5

BIG IDEA 2: LIQUIDS AND SOLIDS

Big Idea 2

Chemical and physical properties of materials can be explained by the structure and the arrangement of atoms, ions, or molecules and the forces between them.

The forces that hold together solids and liquids, the condensed states of matter, are similar. The effect of these forces on properties such as surface tension and vapor pressure will be reviewed. The bonding models, structure, and properties of liquids and solids will be discussed. Changes in state from solid to liquid to gas will also be considered.

You should be able to

- Describe the intermolecular forces that account for observed properties of liquids such as surface tension, capillary action, viscosity, vapor pressure, and boiling point.
- Draw pictures that illustrate the observed differences between solids and liquids, and identify the interparticle forces (also known as intermolecular forces) that account for those differences.
- Draw pictures of or explain atomic level representations that illustrate the observed differences in physical properties between solids of a specific type or solids of different types, and identify the interparticle forces that account for those differences.
- Use your understanding of the type of bonding present in solids to draw pictures that illustrate the observed differences

between solids and liquids, and identify the interparticle forces that account for those differences.

AP Tip

In essay questions about this topic, you may be asked to draw pictures illustrating interactions between molecules.

INTERMOLECULAR FORCES

(*Chemistry* 8th ed. pages 440–443/9th ed. pages 455–458)

Intermolecular forces were introduced in Chapter 3. In this chapter, you will see the effect of intermolecular forces on properties of liquids such as boiling point, surface tension, and vapor pressure.

When molecular compounds such as water undergo changes in state, a disruption of forces that attract molecules to each other, the intermolecular forces, is involved. The covalent bonds in the molecules are not broken. When ionic compounds such as sodium chloride change state, ionic bonds are broken.

PROPERTIES OF LIQUIDS

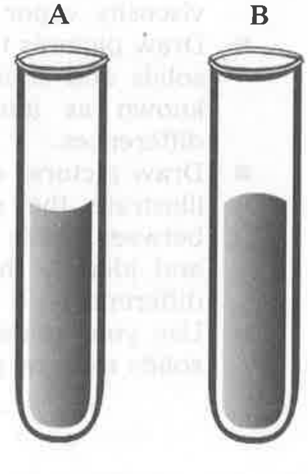
SURFACE TENSION

(*Chemistry* 8th ed. page 443/9th ed. page 458)

Molecules at the surface of a liquid are pulled inward by the molecules beneath them. The surface tension of a liquid is the resistance of a liquid to increasing its surface area. Liquids with strong intermolecular forces tend to have high surface tensions.

EXAMPLE: Equal-sized drops of Hg, Br_2, or H_2O are placed onto the same glass surface. Which of the three liquids will have the most spherical shape?

SOLUTION: Hg will have the most spherical shape due to the metallic bonding which occurs between mercury atoms. Metallic bonding is stronger than both the hydrogen bonding in water and the London dispersion forces of bromine.



CAPILLARY ACTION

(*Chemistry* 8th ed. page 443/9th ed. page 458)

The rise of liquids up very narrow tubes is called capillary action. Water and dissolved nutrients move upward through plants via capillary action.

Adhesive forces, the attractions between a liquid and its container, cause the liquid to creep up the walls of the container. Adhesive forces are opposed by cohesive forces, the intermolecular forces in the liquid that try to decrease the liquid's surface area. Molecules with strong intermolecular attractions will have stronger cohesive forces than adhesive forces.

EXAMPLE: Two different liquids are placed in separate glass tubes. Liquid A forms a concave meniscus. Liquid B forms a convex meniscus. Why do the meniscuses of Liquids A and B have two different shapes? Suggest a possible identity for each liquid.

SOLUTION: Liquid A's adhesive forces are stronger than its cohesive forces, as in water. Liquid B's cohesive forces are stronger than its adhesive forces, as in mercury.

