

# 11 Liquids, Solids, and Intermolecular Forces

## Review Questions

- 11.1 The key to the gecko's sticky feet lies in the millions of microhairs, called setae, that line its toes. Each seta is between 30 and 130  $\mu\text{m}$  long and branches out to end in several hundred flattened tips called spatulae. This unique structure allows the gecko's toes to have unusually close contact with the surfaces it climbs. The close contact allows intermolecular forces—which are significant only at short distances—to hold the gecko to the wall.
- 11.2 Intermolecular forces are important because they are the forces that hold many liquids and solids—such as water and ice, for example—together. These intermolecular forces determine many of the physical properties of a substance. All living organisms depend on intermolecular forces for many physiological processes. Intermolecular forces are responsible for the very existence of the condensed phases.
- 11.3 The main properties of liquids are that liquids have much higher densities in comparison to gases and generally have lower densities in comparison to solids; liquids have an indefinite shape and assume the shape of their container; liquids have a definite volume; and liquids are not easily compressed.
- 11.4 The main properties of solids are that solids have much higher densities in comparison to gases, and usually higher densities than liquids; solids have a definite shape; they do not assume the shape of their container; solids have a definite volume; they are not easily compressed; and solids may be crystalline (ordered) or amorphous (disordered).
- 11.5 Solids may be crystalline, in which case the atoms or molecules that compose them are arranged in a well-ordered three-dimensional array, or they may be amorphous, in which case the atoms or molecules that compose them have no long-range order.
- 11.6 One phase of matter can be transformed to another by changing the temperature, pressure, or both. A liquid can be converted to a gas by heating, and a gas can be condensed into a liquid by cooling. In general, increases in pressure favor the denser phase, so increasing the pressure of a gas sample can result in a transition to the liquid phase. A solid can be converted to a liquid by heating, and a liquid can be converted to a solid by cooling. In general, increases in pressure favor the denser phase (since atoms are pushed closer together), so increasing the pressure of most liquids can result in a transition to the solid phase.
- 11.7 Since there is the most molecular motion in the gas phase and the least molecular motion in the solid phase (atoms are pushed closer together), a substance will be converted from a solid then to a liquid and finally to a gas as the temperature increases. The strength of the intermolecular interactions is least in the gas phase, since there are large distances between particles and they are moving very fast. Intermolecular forces are stronger in liquids and solids, where molecules are "touching" one another. The strength of the interactions in the condensed phases will determine at what temperature the substance will melt and boil.
- 11.8 Intermolecular forces originate from the interactions between charges, partial charges, and temporary charges on molecules (or atoms and ions), much as bonding forces originate from interactions between charged particles in atoms.

11.9 Intermolecular forces, even the strongest ones, are generally much weaker than bonding forces. The reason for the relative weakness of intermolecular forces compared to bonding forces is related to Coulomb's law ( $E = \frac{1}{4\pi\epsilon_0} \frac{q_1q_2}{r}$ ). Bonding forces are the result of large charges (the charges on protons and electrons,  $q_1$  and  $q_2$ ) interacting at very close distances ( $r$ ). Intermolecular forces are the result of smaller charges (as we shall see in the following discussion) interacting at greater distances.

11.10 Dispersion forces (also called London forces) are the result of fluctuations in the electron distribution within molecules or atoms. Since all atoms and molecules have electrons, they all exhibit dispersion forces. The electrons in an atom or molecule may, at any one instant, be unevenly distributed.

The magnitude of the dispersion force depends on how easily the electrons in the atom or molecule can move or polarize in response to an instantaneous dipole (a temporary change in charge distribution), which in turn depends on the size (or volume) of the electron cloud. A larger electron cloud results in a greater dispersion force because the electrons are held less tightly by the nucleus and can therefore polarize more easily. If all other variables are constant, the dispersion force increases with increasing molar mass because molecules or atoms of higher molar mass generally have more electrons dispersed over a greater volume. The shape of the molecules can also affect the magnitude of the dispersion forces. The larger the area of interaction between two molecules, the larger the dispersion forces.

