

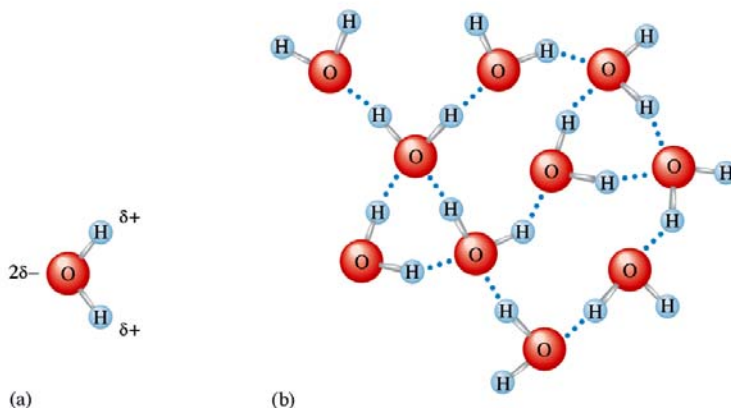
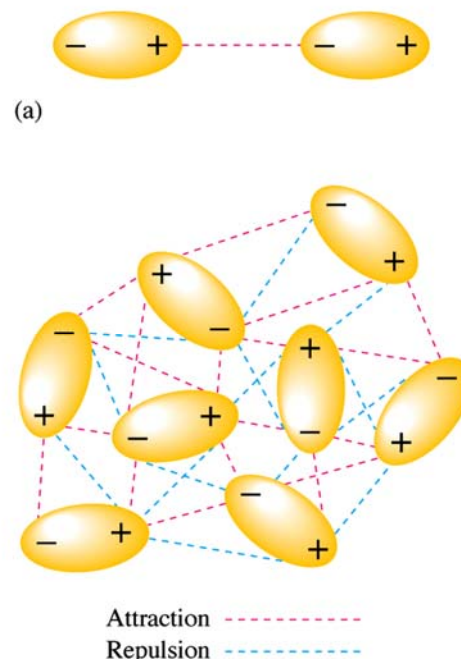
Chapter 10 Outline – Liquids and Solids

Intermolecular Forces

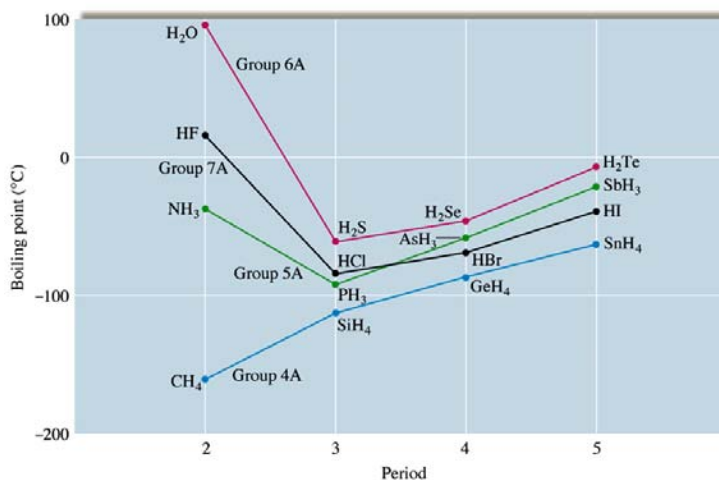
- The solid and liquid states are referred to as the **condensed states of matter**.
- Intramolecular forces exist within a molecule (covalent bonds).
- Intermolecular forces exist between molecules (dipole-dipole forces, hydrogen bonds and London forces)
- When a substance changes from solid to liquid to gas the molecules stays intact. The changes in state are due to changes in the forces among the molecules rather than in those within the molecules.

Dipole-Dipole Forces

- Molecules with polar bonds often behave in an electric field as if they had a center of positive charge and a center of negative charge. They exhibit a dipole moment.
- Molecules with dipole moments can attract each other electrostatically by lining up so that the positive and negative ends are close to each other. This is called a dipole-dipole attraction.
- Dipole-dipole forces are typically only about 1% as strong as covalent or ionic bonds and they rapidly become weaker as the distance between the dipoles increases.
- Particularly strong dipole-dipole interactions are seen in molecules in which hydrogen is bound to a highly electronegative atom, such as nitrogen, oxygen or fluorine.
- Two factors account for the strength of these interactions: the great polarity of the bond and the close approach of the dipoles, allowed by the very small size of the hydrogen atom. Because dipole-dipole attractions of this type are so unusually strong, they are called **hydrogen bonding**. Below, note the hydrogen bonding that occurs between water molecules.

