TOPIC

11

INTERMOLECULAR FORCES, LIQUIDS, AND SOLIDS

Intermolecular forces, especially hydrogen bonding, explain many macroscopic behaviors of matter in terms of unseen atoms, ions, and molecules, including vapor pressures of liquids, the structure of ice, and the melting and boiling points of substances. Know what kinds of intermolecular forces exist, how they affect the properties of molecules, and how to interpret phase diagrams. Focus especially on these sections:

11.2 **Intermolecular Forces**

11.5 **Vapor Pressure**

11.6 **Phase Diagrams**

Intermolecular Forces

Section 11.2

Intramolecular forces are the attractive forces **within** molecules that we call covalent bonds. Intramolecular forces give rise to 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 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 11.1 illustrates the molecular level differences between solids, liquids, and gases.

In general, the higher the intermolecular forces, the higher the melting points of solids and the higher the boiling points of liquids.

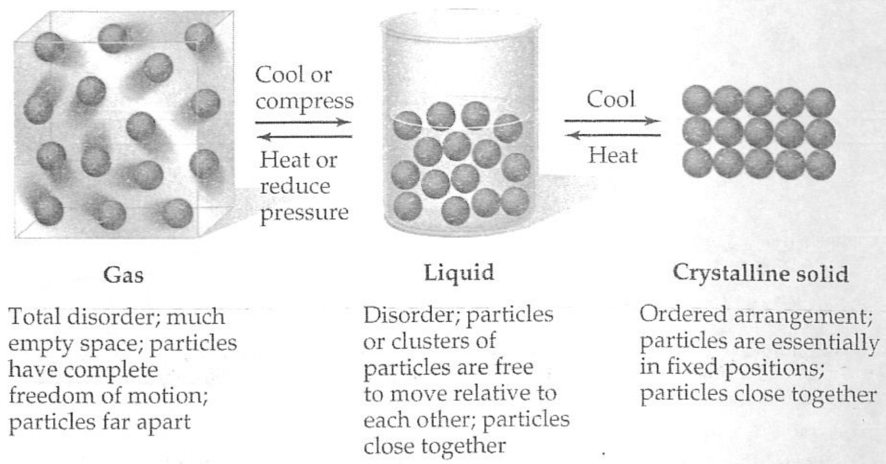

Figure 11.1. Each phase of a substance, solid, liquid, and gas differs in kinetic energy. Higher temperatures impart higher kinetic energy, which makes attractive forces less significant.

Ion–dipole forces exist between an ion and a polar molecule. For example, when sodium chloride dissolves in water, the partial negative end of the water molecule and the positive sodium ion are held together by an ion–dipole force of attraction. (See Figure 11.2a.)

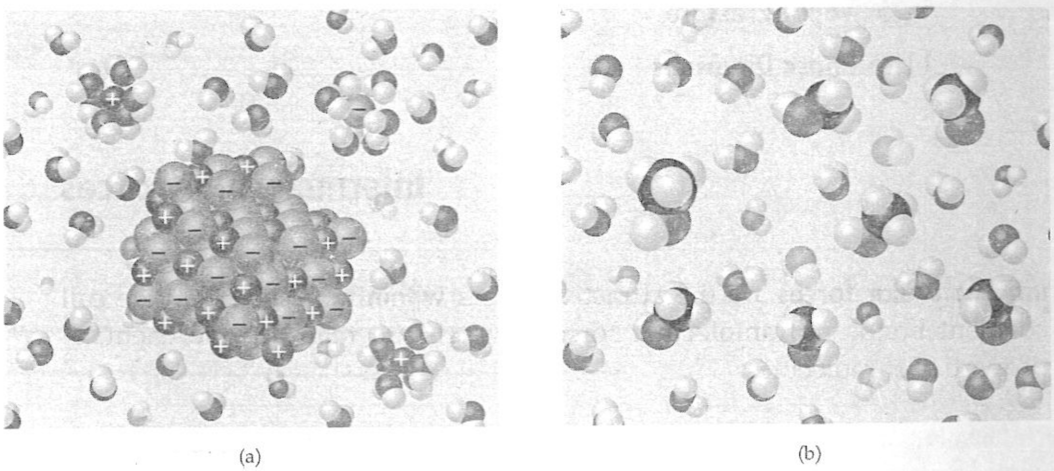

Figure 11.2. (a) Ion–dipole forces between water molecules and sodium and chloride ions; (b) dipole–dipole forces between molecules of water and polar methanol molecules.