11.11 The dipole-dipole force exists in all molecules that are polar. Polar molecules have permanent dipoles that interact with the permanent dipoles of neighboring molecules. The positive end of one permanent dipole is attracted to the negative end of another; this attraction is the dipole-dipole force.

11.12 Miscibility is the ability to mix without separating into two phases. In general, polar liquids are miscible with other polar liquids, but are not miscible with nonpolar liquids. Nonpolar liquids are miscible with other nonpolar liquids.

11.13 The hydrogen bond is a sort of super dipole-dipole force. Polar molecules containing hydrogen atoms bonded directly to fluorine, oxygen, or nitrogen exhibit an intermolecular force called hydrogen bonding. The large electronegativity difference between hydrogen and these electronegative elements means that the H atoms will have fairly large partial positive charges ( $\delta^+$ ), while the F, O, or N atoms will have fairly large partial negative charges ( $\delta^-$ ). In addition, since these atoms are all quite small, they can approach one another very closely. The result is a strong attraction between the hydrogen in each of these molecules and the F, O, or N on its neighbors, an attraction called a hydrogen bond.

11.14 The ion-dipole force occurs when an ionic compound is mixed with a polar compound and is especially important in aqueous solutions of ionic compounds. For example, when sodium chloride is mixed with water, the sodium and chloride ions interact with water molecules via ion-dipole forces. The positive sodium ions interact with the negative poles of water molecules, while the negative chloride ions interact with the positive poles. Ion-dipole forces are the strongest of the types of intermolecular forces discussed here and are responsible for the ability of ionic substances to form solutions with water.

11.15 Surface tension is the tendency of liquids to minimize their surface area. Molecules at the surface have relatively fewer neighbors with which to interact, because there are no molecules above the surface. Consequently, molecules at the surface are inherently less stable—they have higher potential energy—than those in the interior. In order to increase the surface area of the liquid, some molecules from the interior have to be moved to the surface, a process requiring energy. The surface tension of a liquid is the energy required to increase the surface area by a unit amount. Surface tension decreases with decreasing intermolecular forces.

11.16 Viscosity is the resistance of a liquid to flow. Viscosity is measured in a unit called the poise (P), defined as 1 g/cm·s. The centipoise (cP) is a convenient unit because the viscosity of water at room temperature is approximately one centipoise. Viscosity is greater in substances with stronger intermolecular forces because molecules are more strongly attracted to each other, preventing them from flowing around each other as freely. Viscosity also depends on molecular shape, increasing in longer molecules that can interact over a greater area and possibly become entangled. Viscosity increases with increasing molar mass (and therefore increasing magnitude of dispersion forces) and with increasing length (and therefore increasing potential

for molecular entanglement). Viscosity also depends on temperature because thermal energy partially overcomes the intermolecular forces, allowing molecules to flow past each other more easily.

11.17

Capillary action is the ability of a liquid to flow against gravity up a narrow tube. Capillary action results from a combination of two forces: the attraction between molecules in a liquid, called cohesive forces, and the attraction between these molecules and the surface of the tube, called adhesive forces. The adhesive forces cause the liquid to spread out over the surface of the tube, while the cohesive forces cause the liquid to stay together. If the adhesive forces are greater than the cohesive forces (as is the case for water in a glass tube), the attraction to the surface draws the liquid up the tube while the cohesive forces pull along those molecules not in direct contact with the tube walls. The liquid rises up the tube until the force of gravity balances the capillary action—the thinner the tube, the higher the rise. If the adhesive forces are smaller than the cohesive forces (as is the case for liquid mercury), the liquid does not rise up the tube at all (and in fact will drop to a level below the level of the surrounding liquid).

