TOPIC

11

LIQUIDS AND INTERMOLECULAR FORCES

The content in this topic is the basis for mastering Learning Objectives 2.1, 2.3, 2.8, 2.11, 2.13, 2.14, 2.15, 2.16, 5.9, and 5.10 as found in the Curriculum Framework.

When you finish reviewing this topic, be sure you are able to:

- Know what kinds of intermolecular forces exist and how they affect the properties of molecules
- Explain the macroscopic differences between solids, liquids, and gases using their molecular structures and behaviors and the forces that hold them together
- Use particle representations to explain the differences between solids, liquids, and gases
- Use intermolecular forces to explain the properties of liquids such as melting point, boiling point, vapor pressure, viscosity, and surface tension
- Use the structures of molecules to predict the types of intermolecular forces that exist between them
- Describe the relationships between the structures of polar molecules and their dipole–dipole intermolecular forces
- Use London dispersions to explain property trends in nonpolar atoms and molecules

A Molecular Comparison of Gases, Liquids, and Solids

Section 11.1

The three phases of matter are solids, liquids, and gases. The phase of a substance depends largely on the balance between the kinetic energy of the particles, which keep the particles moving, and the attractive forces between them, which hold the particles together. The differences in the atomic- and molecular-level structures of solids, liquids, and gases explain their differences in macroscopic properties. Figure 11.1 illustrates macroscopic and molecular views of solids, liquids, and gases.