Dipole–dipole forces exist between neutral polar molecules in the liquid or solid state. (See Figure 11.2b.)

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 for all atoms and molecules and are the weakest of the intermolecular forces.

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 molar mass.

Your Turn 11.1

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

Figure 11.3 illustrates the various kinds of intermolecular forces.

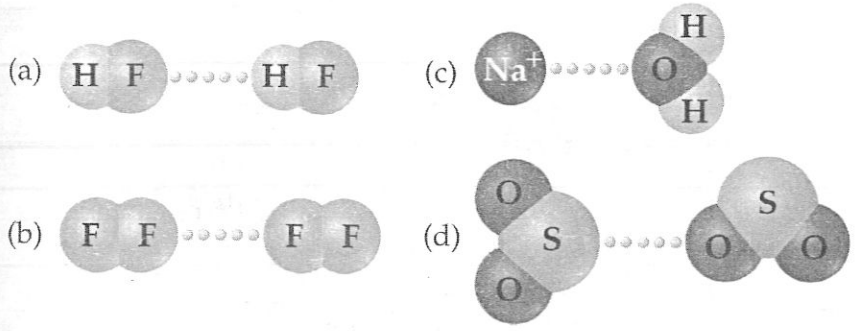

Figure 11.3. Four major intermolecular forces: (a) hydrogen bonding, (b) London Dispersion, (c) ion–dipole, (d) dipole–dipole.

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 become very close to and form a strong force of attraction with a nonbonding electron pair on very electronegative F, O, or N atoms.

Figure 11.4 shows some examples of hydrogen bonding.

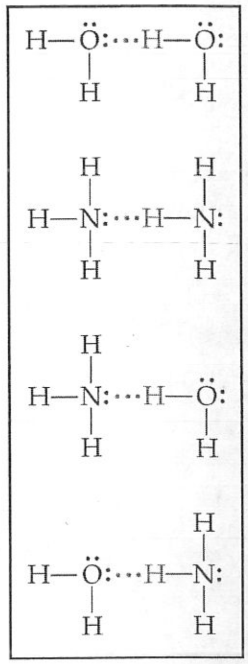

Figure 11.4. Hydrogen bonding exists between electropositive hydrogen atoms and nonbonding pairs of electrons on electronegative oxygen, nitrogen, or fluorine atoms.

Hydrogen bonding accounts for many unique properties of water. For example, Figure 11.5 illustrates the exceptionally high boiling point of water and Figure 11.6 shows the open, hexagonal arrangement of ice, which causes solid water to float on liquid water.

