as

$$\begin{aligned} \text{volume} &= (3.63 \text{ \AA})^3 = 47.8 \text{ \AA}^3 \\ &= 47.8 \times 10^{-24} \text{ cm}^3/\text{unit cell} \end{aligned}$$



(c) Density = mass/volume. To find the density, we must calculate the mass in the unit cell. The atomic weight of nickel is 58.70. The weight of a single atom is

$$\frac{58.70 \text{ g/mole}}{6.02 \times 10^{23} \text{ atoms/mole}} = 9.75 \times 10^{-23} \text{ g/atom}$$

Since there are four atoms in a face-centered unit cell, the mass of the unit cell is

$$4 \frac{\text{atoms}}{\text{unit cell}} \times 9.75 \times 10^{-23} \text{ g/atom} = 39.0 \times 10^{-23} \text{ g/unit cell}$$

The density of the unit cell is

$$\frac{39.0 \times 10^{-23} \text{ g/unit cell}}{47.8 \times 10^{-24} \text{ cm}^3/\text{unit cell}} = 8.15 \text{ g/cm}^3$$

At this point the reader may be wondering why a given substance crystallizes in a particular lattice type and not in another. There are a number of factors that determine this. For example, we must take account of the forces within the crystal, the relative size of the atoms that make up the crystal, and finally the different kinds of atoms, molecules, or ions that make up the crystal.

15-3

Close Packing of Spheres

In many cases, substances made up of atoms or ions form crystals in such a way that the atoms or ions get as close together as possible. This maximizes any attractive forces between them and results in the greatest possible stability for the crystal. If we assume that atoms and ions are spheres,* we can see for ourselves which arrangements lead to the closest possible packing in three dimensions.

We will start with a layer of spheres laid out on a flat surface. Figure 15-11 shows

*In most cases, this is a pretty good approximation of the shape of atoms and ions.

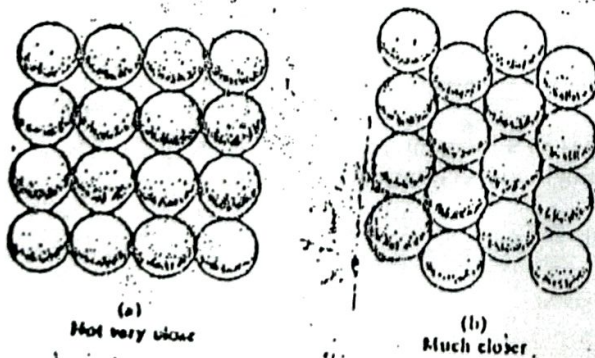


Figure 15-11 Two ways to form a regular layer of spheres on a flat surface. The spheres in (b) are more closely packed than those in (a).

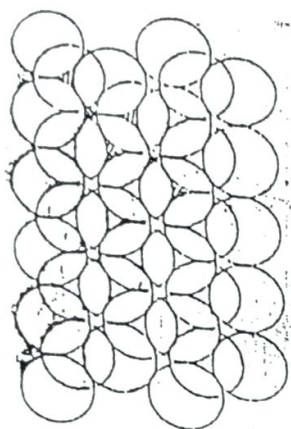
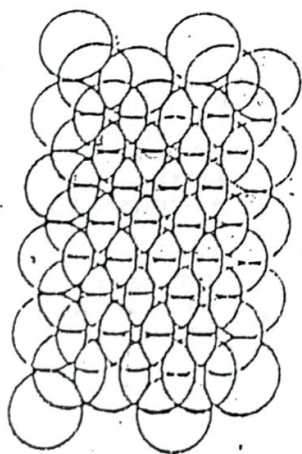