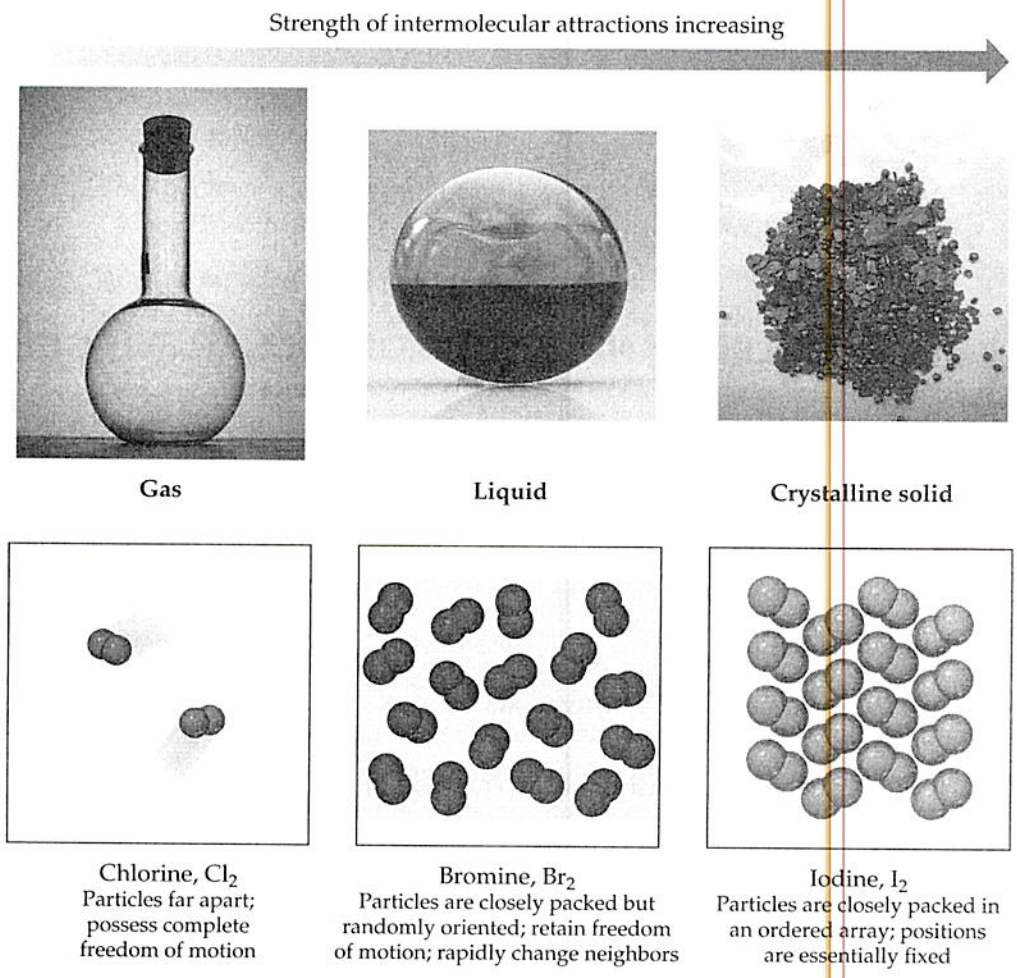


Figure 11.1 Gases, liquids, and solids. Chlorine, bromine, and iodine are all made up of diatomic molecules as a result of covalent bonding. However, because of differences in the strength of the intermolecular forces, they exist in three different states at room temperature and standard pressure: Cl_2 is gaseous, Br_2 is liquid and I_2 is solid.

In **crystalline solids**, the particles are packed closely together in a regular three-dimensional structure called a **crystal**. The close spacing and the relatively strong attractive forces between the individual particles limit their motion. The particles can vibrate in place but do not change positions with respect to each other. Figure 11.2 shows the well-ordered crystalline structure of sodium chloride.

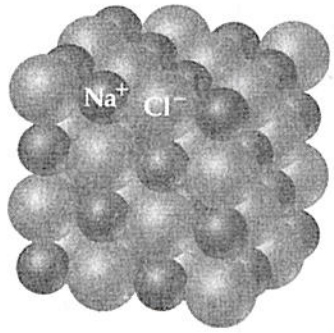


Figure 11.2 Crystal structure of sodium chloride.

Amorphous solids differ from crystalline solids because they are not arranged in a regular ordered crystal pattern. Like crystalline solids, the particles of amorphous solids are packed closely together with motion limited to vibrations in place.

Liquids differ from solids because the forces of attraction in a liquid do not hold the particles in rigid positions. Particles in a liquid are constantly moving and colliding, changing locations as they slip and slide past each other. Like solids, liquids have particles that are close together.

Typically, when a substance changes from solid to liquid, its volume usually changes little because of the relatively close packing in both phases.

In **gases,** the particles are far apart, in rapid, random motion, and their intermolecular forces are negligible.

Table 11.1 compares the macroscopic properties of gases, liquids, and solids.

Table 11.1 Some characteristic properties of the states of matter.

Gas	Assumes both volume and shape of its container Expands to fill its container Is compressible Flows readily Diffusion within a gas occurs rapidly
Liquid	Assumes shape of portion of container it occupies Does not expand to fill its container Is virtually incompressible Flows readily Diffusion within a liquid occurs slowly
Solid	Retains own shape and volume Does not expand to fill its container Is virtually incompressible Does not flow Diffusion within a solid occurs extremely slowly

Your Turn 11.1

Use the particle nature of matter shown in Figure 11.1 to explain the following properties of solids, liquids, and gases listed in Table 11.1.

a. Compressibility
b. Volume and shape
c. Diffusion

Write your answer in the space provided.

Section 11.2 Intermolecular Forces

Intramolecular forces are the attractive forces **within** molecules that we call covalent bonds. Intramolecular forces cause many of the chemical properties of molecules.

Intermolecular forces are the forces that exist **between** molecules. They are largely responsible for the physical properties of solids and liquids.

The physical state of a substance depends largely on the balance between the kinetic energies of the particles and the intermolecular attractive forces between the particles. For example, a gas condenses to a liquid at low temperature because the kinetic energy of the particles decreases to a point where the intermolecular attractive forces become significant. Figure 11.3 illustrates the molecular-level differences between solids, liquids, and gases.