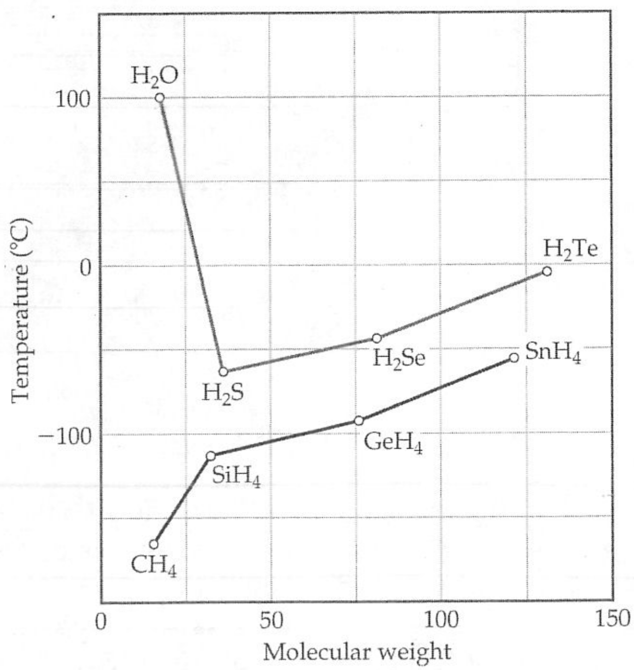

Figure 11.5. Boiling point generally increases with molar mass. Strong hydrogen bonding in water accounts for its unusually high boiling point.

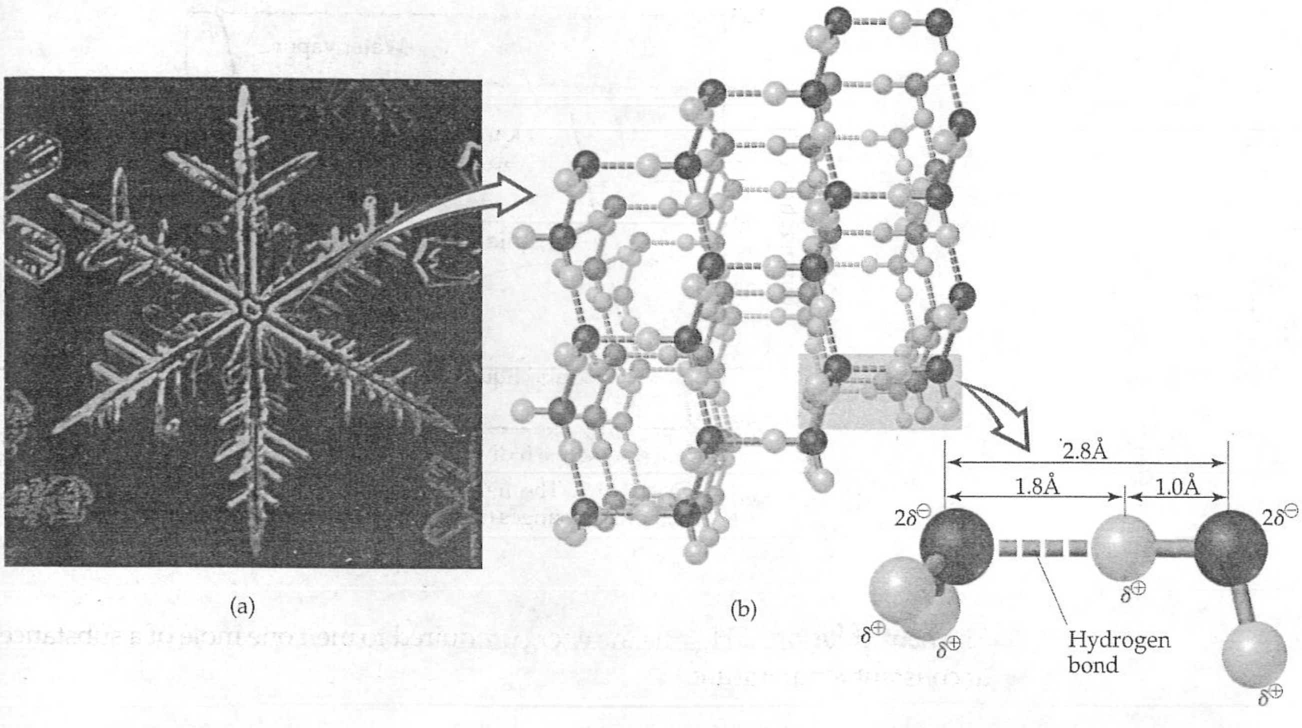

Figure 11.6. The hexagonal geometry of snowflakes (a) and the open, low density structure of ice (b) is due to strong hydrogen bonding of water molecules (c).