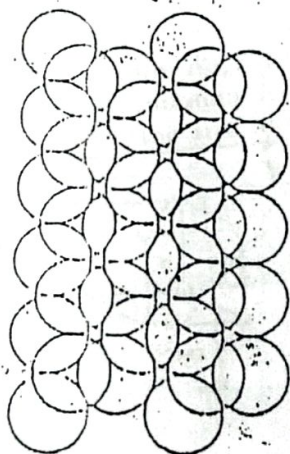
Figure 15-12 Two layers of closely packed spheres. The lower layer is in black, the upper layer is in color. Note that some of the holes in the lower layer (two of them are marked \square) are completely covered by the upper layer, but that others (marked \square) are uncovered. Note that half of the holes in the upper layer (two of them are marked \square) cover atoms, the others cover holes in the lower layer.

two possible regular patterns. The one on the right (in color) allows much closer packing than the square pattern on the left and is the one adopted by most atoms or ions. In a three-dimensional structure, a second layer is placed on top of the first. We could put the spheres of the second layer directly over those in the first layer, but, like the square arrangement in Figure 15-11a, this is not the closest packing. A much more efficient arrangement is for each sphere in the second layer to be placed over a hole in the first layer (Figure 15-12). Note that we cannot cover *all* the holes in the first layer; the size of the spheres will not allow this. We cover every other hole. Note also that the second layer has the same triangular arrangement as the first layer.

When it comes to putting on a third layer, there are two ways, both of which are equally efficient, and both of which cover holes in the second layer. We can cover those holes in the second layer which cover holes in the first layer (two of them are marked \square in Figure 15-12) or we can cover those holes in the second layer which cover spheres in the first layer (two of them are marked \square in Figure 15-12). The two possibilities are shown in Figure 15-13; as shown, if the third layer spheres are directly over first-layer spheres, then the third layer has the same position as the first layer. Additional layers will continue in the pattern *abababab...*, where *a* stands for the first-layer arrangement and *b* for the second layer. This arrangement is called hexagonal close packing (hcp). In the other arrangement, the third layer does not have the same position as the first layer; however, the fourth layer will have the same arrangement as the first, so the pattern will be *abcabcabc...*. This is called cubic close packing (ccp). Figure 15-14 shows three-dimensional views of the two types of packing. You can see them even better if you make models of them yourself, using plastic balls, or even gumdrops.



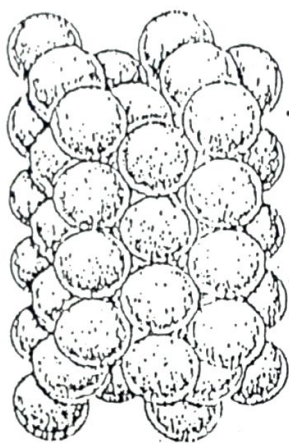
(a) ccp



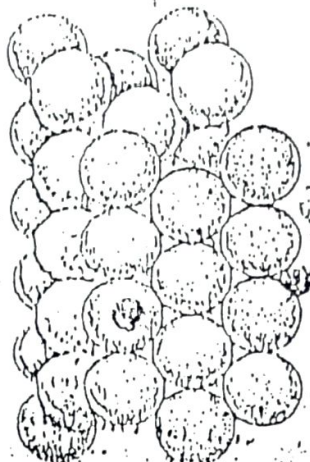
(b) hcp

Figure 15-13 Two ways to obtain three layers of closely packed spheres. (a) Each third-layer sphere is over a first-layer hole (ccp). (b) Each third-layer sphere is over a first-layer sphere (hcp). Note that in (b) the first layer cannot be seen because each sphere in it is directly under a sphere in the third layer.

Figure 13-14 The ccp and hcp structures. The second layer is in color.



(a) ccp



(b) hcp

As previously noted, the ccp and hcp are equally efficient; in each, the spheres cover about 74% of the total volume, leaving about 26% for the holes. This is the minimum amount of empty space that can be achieved when spheres are packed into a volume. Note that the ccp structure is equivalent to the face-centered cubic lattice discussed in Section 15-2.