VISCOSITY

(*Chemistry* 8th ed. pages 443–444/9th ed. pages 458–459)

Viscosity is a measure of a liquid's resistance to flow. The greater its resistance, the more slowly it will flow. Molasses, motor oil, and glycerol are viscous liquids. Highly viscous liquids have large intermolecular forces or are very complex molecules with large molar masses and many electrons, such as polymers. For example, grease is viscous because it contains long hydrocarbon chains which can get tangled. Gasoline consists of shorter carbon chains three to eight carbons long and is therefore a nonviscous liquid. Viscosity decreases with increasing temperature because more molecules will have greater average kinetic energy to overcome the intermolecular forces of the liquid.

VAPOR PRESSURE

(*Chemistry* 8th ed. pages 471–475/9th ed. pages 483–487)

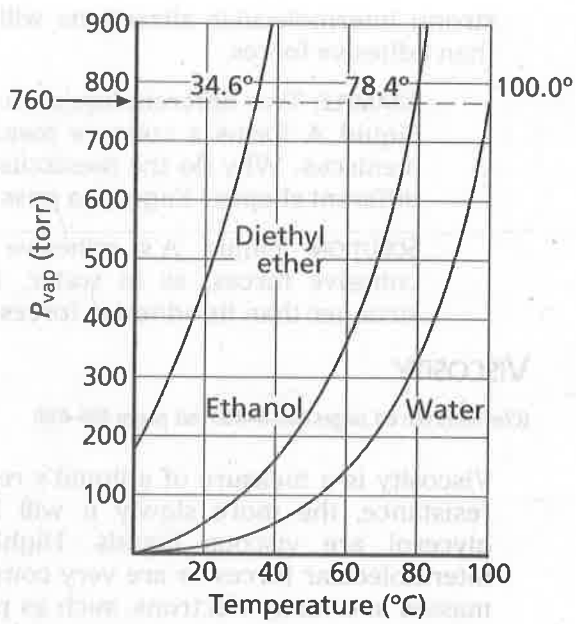
In the process of vaporization (evaporation), liquid molecules leave the surface and form a vapor. The heat of vaporization (enthalpy of vaporization, ΔH_{vap}) is the energy required to vaporize 1 mole of a liquid at its normal boiling point (1 atm). This quantity is endothermic because energy is required to overcome the intermolecular forces. In the reverse process, condensation, energy is released as the IMFs form between the particles when the gas molecules get close enough to interact with each other.

In a closed container, a liquid and its vapor are at equilibrium when the rate of evaporation equals the rate of condensation. The equilibrium vapor pressure is the pressure above the liquid from the molecules of the liquid in the gas phase.

Volatile liquids are liquids with high vapor pressures. The vapor pressure at a given temperature is determined by the intermolecular forces of the liquid. Strong intermolecular forces result in lower vapor pressure. Weak intermolecular forces result in higher vapor pressure because the liquid molecules are not held together as strongly and readily escape from the surface.

The vapor pressure of a liquid increases with increasing temperature. At higher temperatures, more molecules will have sufficient kinetic energy to overcome intermolecular forces and break free from the surface of the liquid.

The dependence of vapor pressure on temperature is represented in the figure.



EXAMPLE: Explain why diethyl ether, $CH_3CH_2OCH_2CH_3$, is more volatile than ethanol, CH_3CH_2OH, at 25°C.

SOLUTION: The dipole forces in diethyl ether are weaker than the hydrogen bonding in ethanol. The weaker the intermolecular forces, the higher the liquid's vapor pressure and volatility.

BOILING

(*Chemistry* 8th ed. page 478/9th ed. page 490)

The boiling of a liquid occurs in a container open to the atmosphere when the vapor pressure of the liquid equals atmospheric pressure. Bubbles containing the vapor form within the liquid and rise to the surface due to their reduced density. During boiling, the temperature remains constant until all of the liquid vaporizes. The normal boiling point of a liquid is the temperature at which the vapor pressure of a liquid is equal to standard atmospheric pressure (1 atm = 760 mm Hg). To determine the normal boiling point of a liquid, interpolate the vapor pressure curve for the liquid at 1 atmosphere.

EXAMPLE: What are the normal boiling points of diethyl ether and ethanol?

SOLUTION: The normal boiling points for diethyl ether and ethanol are approximately 34.6°C and 78.4°C, respectively. The normal boiling point occurs at 1 atm and can be found by interpolating the vapor pressure curves above.