Some Properties of Liquids

Section 11.3

Viscosity is the resistance of a liquid to flow. For a series of related compounds, viscosity increases with molar mass.

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.

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. A curved upper surface or **meniscus** results.

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 11.7.

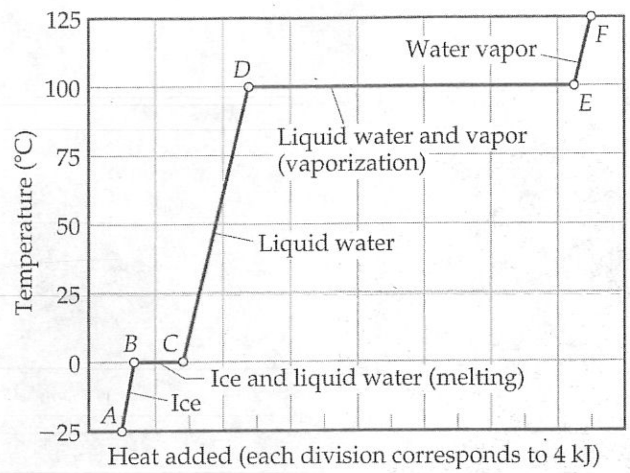

Figure 11.7. The heating curve for water shows that phase changes occur at constant temperature.

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 bring about 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 tend to have low intermolecular forces of attraction and correspondingly low critical temperatures and pressures. Polar substances and substances with higher molar masses have higher critical temperatures and pressures because they tend to have higher intermolecular forces of attraction.

Vapor Pressure

Section 11.5

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 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 11.8.)

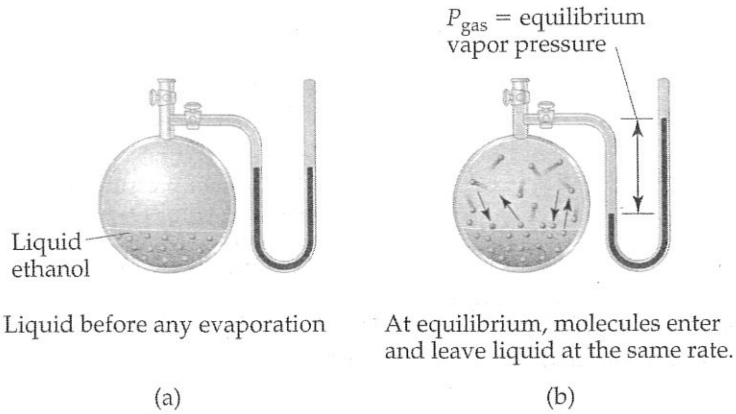

Figure 11.8. Equilibrium vapor pressure arises when a liquid in a closed container evaporates producing a partial pressure of vapor above the liquid. At equilibrium the rate of evaporation equals the rate of condensation.

Liquid substances of low molar mass and weak intermolecular forces tend to have high vapor pressures.

Your Turn 11.2

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

Increasing temperature will increase vapor pressure of a liquid or solid as shown in Figure 11.9. Higher temperatures provide greater kinetic energy of molecules, giving them higher energies to overcome the attractive forces that hold them together.

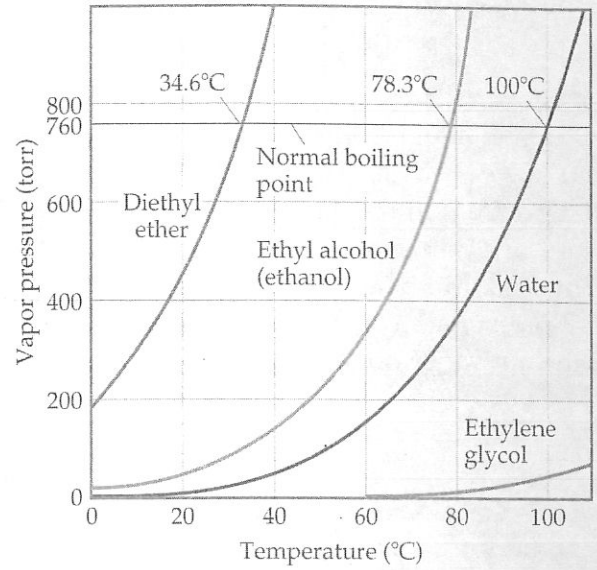

Figure 11.9. Vapor pressure of liquids increase with increasing temperature. The normal boiling point of a liquid is the temperature at which the vapor pressure reaches 760 torr.