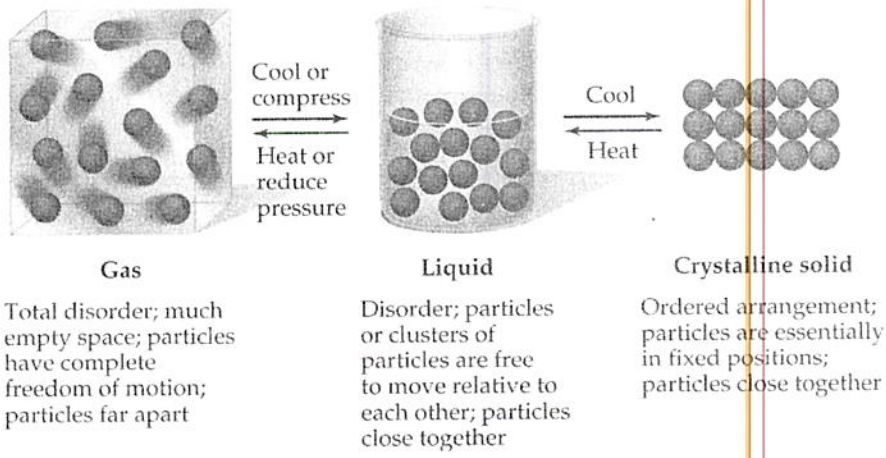


Figure 11.3 Each phase of a substance—solid, liquid, gas—differs in kinetic energy. Higher temperatures impart higher kinetic energy, which makes attractive forces less significant.

Generally, the greater the intermolecular forces, the higher the melting points of solids and the higher the boiling points of liquids.

Ion–dipole forces exist between an ion and a polar molecule. For example, when sodium chloride dissolves in water (see Figure 11.4), the partial negative end of the water molecule and the positive sodium ion are held together by an ion–dipole force of attraction.

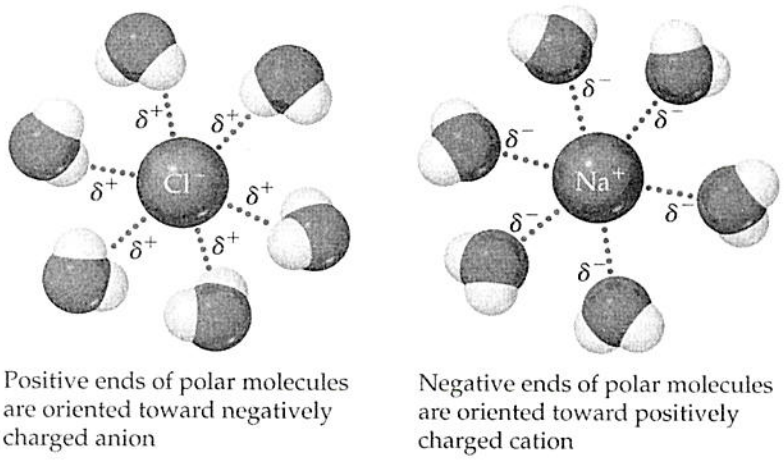


Figure 11.4 Ion–dipole forces between water molecules and sodium chloride ions.

When an ionic substance dissolves in water, the ionic bonds break as the ions separate. Water molecules attract the ions to form ion–dipole interactions. Bond breaking is endothermic and bond making is exothermic. If the energy absorbed when the solid crystal comes apart is less than the energy released when ion–dipole interactions form, the ionic compound will dissolve exothermically.

Dipole–dipole forces exist between neutral polar molecules in the liquid or solid state as illustrated in Figure 11.5.

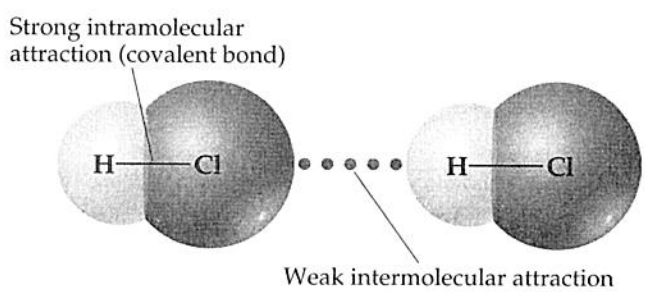


Figure 11.5 The positive end of an HCl molecule attracts the negative end of another, exhibiting a dipole–dipole intermolecular force.

London dispersion forces are the result of attractions between **induced dipoles**. Even though no dipole–dipole forces exist between nonpolar atoms or molecules, they do have attractive forces because they do form liquids and solids. In close proximity,

an induced or temporary dipole forms between nonpolar atoms and molecules when the positive nucleus of one atom or molecule attracts the electrons of another atom or molecule. London dispersion forces exist in all matter because all atoms and molecules have electrons. The greater the number of electrons, the greater the probability that a temporary dipole will form. Dispersion forces, although the weakest of intermolecular forces, are often the dominant forces of attraction.