Most metals crystallize in the ccp, hcp, or body-centered cubic (bcc) structure. The most gases crystallize in ccp structures, while solid H_2 , O_2 , and N_2 have hcp structures. Figure 19-5 shows the crystal structures of most of the metals.

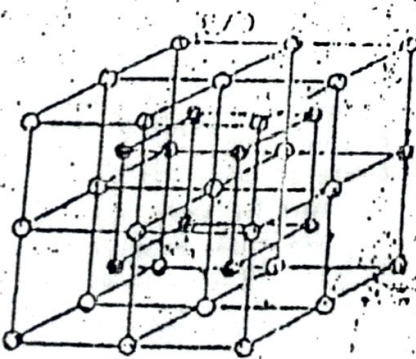
15-4

Ionic Solids

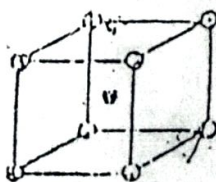
Ionic solids are composed of positive and negative ions. We must suppose that in order to form such a crystal, the ions will so arrange themselves as to achieve the lowest possible energy. This can be accomplished if ions of the same sign are at a maximum distance from each other while ions of opposite sign are at a minimum distance. If this is to happen in three dimensions, each ion will be surrounded by a number of oppositely charged ions. This number is called the coordination number of the ion. The most common coordination numbers in ionic crystals are 4, 6, and 8. We will look at an example of each.

1. Coordination Number 8, Cubic Structure. Figure 15-15 shows a portion of the CsCl crystal. Note that every Cs^+ ion is surrounded by 8 Cl^- ions, each an equal distance away, and each Cl^- is similarly surrounded by Cs^+ ions. This type of structure is called cubic. Note that the lattice type here is simple cubic. A motif consists of one Cs^+ ion and one Cl^- ion, and we may choose our lattice

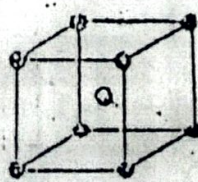
*We have already seen the term "coordination number" used to express a similar concept (Section 6-7).



(a)



(b)



(c)

- Cs^+
- Cl^-

Figure 15-15 The CsCl Crystal. (a) The entire crystal. (b) A small portion of the crystal. Each Cs^+ ion is surrounded by eight Cl^- ions. This is a unit cell if the lattice point is the center of a Cs^+ ion. (c) Each Cl^- ion is surrounded by eight Cs^+ ions.

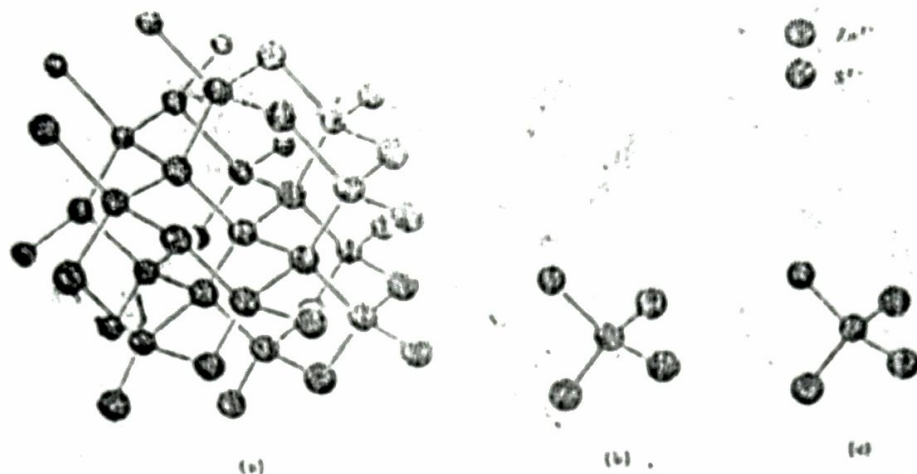


Figure 15-16 The Zincblende Crystal. (a) The entire crystal. (b) A small portion of the crystal. Each Zn^{2+} ion is surrounded by four S^{2-} ions. (c) A small portion of the crystal. Each S^{2-} ion is surrounded by four Zn^{2+} ions.

point to be at the center of a Cl^- ion. The cubic structure of the crystal is then easily seen. However, not every ionic solid in which the coordination number is 8 has a simple cubic lattice.