EXAMPLE: At a location 19,340 ft above sea level, the atmospheric pressure is 350 torr. At what temperature will water boil? Will it take more or less time to cook an egg at this location than at sea level or 1 atm?

SOLUTION: Using the vapor pressure curve above, at 350 torr, water will boil at about 80°C. It will take more time to hard-boil an egg at this elevation because water boils at a temperature lower than that at sea level, and therefore contains less kinetic energy.

EXAMPLE: Pressure cookers heat a small amount of water under high constant pressure. What effect does using a pressure cooker have on cooking time?

SOLUTION: Food in a pressure cooker will take less time to prepare because it will cook at a higher temperature. When the pressure is increased, the boiling point will increase until the vapor pressure of the liquid equals the pressure above the liquid. Once the boiling point is reached, the temperature will not change as long as there is liquid present. Vapor pressure is directly proportional to temperature.

STRUCTURE AND TYPES OF SOLIDS

(*Chemistry* 8th ed. pages 444–446, 449–451/9th ed. pages 459–460, 463–465)

CRYSTALLINE SOLIDS

Crystalline solids are classified according to the type of particle that occupies the lattice points: atoms, molecules, or ions. The four types of crystalline solids are molecular, ionic, metallic, and network covalent. The table below describes each of these solids.

Type of Solid	Molecular	Ionic	Atomic	Metallic	Network Covalent
Examples	$C_6H_{12}O_6$	NaCl	Ar	Cu	C (diamond)
Particles occupying lattice points	Molecule	Ions	Atoms	Atoms	Atoms
Bonds or forces between lattice points	Dispersion forces	Ionic	Dispersion forces	Delocalized nondirectional metallic	Covalent
Melting points	Low	High	Low	High (1083°C)	Very high (3500°C)
Electrical conductivity as solid	None	None	None	Yes	None
Electrical conductivity when melted	None	Yes	None	Yes	None
Other properties		Brittle		Malleable and ductile	Insulator very hard

A lattice is a three-dimensional system of points designating the points of the components (atoms, molecules, or ions) that make up the substance. A unit cell is the smallest repeating unit of a lattice.

AMORPHOUS SOLIDS

Amorphous solids, such as rubber and glass, have particles with no orderly structure.

STRUCTURE AND BONDING IN METALS

Metallic bonding is characterized as an array of positively charged nuclei surrounded by a "sea" of mobile electrons. It is said that the bonding is nondirectional; the metallic atoms can easily slide over each other because the environment will be the same. This model explains the observed properties of metals: they are malleable, conductive, can be formed into thin sheets and pulled into wires (ductile).

ALLOYS

Alloys are mixtures of metallic elements and have metallic properties. Substitutional alloys, like brass and sterling silver, have host metal atoms replaced by atoms of similar size. Brass is a substitutional alloy made of copper and zinc. Interstitial alloys have smaller atoms occupying the empty spaces between the metal atoms within the structure. The presence of the smaller atoms changes the properties of the host making it harder and stronger. Steel is an interstitial alloy containing iron and carbon.

CHANGES IN STATE

HEATING CURVES

(*Chemistry* 8th ed. pages 473–478/9th ed. pages 485–490)

Chapter 11 (Big Idea 5) includes a discussion of the quantitative aspects of the heating curve. Energy is added at a constant rate to a solid and a plot of temperature vs. time is drawn. The first plateau on the heating curve represents the melting point of the substance. The second plateau on the heating curve represents the boiling point of the substance. The temperature does not change during melting or boiling because the energy added is used to overcome intermolecular forces.

Usually, the plateau for the boiling point is longer in duration than the melting plateau because it takes more energy to separate the molecules from a liquid into a gaseous state than from a solid into a liquid state. This greater energy is related to the greater forces that must be overcome.

MULTIPLE-CHOICE QUESTIONS

No calculators are to be used in this section.