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 one atmosphere.

Section 11.6 Phase Diagrams

A phase diagram is a graphical representation of the equilibria among the solid, liquid and gas phases of a substance. Figure 11.10 shows a typical phase diagram. The solid lines represent the temperatures and pressures where the phases of the substance are in equilibrium.

Your Turn 11.3

What will happen to the system illustrated in Figure 11.10 if: a) The pressure is decreased at point D? b) The temperature is increased at Point C? c) The temperature is decreased at Point B? Write your answers in the space provided.

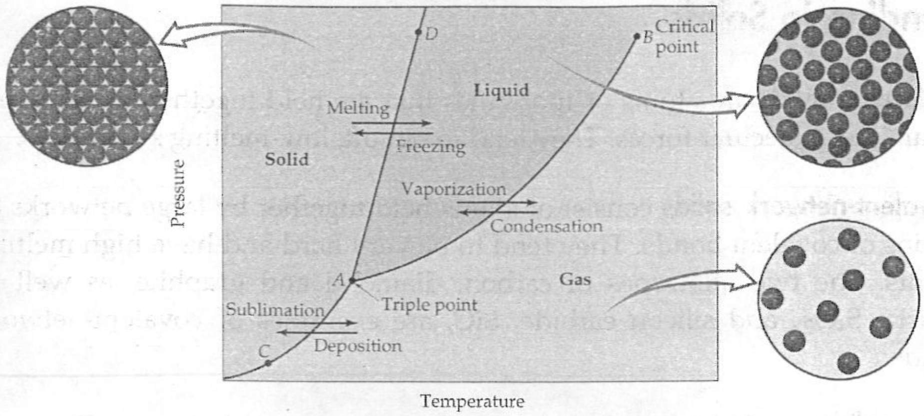

Figure 11.10. A typical phase diagram shows that a substance can exist as a solid, liquid, or gas depending on pressure and temperature.

Figure 11.11 shows the phase diagrams for water and for carbon dioxide. The phase diagram for water is unusual because the slope of the ice-solid equilibrium line is different from most substances and it illustrates that ice melts under pressure. The phase diagram for carbon dioxide shows that liquid CO_2 does not exist at pressures below about five atmospheres.

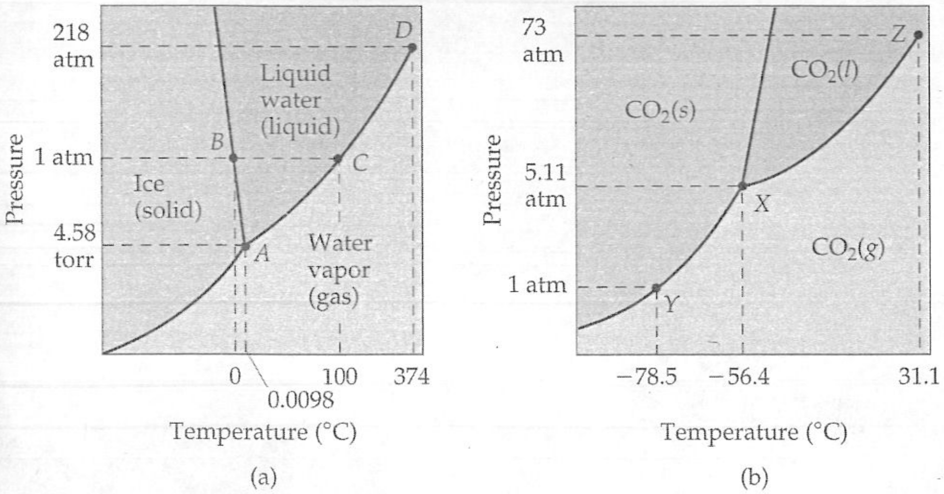

Figure 11.11. Phase diagrams of water and carbon dioxide.