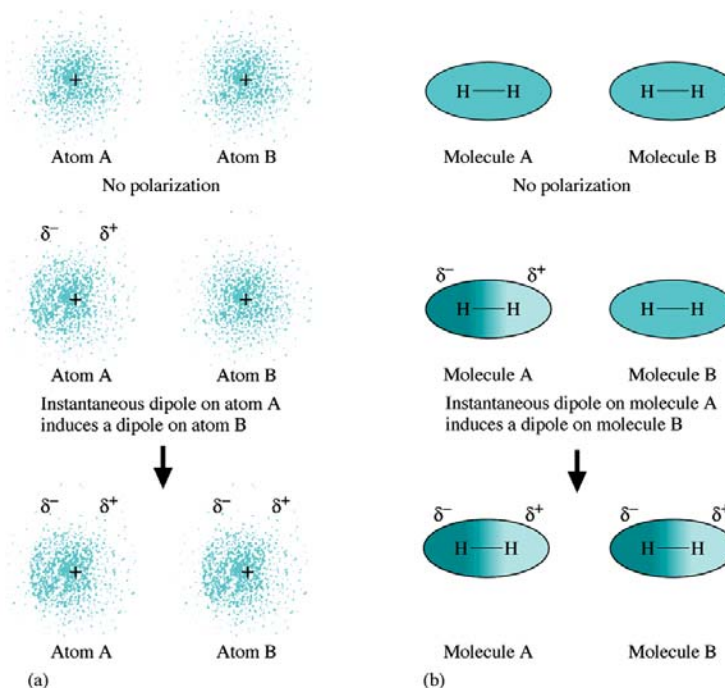


- Hydrogen bonds have an important effect on physical properties. Note in the diagram on the next page that the nonpolar tetrahedral hydrides of group 4A show a steady increase in boiling point with molar mass, whereas for other groups, the lightest member has an unexpectedly high boiling point. This is due to the large hydrogen bonding interactions that exist among the smallest molecules with the most polar X—H bonds. These unusually strong hydrogen bonding forces are due to the high electronegativity values of the lightest elements in each group and the small size of the first element of a group which allows for the close approach of the dipoles.



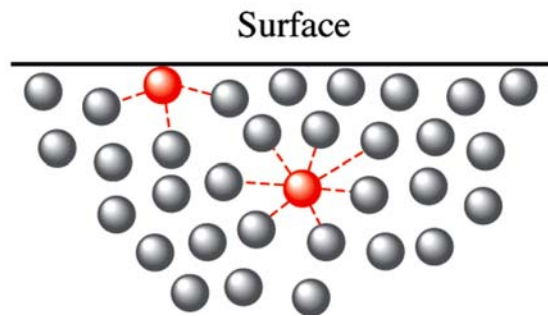
London Dispersion Forces

- Even molecules without dipole moments must exert forces on each other. We know this because even the noble gases exist in solid and liquid states under certain conditions.
- The forces that exist between noble gas atoms and nonpolar molecules are called **London dispersion forces**.
- As the electrons move about the nucleus, a momentary nonsymmetrical electron distribution can develop that produces a temporary dipolar arrangement of charge. The formation of this temporary dipole can, in turn, affect the electron distribution of a neighboring atom. The instantaneous dipole that occurs accidentally in a given atom can then induce a similar dipole in a neighboring atom as seen in the diagram to the right.
- For these reactions to produce a solid, the motions of the atoms must be greatly slowed down. This explains why noble gases have such low freezing points.
- Freezing point increases going down a group. The principle cause for this trend is that as the atomic number increases, the number of electrons increases, and there is an increased chance of the occurrence of momentary dipole interactions. This phenomenon is described using the term **polarizability** which indicates the ease at which the electron “cloud” of an atom can be distorted to give a dipolar distribution.
- The importance of London dispersion forces increases greatly as the size of an atom increases.