1. Water has a higher capillary action than mercury due to
   (A) higher dipole–dipole forces between the water molecules
   (B) strong cohesive forces within water
   (C) weak adhesive forces in water
   (D) strong cohesive forces in water which work with strong adhesive forces

2. Small drops of water tend to bead up because of
   (A) high capillary action
   (B) the shape of the meniscus
   (C) the resistance to increased surface area
   (D) low London dispersion forces

3. The vapor pressure increases in a predictable order as shown as
   (A) $CH_4 < C_2H_5OH < C_2H_5–O–C_2H_5 < Ne$
   (B) $Ne < CH_4 < C_2H_5–O–C_2H_5 < C_2H_5–OH$
   (C) $C_2H_5–OH < C_2H_5–O–C_2H_5 < CH_4 < Ne$
   (D) $C_2H_5–O–C_2H_5 < C_2H_5–OH < Ne < CH_4$

4. Several liquids are compared by adding them to a series of 50-mL graduated cylinders, then dropping a steel ball of uniform size and mass into each. The time required for the ball to reach the bottom of the cylinder is noted. This is a method used to compare the differences in a property of liquids known as
(A) surface tension
(B) buoyancy
(C) capillary action
(D) viscosity

5. The properties of solids vary with their bonding. An example of this is shown by
(A) ionic solids with strong electrostatic attractions called ionic bonds, which have high melting temperatures
(B) molecular solids with high intermolecular forces which have high melting temperatures
(C) ionic solids with highly mobile ions which have high conductance
(D) amorphous solids with strong London dispersion forces and high vapor pressure

6. As you go down the noble gas family on the periodic table, the boiling temperature increases. This trend is due mainly to
(A) an increase in hydrogen bonding
(B) a decrease in dipole–dipole forces
(C) the lower atomic masses as you go down the family
(D) an increase in London dispersion forces

7. Graphite and diamond are network solids, but graphite is slippery, black, and a conductor, while diamond is hard, colorless, and an insulator. This is because
(A) graphite and diamond are made of different elements
(B) diamond is made up of tetrahedrally bonded carbon atoms, while graphite is made up of fused six-membered rings arranged in sheets
(C) graphite contains impurities that result in a less dense solid
(D) diamond contains covalent bonds, while graphite contains ionic bonds

8. Which of the following properties of water is/are due to the intermolecular hydrogen bonding between the water molecules?
(A) Ice floats on water.
(B) Water has a high heat of vaporization.
(C) The specific heat of water (4.184 J/°C·g) is much higher than that of lead (0.128 J/°C·g).
(D) All of the above.

9. The substances neon, sodium fluoride, carbon monoxide, and methylamine all have low molar masses. Order these substances in increasing boiling points or melting points.
(A) Ne < CO < CH_3NH_2 < NaF
(B) NaF < CO < CH_3NH_2 < Ne
(C) Ne < CH_3NH_2 < CO < NaF
(D) CH_3NH_2 < CO < NaF < Ne

10. A substance with strong intermolecular forces of attraction would be expected to have
(A) a low boiling point
(B) a high vapor pressure
(C) a high heat of vaporization
(D) a high solubility in water

11. Consider a closed flask containing a liquid and its vapor. Which statement is *incorrect*?
(A) The vapor exerts a pressure called the vapor pressure.
(B) Increasing the temperature of the liquid would lead to a greater vapor pressure.
(C) Evaporation and condensation will eventually cease after a constant pressure has been attained.
(D) Increasing the volume of the container at constant temperature would cause increased condensation until the pressure of the vapor was once again the same as it had been.

12. 1-Butanol ($CH_3CH_2CH_2CH_2OH$) would be expected to have a higher boiling temperature than 1-propanol ($CH_3CH_2CH_2OH$) because
(A) it has a higher molar mass
(B) its longer carbon chain and greater number of electrons result in more London dispersion forces
(C) its hydrogen bonding is stronger
(D) it is a less polar molecule

13. A substance is found to be nonconductive, to have a relatively low melting point, and to be insoluble in water. This is most likely
(A) a metal
(B) an ionic solid
(C) a molecular solid
(D) a network covalent solid