Your Turn 11.4

The phase diagram for water shows that ice melts under pressure. What does this say about the relative densities of ice and liquid water? What other common observation supports your answer? Write your answer in the space provided.

Section 11.8 Bonding in Solids

Molecular solids are atoms or molecules that are held together by relatively weak intermolecular forces. They tend to be soft, low-melting substances.

Covalent-network solids consist of atoms held together by large networks or chains of covalent bonds. They tend to be very hard and have high melting points. The two allotropes of carbon, diamond and graphite, as well as quartz, SiO_2, and silicon carbide, SiC, are examples of covalent-network solids.

Ionic solids are held together by relatively strong ionic bonds. They are characterized by high melting point and brittle structures.

Metallic solids consist entirely of metal atoms. Bonding in metallic solids is due to attractions of metal nuclei to delocalized electrons throughout the solid. The loosely held electrons give metals their characteristic properties of malleability, ductility, and conduction of heat and electricity.

Multiple Choice Questions

1. *Which compound is most likely to form intermolecular hydrogen bonds?*
   - A) C_4H_{10}
   - B) *NaH*
   - C) C_2H_5OH
   - D) C_2H_5SH
   - E) CH_4
2. *Which best explains why bromine is soluble in mineral oil?*
   - A) *Both substances are liquids.*
   - B) *Both substances have similar densities.*
   - C) *Both substances are made up of nonpolar molecules.*
   - D) *One substance is made up of polar molecules and the other substance is made up of nonpolar molecules.*
   - E) *Both substances dissolve in water.*
3. *The strongest interaction between hexane and iodine is:*
   - A) *An instantaneous dipole–dipole interaction.*
   - B) *A dipole–dipole interaction.*
   - C) *A hydrogen bond.*
   - D) *A covalent bond.*
   - E) *An ionic bond.*
4. *In general, the strongest interaction with water molecules in aqueous solution are for ions that have:*
   - A) *Large charge and large size.*
   - B) *Large charge and small size.*
   - C) *Small charge and large size.*
   - D) *Small charge and small size.*
   - E) *Zero charge and small size.*

5. *Water and ethanol are completely miscible largely due to which intermolecular forces?*

   A) *Covalent bonds*

   B) *London dispersions*

   C) *Ionic bonds*

   D) *Hydrogen bonds*

   E) *Ion–dipole attractions*

6. *The energy absorbed when dry ice sublimes is required to overcome which type of interaction?*

   A) *Covalent bonds*

   B) *Ion–dipole forces*

   C) *Dipole–dipole forces*

   D) *Dispersion forces*

   E) *Hydrogen bonds*

7. *A container is half filled with a liquid and sealed at room temperature and atmospheric pressure. What happens inside the container?*

   A) *Evaporation stops.*

   B) *Evaporation continues for a time then stops.*

   C) *The pressure in the container remains constant.*

   D) *The pressure inside the container increases for a time and then remains constant.*

   E) *The liquid evaporates until it is all in the vapor phase.*

8. *Acetone, $(CH_3)_2C{=}O$, is a volatile, flammable liquid. The central carbon is sp^2 hybridized. The strongest intermolecular forces present in acetone are:*

   A) *Dipole–dipole forces.*

   B) *London dispersions.*

   C) *Hydrogen bonds.*

   D) *Covalent bonds.*

   E) *Ion–dipole forces.*

9. *Which of the factors affect the vapor pressure of a liquid at equilibrium?*

   I. *Intermolecular forces of attraction within the liquid*

   II. *The volume and/or surface area of liquid present*

   III. *The temperature of the liquid*

A) I only

B) II only

C) III only

D) I and II only

E) I and III only

10. *The molar masses of a series of similar polar molecules increases in this order: A < B < C < D < E. The boiling points, in degrees Celcius, of molecules A, B, C, D, and E are respectively, 20°, 50°, 150°, 100°, and 200°. Which molecule is likely to form hydrogen bonds?*