11.18

Molecules are in constant motion. The higher the temperature, the greater the average energy of the collection of molecules. However, at any one time, some molecules will have more thermal energy than the average and some will have less. The molecules with the highest thermal energy have enough energy to break free from the surface—where molecules are held less tightly than in the interior due to fewer neighbor–neighbor interactions—and into the gas phase. This process is called vaporization, the phase transition from liquid to gas. The greater the temperature the greater the rate of vaporization. Some of the water molecules in the gas phase, at the low end of the energy distribution curve for the gaseous molecules, can plunge back into the liquid and be captured by intermolecular forces. This process—the opposite of vaporization—is called condensation, the phase transition from gas to liquid.

11.19

The molecules that leave the liquid are the ones at the high end of the energy curve—the most energetic. If no additional heat enters the liquid, the average energy of the entire collection of molecules goes down—much as the class average on an exam goes down if you eliminate the highest-scoring students. So vaporization is an endothermic process; it takes energy to vaporize the molecules in a liquid. Also, vaporization requires overcoming the intermolecular forces that hold liquids together. Since energy must be absorbed to pull the molecules apart, the process is endothermic. Condensation is the opposite process, so it must be exothermic. Also, gas particles have more energy than those in the liquid. It is the least energetic of these that condense, adding energy to the liquid.

11.20

The weaker the intermolecular forces, the more likely it is that molecules are to evaporate at a given temperature, making the liquid more volatile.

11.21

The heat of vaporization ( $\Delta H_{\text{vap}}$ ) is the amount of heat required to vaporize one mole of a liquid to a gas. The heat of vaporization of a liquid can be used to calculate the amount of heat energy required to vaporize a given mass of the liquid (or the amount of heat given off by the condensation of a given mass of liquid), and can be used to compare the volatility of two substances.

11.22

Molecules are in constant motion. Molecules leave the liquid for the gas phase and gas phase molecules condense to become a liquid. Dynamic equilibrium has been reached when the rate of condensation and the rate of vaporization become equal. Although condensation and vaporization continue, at equal rates, the concentration of water vapor above the liquid is constant. The pressure of a gas in dynamic equilibrium with its liquid is called its vapor pressure.

11.23

When a system in dynamic equilibrium is disturbed, the system responds so as to minimize the disturbance and return to a state of equilibrium.

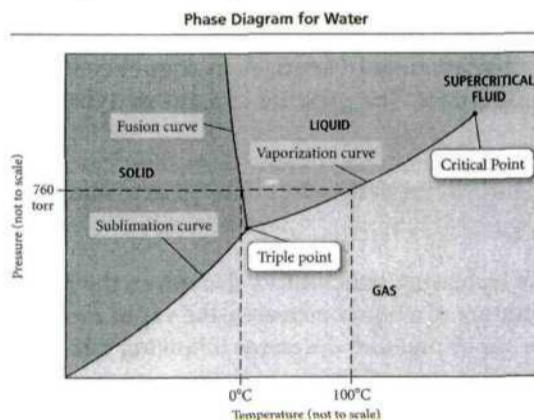
11.24

The vapor pressure of a liquid increases with increasing temperature. However, the relationship is not linear, but rather, it is exponential. As the temperature of a liquid increases, the vapor increases more and more quickly. As the temperature is decreased, the vapor pressure decreases following this same relationship.