14. The fact that metals are conductive is best explained by which of the following statements?
(A) The metal nuclei reside in a "sea" of delocalized electrons.
(B) The metals form anions and cations which allow electrons to travel.
(C) The metals have extra electrons which can carry a charge.
(D) all of these

15. The type of bonding in a solid can be tested by placing the substance in water because
(A) soluble ionic substances form conductive aqueous solutions
(B) soluble covalently bonded substances form aqueous solutions that are not conductive
(C) most network solids are not soluble in water
(D) all of the above are true

FREE-RESPONSE QUESTIONS

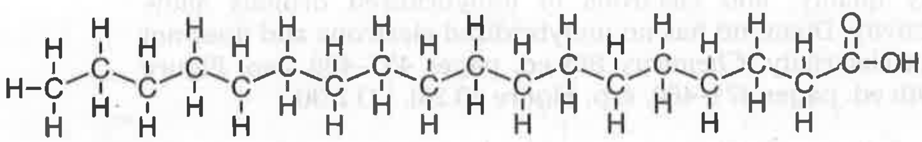
Calculators and equation tables may be used.

1. Four solids are tested for conductivity as solids, solubility in water, and conductivity in aqueous solution if soluble. The results are listed below.

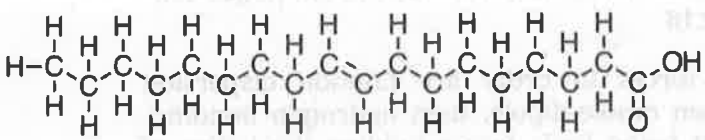
	A	B	C	D
Conducts as solid?	Y	N	N	N
Soluble in water?	N	Y	N	Y
Forms conductive solution?	N	Y	N	N

Identify the type of bonding present in each solid based on these data. Describe explicitly how the data lead to your conclusions.

2. Stearic acid is a primary component of animal fat, which is solid at room temperature. Oleic acid is a component of olive oil, which is liquid at room temperature. What intermolecular forces account for these observations?



Stearic acid



Oleic acid

Answers

MULTIPLE-CHOICE QUESTIONS

1. **D** The strong adhesive forces lead to a creeping effect as water moves up the narrow tubing and the strong cohesive forces attempt to minimize the surface area (*Chemistry* 8th ed. pages 443–444/9th ed. pages 458–459). LO 2.3

2. **C** This is a description of surface tension, which is a result of high dipole–dipole forces between water molecules. These intermolecular forces are also called hydrogen bonds (*Chemistry* 8th ed. pages 443–444/9th ed. pages 458–459). LO 2.3

3. **C** Examining the IMF will suggest that only the alcohol (C_2H_5–OH) has an exposed –OH, suggesting strong hydrogen bonding. The other three are essentially controlled by weaker London dispersion

forces, which are greater in the larger, more massive compound. Realize also that the higher the IMF, the lower the vapor pressure (*Chemistry* 8th ed. pages 471–473/9th ed. pages 483–485). LO 2.16

4. D The resistance to flow of any fluid is called viscosity. As you would predict, liquids with high viscosity (e.g., maple syrup) have large intermolecular forces (*Chemistry* 8th ed. pages 443–444/9th ed. pages 458–459). LO 2.3

5. A Ionic bonds are unusually strong, requiring high temperatures to melt ionic substances. Table salt, for example, which is Na^+Cl^-, melts at 804°C (*Chemistry* 8th ed. pages 466–471, esp. Table 10.7/9th ed. pages 479–483, esp. Table 10.7). LO 2.19, LO 2.26, LO 2.32

6. D These very symmetrical atoms are nonpolar; except for the induced dispersion forces, they would all boil at 0 K. As it is, He boils at 4 K and Ne at 25 K (*Chemistry* 8th ed. pages 440–443/9th ed. pages 455–458). LO 2.11

7. B Both graphite and diamond are made up of the same element, carbon, and in both cases the atoms are covalently bonded to each other. The sheets of graphite can slip over each other, giving it a slippery quality, and electrons in unhybridized orbitals allow conductivity. Diamond has no unhybridized electrons and does not conduct electricity (*Chemistry* 8th ed. pages 457–468, esp. Figure 10.22/9th ed. pages 471–480, esp. Figure 10.26). LO 2.30