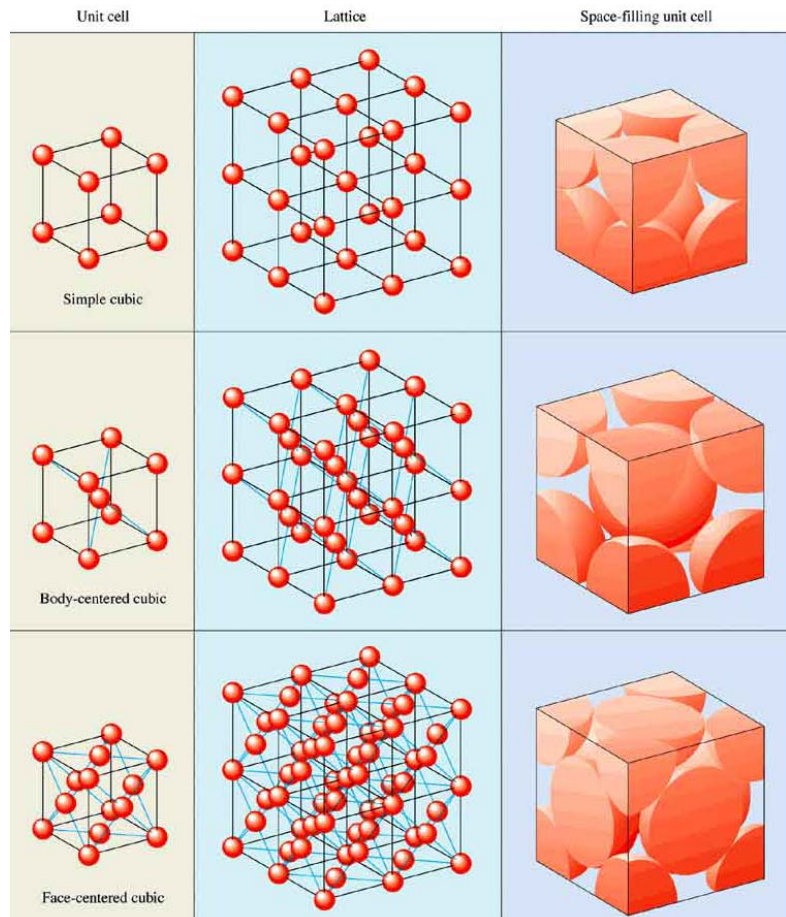
The Liquid State

- Liquids exhibit low compressibility, lack of rigidity and high density when compared with gases.
- The beading of liquids is due to intermolecular forces. Although molecules in the interior of the liquid are completely surrounded by other molecules, those at the liquid surface are subject only to attractions from the side and below. The effect of this uneven pull on the surface molecules tends to draw them into the body of the liquid and cause a droplet of liquid to assume the shape that has the minimum surface area – a sphere.
- The resistance of a liquid to increase in its surface area is called the **surface tension of a liquid**. Liquids with strong intermolecular forces, such as those with polar molecules, tend to have relatively high surface tensions.
- Polar liquids exhibit capillary action, the spontaneous rising of a liquid in a narrow tube. Two different forces are responsible for this behavior: cohesive forces, the intermolecular forces among the molecules of the liquid, and adhesive forces, the forces between the liquid molecules and their container.
- Adhesive forces occur when a container is made of a substance that has polar bonds. Glass surfaces contain many oxygen atoms with partial negative charges that are attractive to the positive end of a polar molecule such as water.
- Because water has strong cohesive (intermolecular) forces and strong adhesive forces to glass, it pulls itself up a glass capillary tube to a height where the weight of the column of water just balances the water's tendency to be attracted to the glass surface.
- The concave shape of the meniscus shows water's adhesive forces toward glass are stronger than its cohesive forces. A nonpolar liquid such as mercury shows a convex meniscus. This behavior is characteristic of a liquid in which the cohesive forces are stronger than the adhesive forces toward glass.
- Viscosity** is a measure of a liquid's resistance to flow. Liquids with large intermolecular forces tend to be highly viscous.



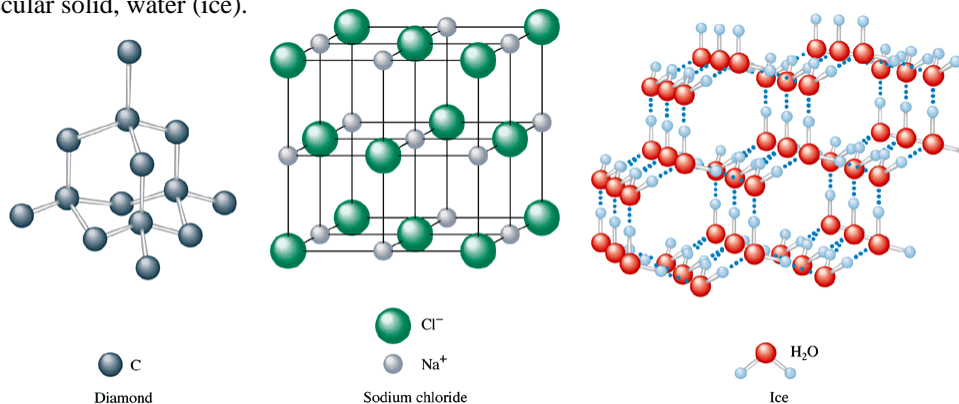
An Introduction to Structure and Types of Solids

- Crystalline solids** are solids with a highly regular arrangement of their components.
- Amorphous solids** (example: glass) are solids with considerable disorder in their structures.
- The positions of the components in a crystalline solid are usually represented by a **lattice**, a three-dimensional system of points designating the positions of the components (atoms ions or molecules) that make up the substance.
- The smallest repeating unit of the lattice is called a **unit cell**.
- The structures of crystalline solids are most commonly determined using **X-ray diffraction**.



Types of Crystalline Solids

- **Ionic solids**, such as sodium chloride, have ions at the points of the lattice that describe the structure of the solid.
- A **molecular solid**, such as ice, has discrete covalently bonded molecules at each of its lattice points.
- **Atomic solids**, such as carbon, silicon and all metals, have atoms at the lattice points that describe the structure of the solid.
- The images below show an atomic solid, carbon (diamond), an ionic solid, sodium chloride, and a molecular solid, water (ice).



- Atomic solids can be subdivided into the following subgroups based on the bonding that exists among the atoms in the solid: **metallic solids, network solids, and Group 8A solids**.
 - In metallic solids a special type of delocalized nondirectional covalent bonding occurs.
 - In network solids, the atoms bond to each other with strong directional covalent bonds that lead to giant molecules, or networks, of atoms.
 - In Group 8A solids, the noble gas elements are attracted to each other with London dispersion forces.