Polarizability refers to the degree to which a dipole can be induced in a nonpolar species. Polarizability and, thus, dispersion forces tend to increase with increasing numbers of electrons and, therefore, with increasing molar mass.

Your Turn 11.2

Order the halogens according to increasing boiling points. Explain your reasoning. Write your answer in the space provided.

Figure 11.6 illustrates the various kinds of intermolecular forces.

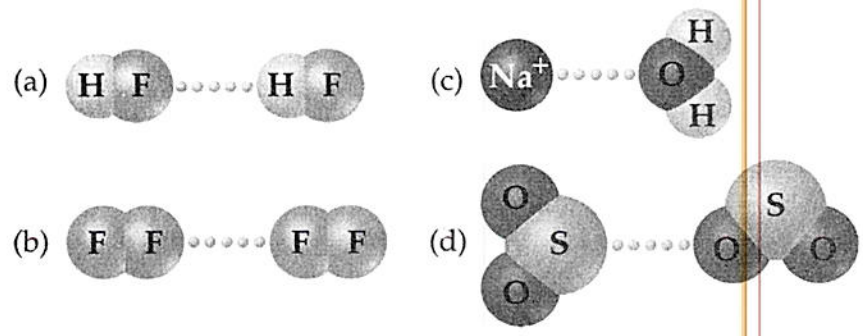


Figure 11.6 Four major intermolecular forces: (a) hydrogen bonding, (b) London dispersion, (c) ion–dipole, and (d) dipole–dipole.

Hydrogen bonding is an especially strong form of a dipole–dipole force. Hydrogen bonding exists only between hydrogen atoms bonded to F, O, or N of one molecule and F, O, and N of another molecule. The small size of electropositive hydrogen allows it to approach and form a strong force of attraction with a nonbonding electron pair on very electronegative F, O, or N atoms. Figure 11.7 shows some examples of hydrogen bonding.

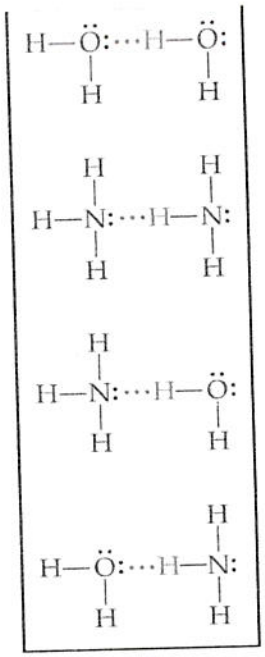


Figure 11.7 Hydrogen bonding exists between electropositive hydrogen atoms and nonbonding pairs of electrons on electronegative oxygen, nitrogen, or fluorine atoms.

Hydrogen bonding accounts for many unique properties of water. For example, Figure 11.8 illustrates the exceptionally high boiling point of water and Figure 11.9 shows the open, hexagonal arrangement of ice, which causes solid water to float on liquid water.