8. D All of the anomalous properties of water are due to the exceptionally effective intermolecular hydrogen bonding (*Chemistry* 8th ed. pages 439–444, 450, 467–468/9th ed. pages 455–459, 464, 479–480). LO 2.16

9. A The intermolecular forces in order are London dispersion forces, the weakest, then dipole-dipole, then hydrogen bonding, and lastly the strongest being ionic forces holding the lattice of NaF together (*Chemistry* 8th ed. pages 440–443/9th ed. pages 455–458). LO 2.16

10. C A high heat of vaporization would be expected of a substance with strong intermolecular forces because a significant amount of energy would be required to liberate the molecules from the liquid to gaseous state. Low boiling point, low melting point, high solubility in water, and a high vapor pressure would indicate that the forces holding the molecules together are relatively weak; therefore, the molecules are able to be separated more easily by added energy or outside forces of attraction, as is the case with the solvent in its ability to act on the solute (*Chemistry* 8th ed. pages 440–443/9th ed. pages 455–458). LO 2.16

11. C Once an equilibrium vapor pressure has been reached at a given temperature within the container, the rate of condensation and rate of evaporation become equal but neither one ceases (*Chemistry* 8th ed. pages 471–478/9th ed. pages 483–490). LO 2.16

12. **B** The longer carbon chain, rather than the molar mass per se, leads to greater London dispersion forces holding the molecules together (*Chemistry* 8th ed. pages 440–443, 471–474/9th ed. pages 455–458, 483–486). LO 2.16

13. **C** In network solids, atoms or molecules bond together with strong directional covalent bonds. Two important network solids are diamond and silica (*Chemistry* 8th ed. pages 449–451, 457–462/9th ed. pages 463–465, 471–476). LO 2.22

14. **A** The "electron sea" model was developed to explain metal conductivity. Although metals do form cations, this does not explain why elemental metals are conductive. Anions are substances with "extra" electrons, and metals generally do not form anions (*Chemistry* 8th ed. pages 454–455/9th ed. pages 468–469). LO 2.26

15. **D** (*Chemistry* 8th ed. pages 440–443, 471–474/9th ed. pages 455–458, 483–486). LO 2.22

FREE-RESPONSE QUESTIONS

1. Solid A is most likely metallic. The delocalized "sea of electrons" results in high conductivity. Lack of solubility in water indicates that the intermolecular forces are very strong (*Chemistry* 8th ed. pages 454–455/9th ed. pages 468–469). LO 2.22

   Solid B is most likely ionic. Ionic solids are not conductive because their electrons are localized around their respective nuclei. Many ionic solids are soluble in water, and when they dissolve they split up into cations and anions which are attracted to the polar water molecules. The separation of charges leads to formation of a conductive solution (*Chemistry* 8th ed. pages 132–136, 341–343/9th ed. pages 141–145, 352–355). LO 2.22

   Solid C is most likely network covalent, such as sand or diamond. These solids are not particularly conductive because the electrons are localized in the covalent bonds between the atoms. They are also not soluble in polar solvents because the molecules themselves are covalently bonded to each other (*Chemistry* 8th ed. pages 444–446, 449–451/9th ed. pages 458–460, 463–465). LO 2.22

   Solid D is most likely molecular. Like network covalent solids, the electrons are localized in the covalent bonds between the atoms. However, many are soluble in water because they are attracted to each other primarily by London dispersion forces, which can be overcome by the attraction of polar parts of the molecules to polar water (*Chemistry* 8th ed. pages 444–446, 449–451/9th ed. pages 458–460, 463–465). LO 2.22

2. Both molecules are essentially nonpolar because of their very long carbon chains. The primary intermolecular attraction is London dispersion forces. Stearic acid is solid because it has a straight chain so its molecules have many contact points and strong London dispersion forces overall. The double bond in oleic acid creates a kink so there are fewer contact points and weaker London dispersion forces. Therefore, oleic acid is a liquid (*Chemistry* 8th ed. pages 442–443/9th ed. pages 457–458). LO 2.16