2. **Coordination Number 4. Tetrahedral Structure.** Figure 15-16 shows the structure of zincblende, a form of ZnS . In this crystal each Zn^{2+} ion is equidistant from 4 S^{2-} ions, and each S^{2-} ion is equidistant from 4 Zn^{2+} ions. In each case, the four equidistant ions are located at the corners of a regular tetrahedron, and this type of structure is called **tetrahedral**. The lattice here is face-centered cubic. It is not easy to see this from Figure 15-16, and it is helpful to look at a model of this system.

3. **Coordination Number 6. Octahedral Structure.** An example of this system is NaCl (Figure 15-17). If we examine this figure carefully, we see (Figure 15-17) that each Na^+ is surrounded by 6 equidistant Cl^- ions, and each Cl^- ion is surrounded by 6 equidistant Na^+ ions. In each case the six equidistant ions are located at the corners of a regular octahedron, and this type of structure is called **octahedral**. We have already seen that the lattice here is face-centered cubic.

In each of our examples, the total number of positive ions is equal to the total number of negative ions, because the formulas are of the type AB . This, of course, is not true for ionic solids such as CaF_2 , Na_2S , K_2O , etc. In these cases, the coordination numbers of the two ions are different. For example, in CaF_2 , each Ca^{2+} ion has a coordination number of 8 and each F^- has a coordination number of 4.

We might expect that the cubic structure would be the structure of choice for all ionic solids of the form AB , since it produces a coordination number of 8, which is the highest of the common coordination numbers. However, another important factor is involved—the size of the ions. The type of structure formed is almost



Figure 15-17 Two small portions of the NaCl crystal. (a) Each Na^+ ion is surrounded by six Cl^- ions. (b) Each Cl^- ion is surrounded by six Na^+ ions.

Coord. No 6
 NaCl , KBr , MgO ,
 AgCl , CsCl
 Coord No 8
 CaS , Cu_2O , CsCl , CsBr

Table 15-2 Crystal Structure Determined by the Limiting Values of r_+/r_-

Limiting values of r_+/r_-	Crystal structure	Coordination number of cation
> 0.732	Cubic	8
$0.414-0.732$	Octahedral	6
$0.225-0.414$	Tetrahedral	4

exclusively determined by the larger of the ions, and usually this is the anion. The anions tend to form close packed structures with the smaller cations fitting into the voids. Since the tetrahedral structure has a coordination number of 4, it has the smallest voids while the cubic structure has the largest voids. Each of the possible structures is limited in how closely the anions can approach each other with the cations in the voids. If we try to push the anions closer together than they already are, we would experience a repulsive force originating from overlapping electron clouds. Since the structures depend on the relative sizes of anion and cation, we will define a term that will help us to decide what structure we might expect given the respective anion and cation sizes. This term, called the radius ratio, is defined as

$$\text{radius ratio} = \frac{r_+}{r_-}$$

where r_+ is the radius of the cation and r_- the radius of the anion (see Section 13-10). It has been determined that there are limiting values of the radius ratio which determine the type of crystal structure formed by ionic solids. Table 15-2 gives these values. Table 15-3 lists a number of ionic solids and their radius ratios.

Remember that in ionic solids there are no molecules. In a crystal of NaCl, we find Na^+ ions and Cl^- ions but never molecules of NaCl. This is in contrast to molecular solids, in which molecules are indeed present. Because of this, an ionic crystal can be imagined as a single giant molecule whose molecular weight is enormous. This explains the very high melting points and heats of fusion found for ionic crystals. Since there are no molecules present in the ionic solids the forces holding the solid together are the electrostatic interactions found between ions (ionic bonds). In order to melt an ionic crystal, enough energy must be supplied to overcome the attractive forces between the ions, which are quite large.