11.25

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

- 11.26 The Clausius–Clapeyron Equation is the relationship between vapor pressure and temperature. It can be expressed as  $\ln P_{\text{vap}} = \frac{-\Delta H_{\text{vap}}}{R} \left( \frac{1}{T} \right) + \ln \beta$ . In this expression  $P_{\text{vap}}$  is the vapor pressure,  $\beta$  is a constant that depends on the gas,  $\Delta H_{\text{vap}}$  is the heat of vaporization,  $R$  is the gas constant (8.314 J/mol K), and  $T$  is the temperature in kelvin. The Clausius–Clapeyron equation gives a linear relationship—not between the vapor pressure and the temperature (which have an exponential relationship)—but between the natural log of the vapor pressure and the inverse of temperature. The Clausius–Clapeyron equation leads to a convenient way to measure the heat of vaporization in the laboratory, or to calculate the vapor pressure of a liquid at a temperature (if the heat of vaporization and a vapor pressure at one temperature are known).
- 11.27 As the temperature rises, more liquid vaporizes and the pressure within the container increases. As more and more gas is forced into the same amount of space, the density of the gas becomes higher and higher. At the same time, the increasing temperature causes the density of the liquid to become lower and lower. At the critical temperature, the meniscus between the liquid and gas disappears and the gas and liquid phases commingle to form a supercritical fluid.
- 11.28 Sublimation is the phase transition from solid to gas, without going through a liquid phase. A common example of sublimation is the carbon dioxide, where “dry ice” converts from a solid to a gas, without going through a “wet” (or liquid) phase.
- 11.29 Fusion, or melting, is the phase transition from solid to liquid. The term fusion is used for melting because, if you heat several crystals of a solid, they will fuse into a continuous liquid upon melting. Fusion is endothermic because solids have less kinetic energy than liquids, so energy must be added to a solid to get it to melt.
- 11.30 The heat of fusion ( $\Delta H_{\text{fus}}$ ) is the amount of heat required to melt 1 mol of a solid. The heat of fusion of a solid, which is related to the strength of the intermolecular forces, can be used to calculate the amount of heat energy required to melt a given mass of the solid (or the amount of heat given off by the freezing of a given mass of liquid).
- 11.31 There are two horizontal lines (i.e. heat is added, but the temperature stays constant) in the heating curve because there are two endothermic phase changes. The heat that is added is used to change the phase from solid to liquid or liquid to gas.
- 11.32 The slopes indicate how much heat is necessary to increase the temperature of the sample. The slope is proportional to  $1/C_s$  (the specific heat capacity of the phase). The amount of molecular motion and the amount of intermolecular interactions is different in each phase, and so the specific heat capacity and the slope is different for each phase and each substance.
- 11.33 A phase diagram is simply a map of the phase of a substance as a function of pressure (on the  $y$ -axis) and temperature (on the  $x$ -axis).



- 11.34 When a line is crossed in a phase diagram it means that a phase transition has occurred.

- of the tetrahedral holes located directly beneath each corner atom. Each unit cell contains four calcium cations ( $[8 \times 1/8] + [6 \times \frac{1}{2}] = 4$ ) and eight fluoride anions (each of the eight fluoride anions is completely contained within the unit cell), resulting in a cation to anion ratio of 1:2, just as in the formula of the compound.
- 11.45 Atomic solids can themselves be divided into three categories—nonbonding atomic solids, metallic atomic solids, and network covalent atomic solids. Nonbonding atomic solids, which include only the noble gases in their solid form, are held together by relatively weak dispersion forces. Metallic atomic solids, such as iron or gold, are held together by metallic bonds, which in the simplest model are represented by the interaction of metal cations with a sea of electrons that surround them. Network covalent atomic solids, such as diamond, graphite, and silicon dioxide, are held together by covalent bonds.
- 11.46 In band theory, bands are the combination atomic orbitals of the atoms within a solid crystal that form orbitals that are not localized on individual atoms, but delocalized over the entire crystal. In band theory, electrons become mobile when they make a transition from the highest occupied molecular orbital into higher-energy empty molecular orbitals. For this reason, the occupied molecular orbitals are often called the valence band and the unoccupied orbitals are called the conduction band.
- 11.47 The band gap is an energy gap that exists between the valence band and conduction band. In metals, the valence band and conduction band are always energetically continuous—the energy difference between the top of the valence band and the bottom of the conduction band is infinitesimally small. In semiconductors, the band gap is small, allowing some electrons to be promoted at ordinary temperatures resulting in limited conductivity. In insulators, the band gap is large, and electrons are not promoted into the conduction band at ordinary temperatures, resulting in no electrical conductivity.
- 11.48 Doped semiconductors contain minute amounts of impurities that result in additional electrons in the conduction band or electron “holes” in the valence band. For example, silicon is a group 4A semiconductor. Its valence electrons just fill its valence band. When silicon is doped with phosphorus, a group 5A element with five valence electrons, its conductivity increases. The phosphorus atoms are incorporated into the silicon crystal structure, but each phosphorus atom brings with it one additional electron. Since the valence band is completely full, the additional electrons must go into the conduction band. These electrons are then mobile and can conduct electrical current. This type of semiconductor is called an n-type semiconductor because the charge carriers are negatively charged electrons in the conduction band. Silicon can also be doped with a group 3A element, such as gallium, which has only three valence electrons. When gallium is incorporated into the silicon crystal structure, it results in electron “holes,” empty molecular orbitals in the valence band. The presence of holes also allows for the movement of electrical current because electrons in the valence band can move between holes. In this way, the holes move in the opposite direction as the electrons. This type of semiconductor is called a p-type semiconductor because the hole acts as a positive charge.