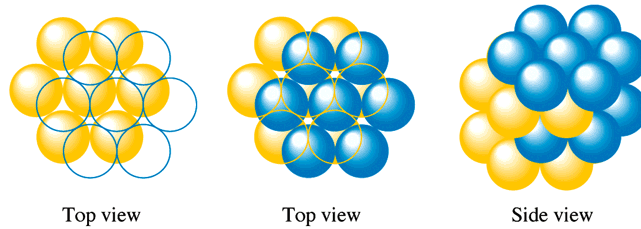
| Summary of Types of Crystalline Solids | | | | | |
|---|----------------------|---|--------------------------|---|--------------|
| | Atomic Solids | | | Compounds | |
| | Metallic | Network | Group 8A | Molecular Solids | Ionic Solids |
| Components that occupy the lattice points | metal atoms | nonmetal atoms | noble gases | discrete molecules | ions |
| Bonding: | delocalized covalent | directional covalent leading to giant molecules | London dispersion forces | dipole-dipole and/or London dispersion forces | ionic |

Structure and Bonding in Metals

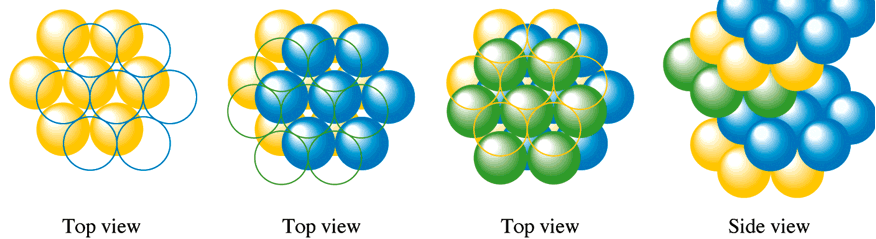
- Metals are characterized by high thermal and electrical conductivity, malleability and ductility. These properties are due to the nondirectional covalent bonding found in metallic crystals.
- A metallic crystal can be pictured as containing spherical atoms packed together and bonded to each other equally in all directions. Such an arrangement is called closest packing.
- The spheres are packed in layers in which each sphere is surrounded by six others. In the second layer the spheres do not lie directly over those in the first layer. Instead, each one occupies an indentation formed by three spheres in the first layer.
- If the third layer is positioned directly beneath the first layer, it is called **aba arrangement**.
- If the third layer is positioned so that no first layer sphere lies over one in the third layer, it is called **abc arrangement**.
- The aba arrangement has the hexagonal unit cell and the resulting name is called the **hexagonal closest packed (hcp)** structure.
- The abc arrangement has a face centered cubic unit cell and the resulting structure is called the **cubic closest packed (ccp)** structure.

- Magnesium and zinc are hexagonal closest packed.
- Aluminum, iron, copper, cobalt and nickel form cubic closest packed solids.
- Why a particular metal adopts the structure it does is not well understood.
- Although the shapes of most metals can be changed relatively easily, most metals are durable and have high melting points. These facts indicate that the bonding in most metals is both strong and nondirectional.

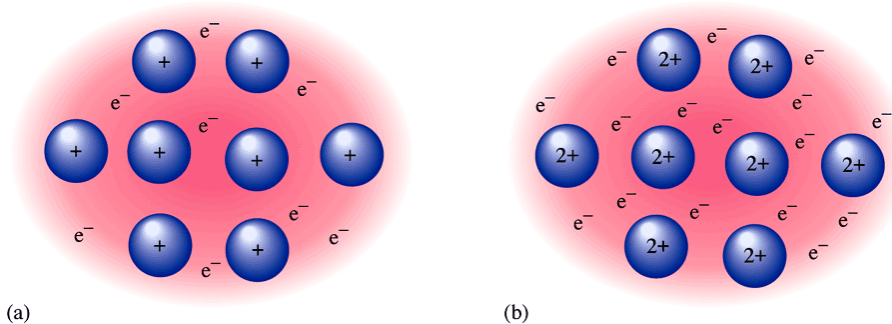
(a) *abab* — Closest packing



(b) *abca* — Closest packing

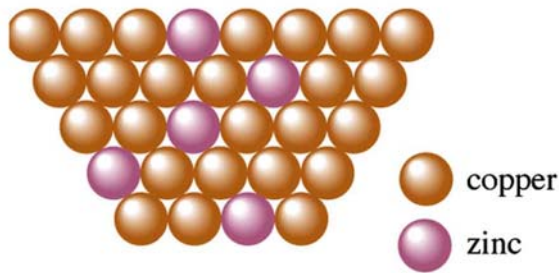


- The simplest picture that explains these observations is the electron sea model, which envisions a regular array of metal cations in a sea of valence electrons. The mobile electrons can conduct heat and electricity, and the metal ions can be easily moved around as the metal is hammered into a sheet or pulled into a wire.