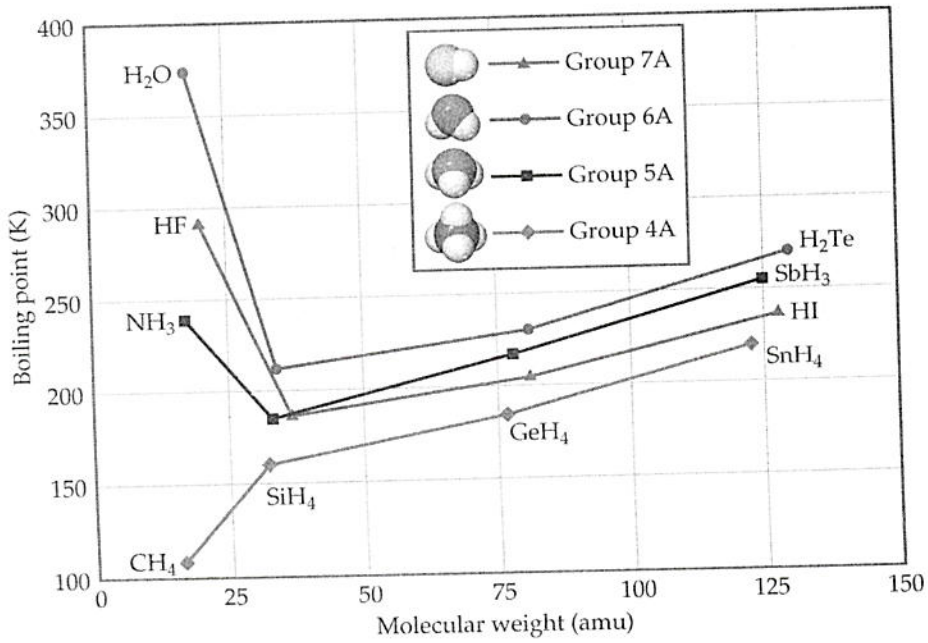


Figure 11.8 Boiling point generally increases with molar mass. Strong hydrogen bonding in water accounts for its unusually high boiling point.

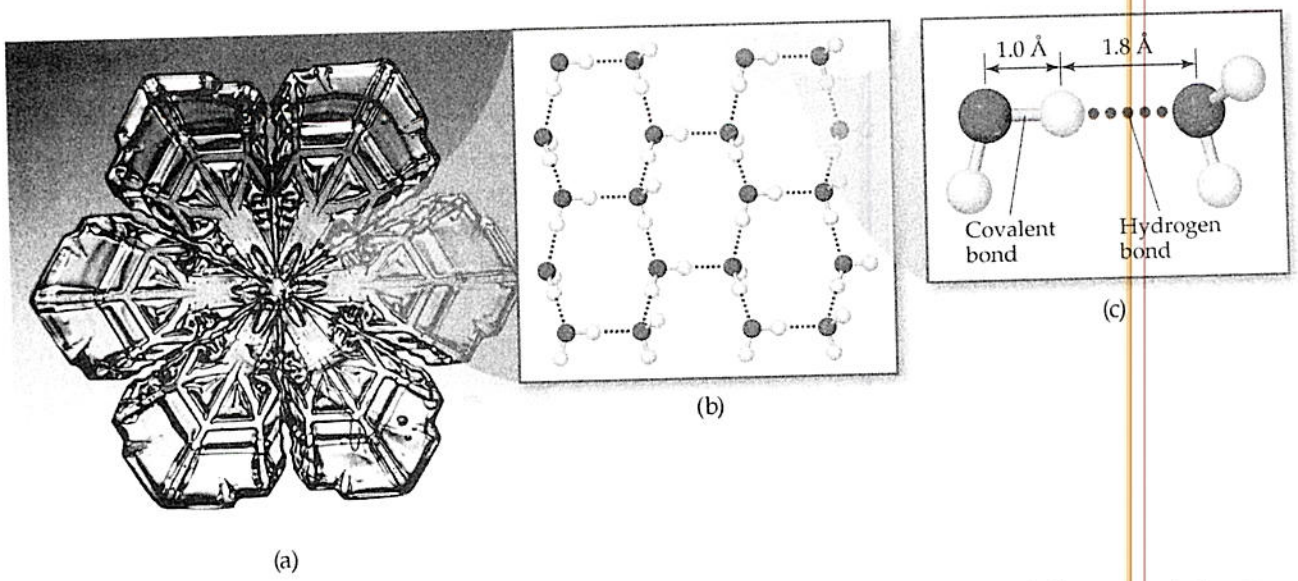


Figure 11.9 The hexagonal geometry of snowflakes (a) and the open, low-density structure of ice (b) result from strong hydrogen bonding of water molecules (c).

Section 11.3 Select Properties of Liquids

Many properties of liquids can be explained by identifying the intermolecular forces that are present.

Viscosity is the resistance of a liquid to flow. Molasses has a higher viscosity than water. Viscosity increases with increased intermolecular forces of attraction. For a series of related nonpolar compounds, viscosity increases with molar mass because larger molecules have more electrons so they are more polarizable and hence have stronger London dispersions.