### Intermolecular Forces

- 11.49 (a) dispersion forces  
(b) dispersion forces, dipole–dipole forces, and hydrogen bonding  
(c) dispersion forces and dipole–dipole forces  
(d) dispersion forces
- 11.50 (a) dispersion forces  
(b) dispersion forces and dipole–dipole forces  
(c) dispersion forces  
(d) dispersion forces, dipole–dipole forces, and hydrogen bonding
- 11.51 (a) dispersion forces and dipole–dipole forces  
(b) dispersion forces, dipole–dipole forces, and hydrogen bonding

- (c) dispersion forces  
(d) dispersion forces
- 11.52 (a) dispersion forces and dipole–dipole forces  
(b) dispersion forces and dipole–dipole forces  
(c) dispersion forces, dipole–dipole forces, and hydrogen bonding  
(d) dispersion forces
- 11.53 (a)  $\text{CH}_4 < \text{(b) CH}_3\text{CH}_3 < \text{(c) CH}_3\text{CH}_2\text{Cl} < \text{(d) CH}_3\text{CH}_2\text{OH}$ . The first two molecules only exhibit dispersion forces, so the boiling point increases with increasing molar mass. The third molecule also exhibits dipole–dipole forces, which are stronger than dispersion forces. The last molecule exhibits hydrogen bonding. Since these are by far the strongest intermolecular forces in this group, the last molecule has the highest boiling point.
- 11.54 (a)  $\text{H}_2\text{S} < \text{(b) H}_2\text{Se} < \text{(c) H}_2\text{O}$ . The first two molecules only exhibit dispersion forces and dipole–dipole forces, so the boiling point increases with increasing molar mass. The third molecule also exhibits hydrogen bonding. Since these are by far the strongest intermolecular forces in this group, the last molecule has the highest boiling point.
- 11.55 (a)  $\text{CH}_3\text{OH}$  has the higher boiling point since it exhibits hydrogen bonding.  
(b)  $\text{CH}_3\text{CH}_2\text{OH}$  has the higher boiling point since it exhibits hydrogen bonding.  
(c)  $\text{CH}_3\text{CH}_3$  has the higher boiling point since it has the larger molar mass.
- 11.56 (a)  $\text{NH}_3$  has the higher boiling point since it exhibits hydrogen bonding.  
(b)  $\text{CS}_2$  has the higher boiling point since it has the larger molar mass.  
(c)  $\text{NO}_2$  has the higher boiling point since it exhibits dipole–dipole forces.
- 11.57 (a)  $\text{Br}_2$  has the higher vapor pressure since it has the smaller molar mass.  
(b)  $\text{H}_2\text{S}$  has the higher vapor pressure since it does not exhibit hydrogen bonding.  
(c)  $\text{PH}_3$  has the higher vapor pressure since it does not exhibit hydrogen bonding.
- 11.58 (a)  $\text{CH}_4$  has the higher vapor pressure since it has the smaller molar mass and it does not exhibit dipole–dipole forces.  
(b)  $\text{CH}_3\text{OH}$  has the higher vapor pressure since it has the smaller molar mass, and both exhibit hydrogen bonding.  
(c)  $\text{H}_2\text{CO}$  has the higher vapor pressure since it has the smaller molar mass and it does not exhibit hydrogen bonding.
- 11.59 (a) This will not form a homogeneous solution, since one is polar and one is nonpolar.  
(b) This will form a homogeneous solution. There will be ion–dipole interactions between the  $\text{K}^+$  and  $\text{Cl}^-$  ions and the water molecules. There will also be dispersion forces, dipole–dipole forces, and hydrogen bonding between the water molecules.  
(c) This will form a homogeneous solution. There will be dispersion forces present among all of the molecules.  
(d) This will form a homogeneous solution. There will be dispersion forces, dipole–dipole forces, and hydrogen bonding among all of the molecules.