    A) A

    B) B

    C) C

    D) D

    E) E

Free Response Questions

1. *Use concepts of chemical bonding and/or intermolecular forces to account for each of the following observations:*

   a. The boiling points of water, ammonia, and methane are 100°C, −33°C and −164°C, respectively.

   b. At 25°C and 1.0 atm, chlorine is a gas, bromine is a liquid, and iodine is a solid.

   c. Calcium oxide (2615°C) melts at a much higher temperature than does potassium chloride (770°C).

   d. Propane is a gas and ethanol is a liquid, even though they have similar molar masses.

2. *Answer the following questions about water using principles of solids, liquids, and gases and intermolecular forces.*

   a. Why does water boil at a lower temperature in Denver, Colorado, than in New York City?

   b. For substances of similar molar mass, why does water have unusually high values for boiling point, heat of vaporization, and surface tension?

   c. What structural features of ice cause it to float on liquid water?

   d. Why does calcium chloride dissolve exothermically in water?

Additional Practice in *Chemistry the Central Science*

For more practice answering questions in preparation for the Advanced Placement examination try these problems in Chapter 11 of Chemistry the Central Science:

Additional Exercises: 11.79, 11.81, 11.83, 11.85, 11.88.

Integrative Exercises: 11.100, 11.101, 11.102, 11.105, 11.106.

Multiple Choice Answers and Explanations

1. *C. Hydrogen bonding occurs between molecules that have H-O, H-N, or H-F bonds. The hydrogen atom on one molecule attracts a non-bonding electron pair on an O, N, or F atom of another molecule.*

2. *C. The adage, "Like dissolves like," means that polar substances will dissolve other polar substances and nonpolar substances will dissolve other nonpolar substances. Polar substances dissolve in each other because of strong dipole–dipole interactions. Nonpolar substances dissolve in each other because of London dispersions. Polar substances generally do not dissolve in nonpolar substances because dipole–dipole interactions among the polar molecules exclude the nonpolar molecules.*

3. *A. Hexane, $CH_3CH_2CH_2CH_2CH_2CH_3$, and iodine, I_2, are both non-polar molecules. The strongest intermolecular forces acting between them are London dispersion forces. London dispersion forces arise when a positive nucleus of one molecule attracts the electrons of another molecule inducing an instantaneous dipole, a momentary shift in electron density.*

4. *B. The equation, $F = KQ_1Q_2/d^2$, where Q_1 and Q_2 are ionic charge and d is the distance between ions, describes the force of attraction between two charged particles. It's also useful in estimating the relative strengths of ion–dipole interactions, such as those between polar water molecules and an aqueous ion. The larger the charge and the smaller the ion, the larger the intermolecular force.*

5. *D. Water and ethanol, CH_3CH_2OH, are both small molecules and both have O-H bonds. The hydrogen atoms on one molecule attract non-bonding electron pairs on an oxygen atom of another molecule, forming an especially strong dipole–dipole interaction called a hydrogen bond.*

6. *D. Carbon dioxide molecules are nonpolar. They are held together only by London dispersion forces. Sublimation is the process where a solid changes directly into a gas. Energy is required to overcome the forces of attraction that hold the molecules together in the solid phase.*

7. *D. The liquid will continue to evaporate without stopping. The pressure will rise until the partial pressure of the vapor equals the vapor pressure of the liquid at the given temperature. Then a dynamic equilibrium is established where the rate of evaporation equals the rate of condensation.*

8. *A. The C=O bond in trigonal planar acetone is very polar, making the molecule a strong dipole. The absence of H-O bonds rule out hydrogen bonding but strong dipole–dipole interactions exist.*