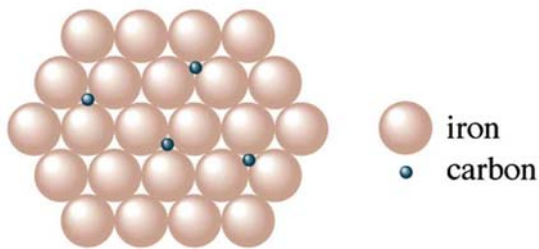
Metal Alloys

- Because of the nature of the structure of metals, other elements can be introduced into a metallic crystal relatively easily to produce a substance called an alloy.
- An alloy is a substance that contains a mixture of elements and has metallic properties.
- There are two types of alloys:
 - In a substitutional alloy some of the host metal atoms are replaced by other metal atoms similar in size. When zinc atoms replace host copper atoms, brass is formed. Brass is a substitutional alloy.
 - In an interstitial alloy some of the interstices (holes) in the closest packed structure are occupied by small atoms. Steel is the best known interstitial alloy. It contains carbon atoms in the holes of an iron crystal. Pure iron is relatively soft, ductile and malleable due to the absence of directional bonding. When carbon, which forms strong directional bonds, is introduced into an iron crystal, the presence of the of the directional carbon-iron bonds makes the resulting alloy harder, stronger and less ductile than pure iron.
 - Mild steels, containing less than 0.2% carbon, are ductile and malleable and used for nails, cables, and chains.
 - Medium steels, containing 0.2 to 0.6% carbon are harder than mild steels and are used in rails and structural steel beams.
 - High carbon steels, containing 0.6-1.5% carbon are tough and hard and are used for springs, tools and cutlery.



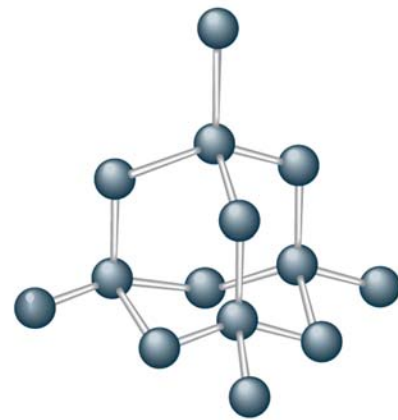
Brass

(a)



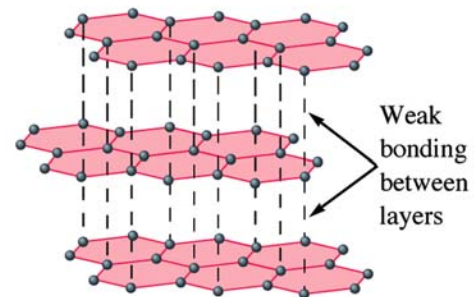
Steel

(b)



(a)

Diamond



(b)

Graphite

Carbon and Silicon: Network Atomic Solids

- Many atomic solids contain strong directional covalent bonds to form a solid that might best be viewed as a “giant molecule”. We call these substances network solids.
- In contrast to metals, these materials are typically brittle and do not efficiently conduct heat or electricity.
- The two most common forms of carbon, diamond and graphite, are typical network solids.
- Graphite is very different from diamond. Diamonds are hard, colorless and an insulator. Graphite is slippery, black and a conductor. These differences in bonding in the two types of solids.
- In contrast to the tetrahedral arrangement of carbon atoms in diamond, the structure of graphite is based on layers of carbon atoms arranged in fused six-membered rings.
- The slipperiness that is characteristic of graphite can be explained by noting that graphite has very strong bonding within the layers of carbon atoms but little bonding between the layers.
- The application of 150,000 atm of pressure at 2800°C converts graphite virtually completely to diamond. The high temperature is needed to break strong bonds in graphite so the rearrangement can occur.
- **Silicon is to geology as carbon is to biology.** The carbon based compounds of biology and the silicon based compounds of geology have markedly different structures. Carbon compounds typically contain long strings of carbon-carbon bonds, whereas the most stable silicon compounds involve chains with silicon-oxygen bonds.
- The fundamental silicon-oxygen compound is silica, SiO_2 .

- When silica is heated above its melting point (about 1600°C) and cooled rapidly, an amorphous solid called glass results.
 - Common glass results when substances such as Na_2CO_3 are added to the silica melt which is then cooled.
 - The addition of B_2O_3 produces borosilicate glass that expands and contracts little under large temperature changes. The most common brand is Pyrex.
 - The addition of K_2O produces an especially hard glass that can be ground to the precise shape needed for eyeglass and contact lenses.

Ceramics

- Ceramics are typically made from clays (which contain silicates).
- Ceramics are nonmetallic materials that are strong, brittle, and resistant to heat and attack by chemicals.
- Like glass, ceramics are based on silicates, but the resemblance ends there. Glass can be melted and re-melted as often as desired, but once a ceramic has been hardened, it is resistant to extremely high temperatures. A glass is a homogeneous, noncrystalline “frozen solution,” and a ceramic is heterogeneous. A ceramic contains two phases: minute crystals of silicates that are suspended in a glassy cement.