- 11.60 (a) This will form a homogeneous solution. There will only be dispersion forces present.
- (b) This will not form a homogeneous solution, since one is polar and one is nonpolar.
- (c) This will form a homogeneous solution. There will be ion-dipole interactions between the  $\text{Li}^+$  and  $\text{NO}_3^-$  ions and the water molecules. There will also be dispersion forces, dipole-dipole forces, and hydrogen bonding between the water molecules.
- (d) This will not form a homogeneous solution, since one is polar and one is nonpolar.

### Surface Tension, Viscosity, and Capillary Action

- 11.61 Water will have the higher surface tension since it exhibits hydrogen bonding, a strong intermolecular force. Acetone cannot form hydrogen bonds.
- 11.62 (a) Water "wets" surfaces that are capable of dipole-dipole interactions. The water will form strong adhesive forces with the surface when these dipole-dipole forces are present and so the water will spread to cover as much of the surface as possible. Water does not experience strong intermolecular forces with oil and other nonpolar surfaces. The water will bead up, maximizing the cohesive interactions, which involve strong hydrogen bonds. So water will bead up on surfaces that can only exhibit dispersion forces.
- (b) Mercury will bead up on surfaces since it is not capable of forming strong intermolecular interactions (only dispersion forces).
- 11.63 Compound A will have the higher viscosity since it can interact with other molecules along the entire molecule. The more branched isomer has a smaller surface area allowing for fewer interactions. Also the molecule is very flexible and the molecules can get tangled with each other.
- 11.64 Multigrade oils contain polymers (long molecules made up of repeating structural units) that coil at low temperatures but unwind at high temperatures. At low temperatures, the coiled polymers—because of their compact shape—do not contribute very much to the viscosity of the oil. As the temperature increases, however, the molecules unwind and their long shape results in intermolecular forces and molecular entanglements that prevent the viscosity from decreasing as much as it would normally. The result is an oil whose viscosity is less temperature-dependent than it would be otherwise, allowing the same oil to be used over a wider range of temperatures.
- 11.65 In a clean glass tube the water can generate strong adhesive interactions with the glass (due to the dipoles at the surface of the glass). Water experiences adhesive forces with glass that are stronger than its cohesive forces, causing it to climb the surface of a glass tube. When grease or oil coats the glass this interferes with the formation of these adhesive interactions with the glass, since oils are nonpolar and cannot interact strongly with the dipoles in the water. Without experiencing these strong intermolecular forces with oil, the water's cohesive forces will be greater and it will be drawn away from the surface of the tube.
- 11.66 Water can generate strong adhesive interactions with the glass (due to the dipoles at the surface of the glass), but hexane is nonpolar and cannot interact strongly with the glass surface.

### Vaporization and Vapor Pressure

11.67 The water in the 12 cm diameter beaker will evaporate more quickly because there is more surface area for the molecules to evaporate from. The vapor pressure will be the same in the two containers because the vapor pressure is the pressure of the gas when it is in dynamic equilibrium with the liquid (evaporation rate = condensation rate). The vapor pressure is dependent only on the substance and the temperature. The 12 cm diameter container will reach this dynamic equilibrium faster.