Surface tension is the energy required to increase the surface area of a liquid by a unit amount. Surface tension is caused by an imbalance of intermolecular forces at the surface of the liquid. Water, which has very strong hydrogen bonding, has an unusually large surface tension.

Cohesive forces are intermolecular forces that bind similar molecules to one another, such as the hydrogen bonding in water.

Adhesive forces are intermolecular forces that bind a substance to a surface. For example, water placed in a glass tube adheres to the glass because the adhesive forces between the water and the glass are stronger than the cohesive forces between the water molecules. The curved upper surface that forms a meniscus in burets results from the high surface tension of water.

Capillary action is the rise of a liquid up a narrow tube. The adhesive forces between the liquid and the walls of the tube increase the surface area of the liquid. The surface tension of the liquid reduces the surface area, thereby pulling the liquid up the tube. The liquid will rise until the force of gravity balances the adhesive and cohesive forces.

Phase Changes Section 11.4

A heating curve is a graph of the temperature of a system versus the amount of heat added as illustrated in Figure 11.10.

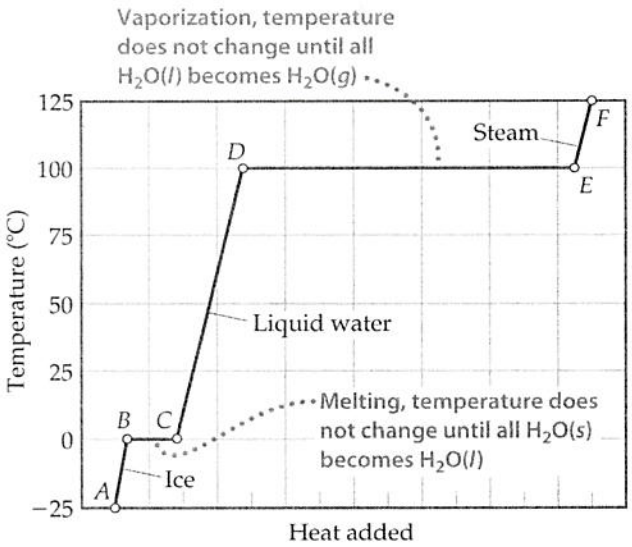


Figure 11.10 The heating curve for water shows that phase changes occur at constant temperature.

The **heat of fusion**, ΔH_{fus}, is the energy required to melt one mole of a substance at constant temperature.

The **heat of vaporization**, ΔH_{vap}, is the energy required to vaporize one mole of a substance at constant temperature.

The horizontal lines of a heating curve represent the heat of fusion, ΔH_{fus}, and heat of vaporization, ΔH_{vap}, of the substance. Notice that the temperature does not change during melting or vaporization. The nearly vertical lines represent the heat required to effect the corresponding temperature change of a single phase.

The **critical temperature** of a substance is the highest temperature at which a liquid can exist. At temperatures higher than the critical temperature, the kinetic energy of the molecules is so great that the substance can only be in the gas phase.

The **critical pressure** is the pressure required to cause liquefaction at the critical temperature. This is the pressure necessary to bring the molecules sufficiently close together, so that the forces of attraction between them can operate at the critical temperature.

Nonpolar substances and those with low molar masses (few electrons) tend to have low intermolecular forces of attraction and correspondingly low critical temperatures and pressures. Polar substances and substances with higher molar masses (many electrons) have higher critical temperatures and pressures because they are more polarizable and have higher intermolecular forces of attraction.

Section 11.5 Vapor Pressure

Vapor pressure is the partial pressure exerted by a vapor in a closed system when it is in equilibrium with its liquid or solid phase. For example, water placed in a closed container will evaporate at a constant rate and produce a partial pressure in the gas phase above the liquid. The partial pressure of water vapor will increase until the rate of evaporation equals the rate of condensation. The system is said to be in a state of **dynamic equilibrium** at this point and the partial pressure of water vapor remains constant. This partial pressure is the equilibrium vapor pressure of water (see Figure 11.11).