Solid	r_+/r_-	Coordination number of cation
MgF_2	0.48	6
NiF_2	0.51	6
CoF_2	0.53	6
ZnF_2	0.54	6
MnF_2	0.59	6
CaF_2	0.71	8
CaF_2	0.73	8
SrF_2	0.83	8
PbF_2	0.88	8
BaF_2	0.99	8
CaCl_2	0.93	8
NaCl	0.62	6
ZnS	0.40	4

Table 15-3 Ionic Solids, r_+/r_- Ratios, and Coordination Numbers of Cations

High melting point & heat of fusion if ionic
In ionic crystals, which require high energy to overcome

Grims.
gray tin Silicon
crystallizes diamond

Covalent Crystals

At the beginning of Chapter 14, it was pointed out that covalent molecules may consist of: comparatively small number of atoms, or of a very large number, so large that an entire crystal is essentially a single molecule made up of perhaps 10^{22} or 10^{23} atoms. We may refer to such crystals as giant molecules. A good example of such a crystal is the diamond structure shown in Figure 15-1a. The bonding between the carbon atoms is purely covalent. Figure 15-1a illustrates a number of interesting features. Each carbon atom is surrounded by four equidistant carbon atoms. The angle between any two bonded atoms is the tetrahedral angle, $109^\circ 28'$. The basic unit cell of the diamond structure is a cubic cell; the covalent bonding permeates throughout the complete crystal. In order to melt such a structure, one must rupture a great many of these strong covalent bonds, which gives diamond its very high melting point. Germanium, gray tin, and silicon also crystallize in the diamond structure. All of them are in group IVA of the periodic table, so that all have four outer-shell electrons. It is not surprising then that all bond in the same way. Other systems that assume the diamond structure are ZnS, AgI, AlP, and SiC. We find in these structures that each atom is tetrahedrally surrounded by four unlike atoms; the bonding is almost exclusively covalent. The covalent structure, as in diamond, permeates the complete crystal.

In small covalent molecules, the atoms are connected to each other by strong covalent bonds within the molecules, but there are no covalent bonds between the molecules. The molecules are held together in the crystal by van der Waals forces. The molecules tend to pack within the crystals as closely as their sizes allow; we may call these molecular crystals. Typical examples of compounds or elements that form molecular crystals are ethane, carbon tetrachloride, nitrogen, argon, benzene, and naphthalene. It is relatively easy to melt molecular crystals, precisely because covalent bonds do not have to be broken. When this type of crystal melts, it is only the weak van der Waals forces that must be overcome. The molecules are still intact in the liquid state, and even in the gaseous state (Figure 15-18). This is the reason that compounds made up of small covalent compounds are usually liquids, gases, or relatively low melting solids. Most nonionic organic substances crystallize as molecular crystals except those in which hydrogen bonding is present.