11.68 The acetone will evaporate more quickly since it is not capable of forming hydrogen bonds, so the intermolecular forces are much weaker. This will result in a larger vapor pressure at the same temperature as the water.

$$\text{Solution: } 1.00 \text{ mol} \times \frac{18.01 \text{ g}}{1 \text{ mol}} = 18.01 \text{ g}$$

$$q_1 = m_{\text{steam}} C_{\text{steam}} (T_{\text{steamf}} - T_{\text{steami}}) = 18.01 \text{ g} \times 2.01 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \times (100.0 ^\circ\text{C} - 145.0 ^\circ\text{C}) = -1629.00 \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$= -1.629 \text{ kJ}$$

$$q_2 = \text{mol} \times \frac{-\Delta H_{\text{vap}}}{1 \text{ mol}} = 1.00 \text{ mol} \times \frac{-40.7 \text{ kJ}}{1 \text{ mol}} = -40.7 \text{ kJ},$$

$$q_3 = m_{\text{water}} C_{\text{water}} (T_{\text{waterf}} - T_{\text{wateri}}) = 18.01 \text{ g} \times 4.18 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \times (0.0 ^\circ\text{C} - 100.0 ^\circ\text{C}) = -7528.2 \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$= -7.5282 \text{ kJ},$$

$$q_4 = \text{mol} \times \frac{-\Delta H_{\text{fus}}}{1 \text{ mol}} = 1.00 \text{ mol} \times \frac{-6.02 \text{ kJ}}{1 \text{ mol}} = -6.02 \text{ kJ},$$

$$q_5 = m_{\text{ice}} C_{\text{ice}} (T_{\text{icef}} - T_{\text{icei}}) = 18.01 \text{ g} \times 2.09 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \times (-50.0 ^\circ\text{C} - 0.0 ^\circ\text{C}) = -1882.0 \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$= -1.8820 \text{ kJ}$$

$$q_{\text{Total}} = q_1 + q_2 + q_3 + q_4 + q_5 = -1.629 \text{ kJ} - 40.7 \text{ kJ} - 7.5282 \text{ kJ} - 6.02 \text{ kJ} - 1.8820 \text{ kJ}$$

$$= -57.8 \text{ kJ} \text{ or } 57.8 \text{ kJ} \text{ released.}$$

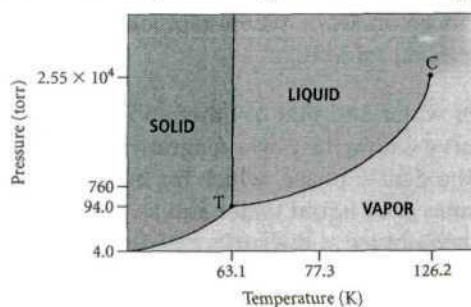
**Check:** The units (kJ) are correct. The amount of heat is dominated by the vaporization step. Since we have exactly 1 mole we expect more than 41 kJ.

## Phase Diagrams

- 11.85 (a) solid  
 (b) liquid  
 (c) gas  
 (d) supercritical fluid  
 (e) solid/liquid equilibrium  
 (f) liquid/gas equilibrium  
 (g) solid/liquid/gas equilibrium

- 11.86 (a) 184.4 °C  
 (b) 113.6 °C  
 (c) solid  
 (d) gas

- 11.87 **Given:** nitrogen, normal boiling point = 77.3 K, normal melting point = 63.1 K, critical temperature = 126.2 K, critical pressure =  $2.55 \times 10^4$  torr, triple point at 63.1 K and 94.0 torr  
**Find:** Sketch phase diagram. Does nitrogen have a stable liquid phase at 1 atm?

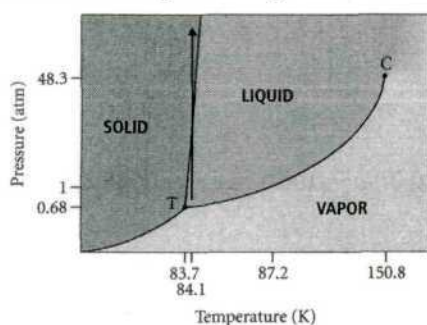


Nitrogen has a stable liquid phase at 1 atm.  
 Note that the axes are not to scale.