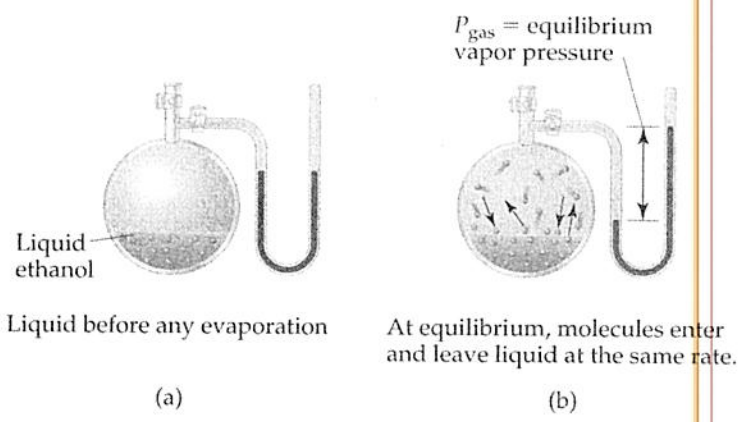


Figure 11.11 Equilibrium vapor pressure arises when a liquid in a closed container (a) evaporates producing a partial pressure of vapor above the liquid. (b) At equilibrium, the rate of evaporation equals the rate of condensation.

Liquid substances having low molar masses, and therefore few electrons, usually have weak intermolecular forces and tend to have high vapor pressures.

Your Turn 11.3

Place the following compounds in order of increasing vapor pressure: CCl_4, CI_4, CBr_4. Justify your answer. Write your answer in the space provided.

Increasing temperature will increase vapor pressure of a liquid or solid as shown in Figure 11.12. Higher temperatures provide greater kinetic energy of molecules, which gives them higher energies to overcome the attractive forces that hold them together.

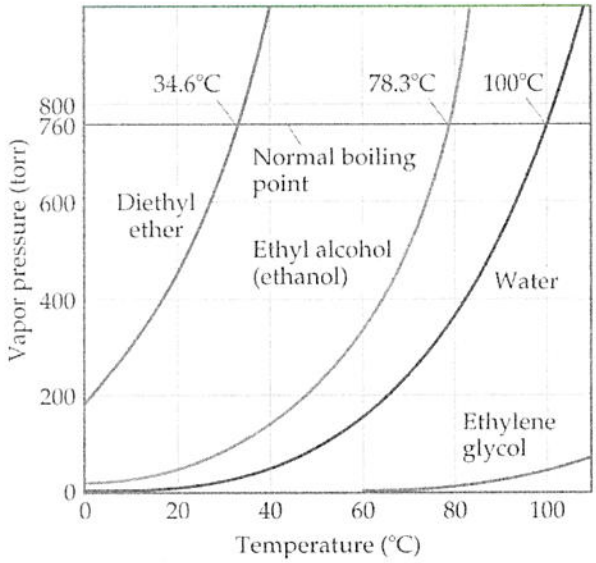


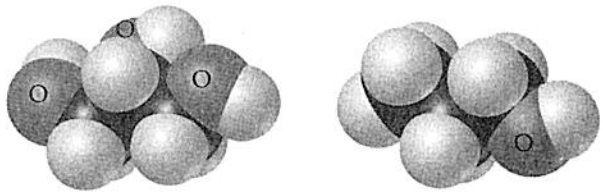
Figure 11.12 Vapor pressure of liquids increase with increasing temperature. The normal boiling point of a liquid is the temperature at which the vapor pressure reaches 760 torr.

The **boiling point** of a liquid is the temperature at which the vapor pressure of the liquid equals the atmospheric pressure.

The **normal boiling point** of a liquid is the temperature at which the vapor pressure equals 1 atm.

Your Turn 11.4

Predict whether glycerol, $C_3H_5(OH)_3$, or 1-propanol, C_3H_7OH, will have the higher: (a) viscosity, (b) vapor pressure, and (c) boiling point. Justify your reasoning. Write your answers in the space provided.



(a) Glycerol (b) 1-Propanol

Your Turn 11.5

Ice skaters demonstrate that ice melts under pressure. A skater glides over a liquid surface of water as her blades impart a force sufficient to temporarily melt the ice. What does this say about the relative densities of ice and liquid water? Describe the molecular structures of liquid and solid water that would explain this unusual property of ice. Write your answer in the space provided.