Molecular Solids

- Molecular solids have strong covalent bonding within the molecules, but relatively weak forces between the molecules.
- Many molecules such as CO_2 , I_2 , P_4 , and S_8 have no dipole moment and the intermolecular forces are London dispersion forces.
- When molecules do have dipole moments, their intermolecular forces are significantly greater, especially when hydrogen bonding is possible.

Ionic Solids

- Ionic solids are stable, high melting substances held together by the strong electrostatic forces that exist between oppositely charged ions.
- The structures of most binary ionic solids, such as sodium chloride, can be explained by the closest packing of spheres. Usually the smaller cation fills the holes between anions.
- There are three types of holes in closest packed structures:
 - Trigonal holes formed by three spheres in the same layer.
 - Tetrahedral holes are formed when a sphere sits in the dimple of three spheres in an adjacent layer.
 - Octahedral holes are formed between two sets of three spheres in adjoining layers of the closest packed structures
- For spheres of a given diameter, the hole increase in size in the order: trigonal < tetrahedral < octahedral
- Trigonal holes are so small they are never occupied in binary ionic compounds. Whether the tetrahedral or octahedral holes in a given binary ionic solid are occupied depends mainly on the relative sizes of the anion and cation.
- The structure of sodium chloride can be described in terms of a cubic closest packed array of Cl^- ions with Na^+ ions in all the octahedral holes.

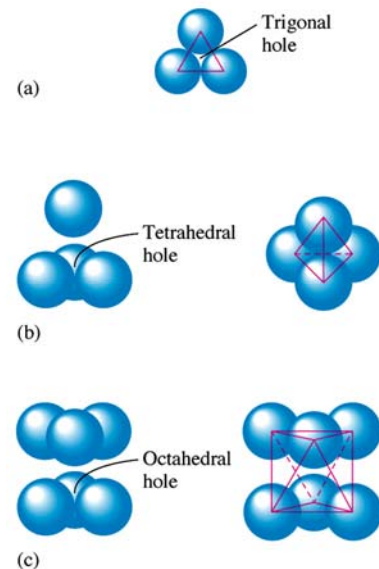


TABLE 10.7 Types and Properties of Solids

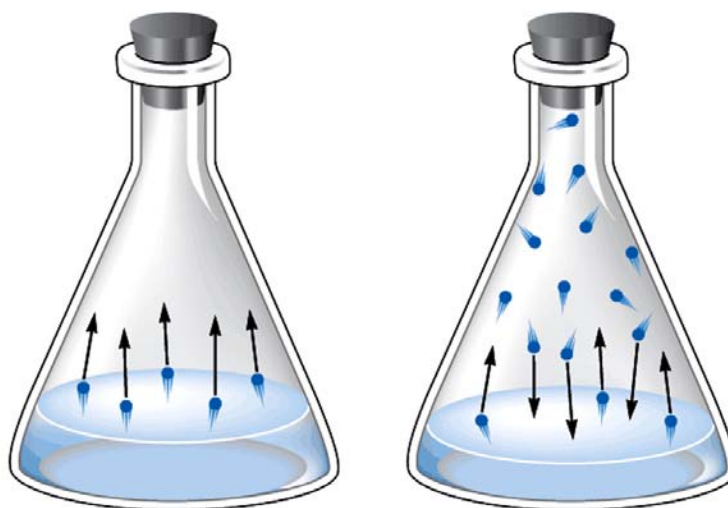
| Type of Solid: | Atomic | | | Molecular | Ionic |
|---------------------|---|---|--------------------------|---|---|
| | Network | Metallic | Group 8A | | |
| Structural Unit: | Atom | Atom | Atom | Molecule | Ion |
| Type of Bonding: | Directional covalent bonds | Nondirectional covalent bonds involving electrons that are delocalized throughout the crystal | London dispersion forces | Polar molecules: dipole–dipole interactions Nonpolar molecules: London dispersion forces | Ionic |
| Typical Properties: | Hard High melting point Insulator | Wide range of hardness Wide range of melting points Conductor | Very low melting point | Soft Low melting point Insulator | Hard High melting point Insulator |
| Examples: | Diamond | Silver Iron Brass | Argon(s) | Ice (solid H ₂ O) Dry ice (solid CO ₂) | Sodium chloride Calcium fluoride |

Vapor Pressure and Changes of State

- There is clear evidence that the molecules of a liquid can escape the liquid's surface and form a gas. This is called **vaporization** or **evaporation**.
- Vaporization is endothermic because energy is required to overcome the relatively strong intermolecular forces in the liquid.
- The energy required to vaporize 1 mole of a liquid at a pressure of 1 atm is called the **heat of vaporization** or the **enthalpy of vaporization, ΔH_{vap}** .
- Because of strong hydrogen bonding among its molecules in the liquid state, water has an unusually large heat of vaporization (40.7 kJ/mol).