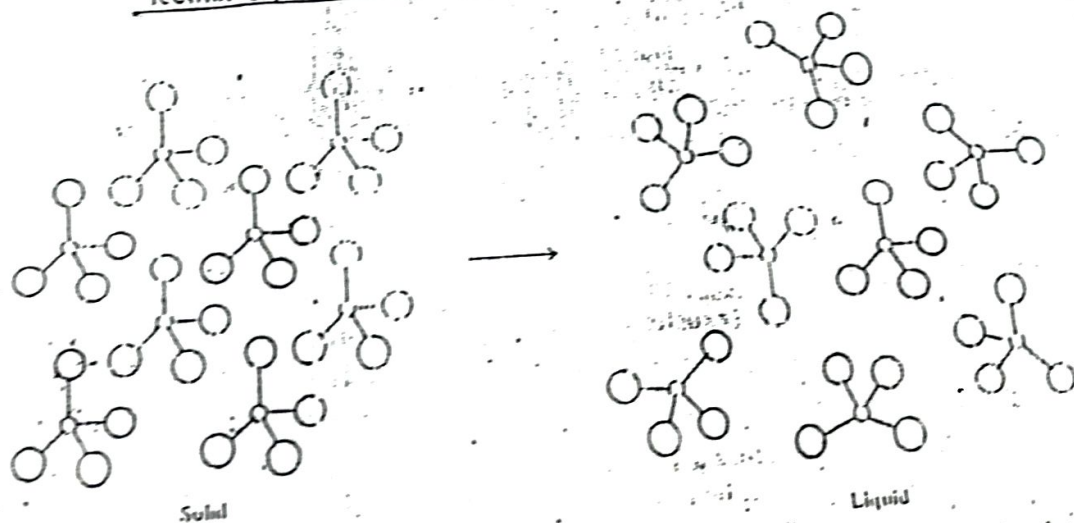


Figure 15-18 The molecules of solid CCl_4 are rigidly held in a crystal lattice by weak van der Waals forces. When the solid melts, the molecules are still intact (no covalent bonds have been broken) but are no longer held in a rigid array.

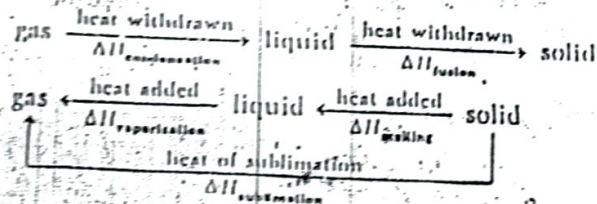
The hydrogen bond is very important in a number of crystal structures. Covalent organic and inorganic acids, as well as many hydrated salts, owe their structure to hydrogen bonds. The ice structure is shown in Figure 6-16. All these crystals exhibit the open structure expected of hydrogen-bonded systems.

15-6

Phase Diagrams

The three states of matter, gas, liquid, and solid, are known as phases. Most substances can exist in any of these three phases, but only under certain conditions of temperature and pressure. For example, at 1 atm pressure, water is a liquid between 0°C and 100°C, but at 5 atm pressure, water is a liquid between about -0.1°C and 152°C.

As the temperature of a gas is lowered at constant pressure, a point is reached where liquid begins to form. As we know, this is the condensation temperature of the gas (or the boiling point of the liquid) at this particular pressure. The gas and liquid are in equilibrium at this T and P and the system is now a two-phase system. We say that the system is at equilibrium since if it was completely isolated it would not change with time. The gas and liquid would remain as such indefinitely. If we continue to withdraw heat from the system, the temperature remains constant while more gas is converted into liquid. Eventually, a point is reached where all the gas is converted into liquid and the system again becomes a one-phase system. Further withdrawal of heat from the liquid system lowers the temperature until a point is reached when solid begins to form. This is, of course, the freezing temperature of the liquid (or the melting point of the solid) at this particular pressure. The two-phase system (liquid and solid) is in equilibrium. Further withdrawal of heat does not lower the temperature but first converts more liquid into solid. Finally, all the liquid has been converted into solid; further withdrawal of heat now would lower the temperature of the solid. If heat is supplied to the system at the same pressure, the whole process can be reversed. This is shown as follows. Note that the terminology changes, depending on which way the process is proceeding.



Note that

$$\begin{aligned} \Delta H_{\text{condensation}} (\text{exothermic}) &= -\Delta H_{\text{vaporization}} (\text{endothermic}) \\ \Delta H_{\text{fusion}} (\text{exothermic}) &= -\Delta H_{\text{melting}} (\text{endothermic}) \\ \Delta H_{\text{sublimation}} &= \Delta H_{\text{melting}} + \Delta H_{\text{vaporization}} (\text{endothermic}) \end{aligned}$$