9. *E. Intermolecular forces and temperature both affect the vapor pressure of a liquid, but vapor pressure is independent of volume and surface area.*

10. *C. Because of increased dispersion forces, the boiling points of a series of similar molecules will increase regularly with increasing molar mass. Molecule C is lighter than molecule D, yet it has a higher boiling point. This can be explained by especially strong dipole–dipole forces called hydrogen bonding in molecule C.*

Free Response Answers

1. a. *Water, H_2O, and ammonia, NH_3, both have higher boiling points than methane, CH_4, because water and ammonia form hydrogen bonds among their molecules and methane does not. Hydrogen bonds are relatively strong intermolecular attractive forces, which tend to hold molecules together in liquids requiring more energy to separate them. Water has a much higher boiling point than ammonia because water has two nonbonding pairs of electrons per molecule versus one nonbonding pair for ammonia. Additionally, oxygen is more electronegative than is nitrogen. These facts work together to allow for stronger and much greater hydrogen bonding in water than in ammonia.*

   b. *Chlorine, bromine, and iodine are all nonpolar diatomic molecules held together by London dispersion forces. The dispersion forces become greater as the molar masses increase. Iodine has the highest molar mass and the largest dispersion forces, large enough to hold the molecules together in a molecular solid. Bromine has weaker dispersion forces but strong enough to hold the molecules together in a liquid. Chlorine has the weakest dispersion forces, too weak to hold the molecules together, so it is a gas.*

   c. *To melt a solid, the temperature must be sufficient to overcome the attractive forces holding the solid together. Calcium oxide, CaO, is composed of small ions of relatively large charge so they are held together with relatively large attractive forces, requiring a high temperature to melt. Potassium chloride is composed of larger ions of smaller charge requiring a relatively low temperature to provide sufficient kinetic energy to overcome the relatively low attractive forces.*

d. *Propane, $CH_3CH_2CH_3$, is a nonpolar molecule held together by relatively weak London dispersion forces. Ethanol, CH_3CH_2OH, is a polar molecule held together by stronger dipole–dipole forces. Additionally, ethanol can form hydrogen bonds which are even stronger forces of attraction.*

2. a. *Boiling point is the temperature at which the vapor pressure of a liquid equals the external pressure. Vapor pressure increases with increasing temperature. Due to its relatively high elevation above sea level, the atmospheric (external) pressure in Denver is lower than that in New York. Consequently, a lower temperature is required to reach the vapor pressure equal to the lower pressure in Denver.*

   b. *Water forms very strong hydrogen bonds among its molecules which hold the molecules together in the liquid phase much more than liquids having the relatively weak dipole–dipole or dispersion attractive forces.*

   c. *The hydrogen bonding in water causes ice to form a relatively open hexagonal structure that is less dense than the more loosely held liquid.*

   d. *The process of dissolving an ionic substance in water breaks the ion–ion bonds (bond breaking is always endothermic) and forms ion–dipole interactions (bond formation is always exothermic) with water. The fact $CaCl_2$ dissolves exothermically means that the ion–dipole interactions formed in the solution are stronger than the ion–ion interactions of the solid ionic lattice.*

Your Turn Answers

11.1. *The boiling points of the halogens will increase in this order: $F_2 < Cl_2 < Br_2 < I_2 <$ At. As the molar mass increases the polarizability of the molecules increases causing greater induced dipoles and stronger London dispersion forces that hold the molecules together.*

11.2. *The vapor pressures increase in this order: $CI_4 < CBr_4 < CCl_4$ Higher molar mass substances have higher dispersion forces and are held together more strongly than are lower molar mass substances.*

11.3. *a) A pressure decrease at Point D will cause any solid present to melt. b) A temperature increase at Point C will cause any solid present to sublime. c) A temperature decrease at Point B will cause most of the vapor present to condense.*

11.4. *The fact that ice melts under pressure indicates that ice is less dense than liquid water. This conclusion is supported by the fact that ice floats on liquid water.*