Vapor Pressure

- When a liquid is placed in a sealed container, the amount of liquid at first decreases but eventually becomes constant. The decrease occurs because there is an initial net transfer of molecules from liquid to the vapor state. This evaporation process occurs at a constant rate at a given temperature.
- The process by which vapor molecules re-form a liquid is called condensation. Eventually, enough vapor molecules are present above the liquid so that the rate of condensation equals the rate of evaporation. At this point no further net change occurs in the amount of liquid or vapor because the two processes exactly balance each other; the system is at equilibrium. This process is highly dynamic.
- Liquids with high vapor pressure are said to be **volatile**. The vapor pressure of a liquid is principally determined by the size of the intermolecular forces in the liquid.



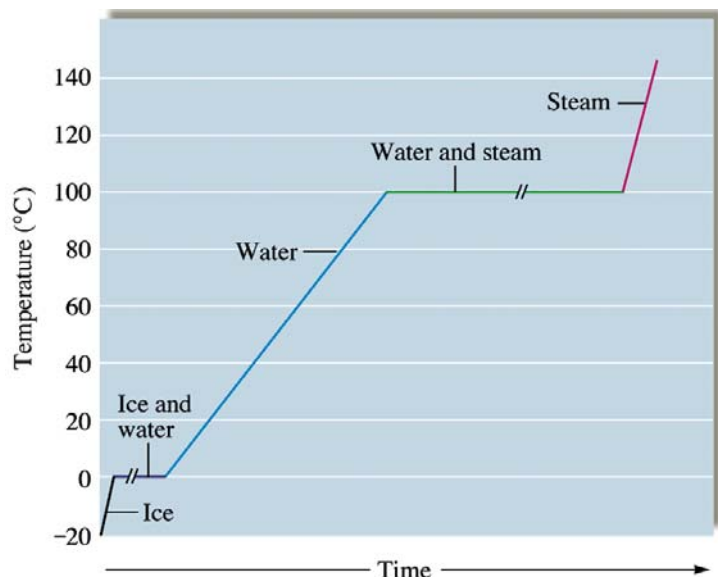
- In general, substances with large molar masses have relatively low vapor pressures, mainly because of the large dispersion forces. The more electrons a substance has, the more polarizable it is, and the greater are the dispersion forces.
- Vapor pressure increases significantly with temperature.
- Like liquids, solids have vapor pressures. Under normal conditions iodine sublimates; it goes directly from the solid to the gaseous state without passing through the liquid state. Sublimation also occurs with dry ice (solid CO_2).

TABLE 10.8
The Vapor Pressure of Water
as a Function of Temperature

| T ($^{\circ}\text{C}$) | P (torr) |
|----------------------------|------------|
| 0.0 | 4.579 |
| 10.0 | 9.209 |
| 20.0 | 17.535 |
| 25.0 | 23.756 |
| 30.0 | 31.824 |
| 40.0 | 55.324 |
| 60.0 | 149.4 |
| 70.0 | 233.7 |
| 90.0 | 525.8 |

Changes of State

- A heating curve is a plot of temperature versus time for a process where energy is added at a constant rate.
- The heating curve for water is shown below.



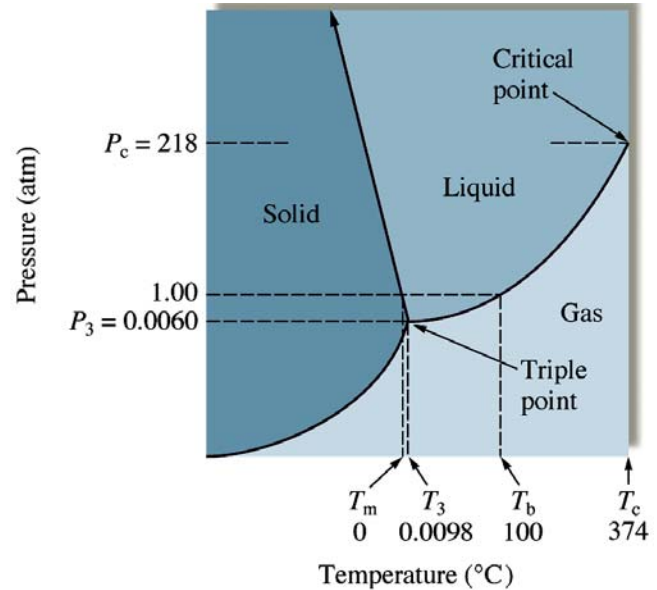
- As energy flows into the ice, the random vibrations of the water molecules increases as the temperature rises.
- At the melting point, all the energy added is used to disrupt the ice structure by breaking hydrogen bonds, increasing the potential energy of the water molecules. The enthalpy change that occurs at the melting point is called the **heat of fusion**, or the **enthalpy of fusion**, ΔH_{fus} .
- The temperature remains constant until all of the solid has completely changed to liquid; then it begins to increase again.
- At 100°C the liquid water reaches its boiling point and the temperature remains constant as the energy added is used to vaporize the liquid.