As we saw in Section 6-3, boiling points and melting points are dependent on the external pressure. How a substance behaves under different conditions of temperature and pressure can be represented on a graph called a phase diagram. A phase diagram condenses a great deal of information into a small figure. To see this, let us consider the phase diagram for water given in Figure 15-19. The various phases are labeled on the graph. The line BC is the liquid-vapor line, which tells us the

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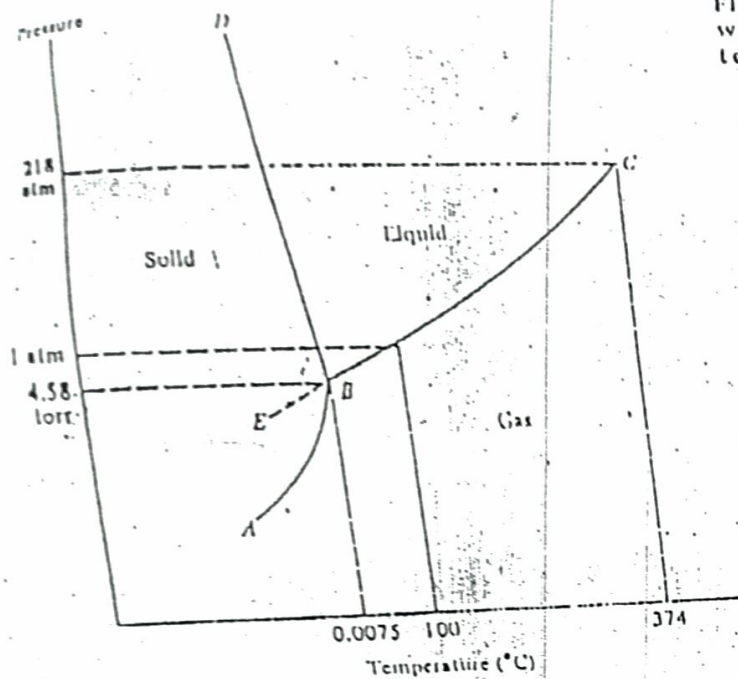


Figure 15-19 The phase diagram of water (not drawn to scale). The letters are explained in the text.

temperature and pressure conditions necessary to condense a gas or to vaporize a liquid. For example, at 1 atm pressure, the temperature must be 100°C, which is the normal boiling point. If the atmospheric pressure is increased to 218 atm, the boiling point of water increases to 374°C. This is also the critical point of water (Section 4-14). DB is the melting point line; it tells us how the equilibrium melting temperatures change with external pressures. Note that there is no critical temperature for a solid-liquid system. At point B, gas, liquid, and solid are in equilibrium. This is known as the triple point, since there are three phases in equilibrium. For water it occurs at 0.0075°C and 4.58 torr. The phase diagram shows that if the temperature or pressure even slightly changes from the triple-point values, the three phases are no longer in equilibrium. AB is the sublimation curve for water. Solid and gas are in equilibrium along this curve. At the temperatures and pressures along this curve, one may convert the solid directly into the gas, or vice versa, without going through a liquid phase.

EB, which is shown as a dashed line in the phase diagram, is a nonequilibrium extension of the liquid-gas equilibrium curve. Water can be supercooled below 0°C, where it would normally freeze. This may occur, since for any liquid to form a solid, crystals of ice or other small solid particles or a rough surface must be present so that other crystals can grow upon them. It is quite similar to the phenomenon of supersaturation discussed in Section 7-2. The EB line is known as a nonequilibrium or metastable equilibrium state. If we drop the temperature low enough, the water will freeze spontaneously even though impurities are absent.

There is one important aspect of the phase diagram of water that is not true of most other substances. The BD line slopes to the left, whereas for most other species, the solid-liquid line slopes to the right. A thermodynamic analysis shows that this occurs when the liquid is more dense than the solid. Bismuth and antimony behave similarly.

Phase diagrams have been experimentally determined for thousands of pure substances as well as for mixtures of two, three, and more components. They are extremely valuable since, as previously noted, they contain such large quantities of information in a single graph.