- When the liquid is completely changed to vapor, the temperature again begins to rise.
- Changes in state are physical changes, only intermolecular forces are overcome.
- As the temperature of the solid is increased, a point is eventually reached where the liquid and solid have identical vapor pressures. This is the melting point.
- The normal melting point is defined as the temperature at which the solid and liquid states have the same vapor pressure under conditions where the total pressure is 1 atm.
- Boiling occurs when the vapor pressure of a liquid becomes equal to the pressure of its environment. The normal boiling point of a liquid is the temperature at which the vapor pressure of the liquid is exactly one atmosphere. The enthalpy change that occurs at the boiling point is called the **heat of vaporization**, or the **enthalpy of vaporization**, ΔH_{vap} .
- Changes of state do not always occur exactly at the boiling point or melting point. Water can be supercooled; it can be cooled below 0°C at 1 atm pressure and remain in the liquid state. **Supercooling** occurs because as it is cooled, the water may not achieve the degree of organization necessary to form ice at 0°C and thus continues to exist as a liquid.
- A liquid can also be **superheated**, or raised above its boiling point, especially if it is heated rapidly. Superheating can occur because bubble formation in the interior of the liquid requires that many high energy molecules gather in the same vicinity, and this may not happen at the boiling point, especially if the liquid is heated rapidly.

- Once a bubble does form, since its internal pressure is greater than that of the atmosphere, it can burst before rising to the surface, blowing the surrounding liquid out of the container. This is called **bumping**. Boiling chips are bits of porous ceramic material containing trapped air that escapes on heating, forming tiny bubbles that act as “starters” for vapor bubble formation.

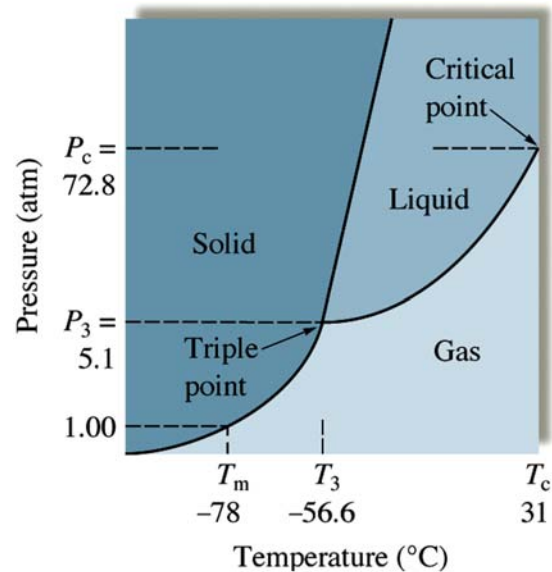
Phase Diagrams

- A phase diagram is a convenient way of representing the phases of a substance as a function of temperature and pressure.
- A phase diagram describes conditions and events in a closed system. The phase diagram for water is shown below.
- Critical temperature** is defined as the temperature above which vapor cannot be liquefied no matter what pressure is applied.
- The **critical pressure** is the pressure required to produce liquefaction at the critical temperature.
- Together the critical pressure and the critical temperature define the **critical point**.
- Note that the solid/liquid boundary on the phase diagram for water has a negative slope.



This means that the melting point of ice decreases as the external pressure increases. This behavior, which is opposite of most substances, occurs because the density of ice is less than that of the liquid water at its melting point. Other substances where the solid form floats (is less dense than) the liquid form include acetic acid, antimony, bismuth, gallium, germanium, silicon and Wood’s metal.

- When water freezes it expands. The low density of ice means that ice formed on rivers and lakes will float, providing a layer of insulation that helps prevent bodies of water from freezing solid in the winter. Aquatic life can therefore continue to live through periods of freezing temperatures.
- A liquid boils at the temperature where the vapor pressure of the liquid equals the external pressure. Thus the boiling point, like the melting point, depends on the external pressure.
- In dry climates (low humidity), snow and ice seem to sublime – a minimum amount of slush is produced.
- Wet clothes put on an outside line at temperatures below 0°C freeze and then dry while frozen. The phase diagram shows that water should not be able to sublime at normal atmospheric pressures. Ice in the environment is not a closed system. Because the vapor produced over the ice can escape from the immediate region as soon as it is formed, the vapor does not come to equilibrium with the solid, and the ice slowly disappears. Sublimation, which seems forbidden by the phase diagram, does in fact occur under these conditions, although it is not the sublimation under equilibrium conditions described by the phase diagram.



- The phase diagram for carbon dioxide is shown below. The solid/liquid line has a positive slope, since solid CO_2 is denser than liquid CO_2 . Carbon dioxide is often used in fire extinguishers, where it exists as a liquid at 25°C under high pressures. Liquid CO_2 released from the extinguisher into the environment at 1 atm immediately changes to a vapor. Being heavier than air, this vapor smothers the fire by keeping oxygen away from the flame. The liquid/vapor transition is highly endothermic, so cooling also results, which helps to put out the fire.