11.88 **Given:** argon, normal boiling point = 87.2 K, normal melting point = 84.1 K, critical temperature = 150.8 K, critical pressure = 48.3 atm, triple point at 83.7 K and 0.68 atm

**Find:** Sketch phase diagram. Which has the greater density, solid or liquid argon?



The solid has the higher density because the slope of the solid/liquid equilibrium line is positive. If we start in the liquid and increase the pressure, we will cross into the solid phase, the dense phase.

Note that the axes are not to scale.

11.89 (a) 0.027 mmHg, the higher of the two triple points

(b) The rhombic phase is denser because if we start in the monoclinic phase at 100 °C and increase the pressure, we will cross into the rhombic phase.

11.90 The triple point marked "O" shows the equilibrium of Ice II, Ice III, and Ice V. Ice II is denser than Ice I because you can generate Ice II from Ice I by increasing the pressure (pushing the molecules closer together). Ice III would sink in liquid water. Note that the slope of the Ice III/liquid line has the typical positive slope.

## The Uniqueness of Water

11.91 Water has a low molar mass (18.01 g/mol), yet it is a liquid at room temperature. Water's high boiling point for its molar mass can be understood by examining the structure of the water molecule. The bent geometry of the water molecule and the highly polar nature of the O-H bonds result in a molecule with a significant dipole moment. Water's two O-H bonds (hydrogen directly bonded to oxygen) allow a water molecule to form very strong hydrogen bonds with four other water molecules, resulting in a relatively high boiling point.

11.92 Water's high polarity also allows it to dissolve many other polar and ionic compounds, and even a number of nonpolar gases such as oxygen and carbon dioxide (by inducing a dipole moment in their molecules). Consequently, water is the main solvent within living organisms, transporting nutrients and other important compounds throughout the body. Water is also the main solvent of the environment, allowing aquatic animals, for example, to survive by breathing dissolved oxygen and allowing aquatic plants to survive by using dissolved carbon dioxide for photosynthesis.

11.93 Water has an exceptionally high specific heat capacity, which has a moderating effect on the climate of coastal cities. Also, its high  $\Delta H_{\text{vap}}$  causes water evaporation and condensation to have a strong effect on temperature. A tremendous amount of heat can be stored in large bodies of water. Heat will be absorbed or released from large bodies of water preferentially over land around it. In some cities, such as San Francisco, for example, the daily fluctuation in temperature can be less than 10 °C. This same moderating effect occurs over the entire planet, two-thirds of which is covered by water. In other words, without water, the daily temperature fluctuations on our planet might be more like those on Mars, where temperature fluctuations of 63 °C (113 °F) have been measured between early morning and midday.

11.94 One significant difference between the phase diagram of water and that of other substances is the fusion curve for water, which has a negative slope. The fusion curve within the phase diagrams for most substances has a positive slope because increasing pressure favors the denser phase, which for most substances is the solid phase. This negative slope means that ice is less dense than liquid water and so ice floats. The solids sink in the liquids of most other substances. The frozen layer of ice at the surface of a winter lake insulates the water in the lake from further freezing. If this ice layer sank, it would kill bottom-dwelling aquatic life and possibly allow the lake to freeze solid, eliminating virtually all life in the lake.

$$\text{Solution: } l = \frac{4r}{\sqrt{3}} = \frac{4 \times 136 \text{ pm}}{\sqrt{3}} = 314.079 \text{ pm} = 314 \text{ pm and}$$

$$V = l^3 = (314.079 \text{ pm})^3 \times \frac{(1 \text{ cm})^3}{(10^{10} \text{ pm})^3} = 3.09823 \times 10^{-23} \text{ cm}^3 \text{ and}$$

$$m = \frac{2 \text{ atoms}}{\text{unit cell}} \times \frac{M}{N_A} = \frac{2 \text{ atoms}}{\text{unit cell}} \times \frac{95.94 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} = 3.186317 \times 10^{-22} \frac{\text{g}}{\text{unit cell}} \text{ then}$$

$$d = \frac{m}{V} = \frac{3.186317 \times 10^{-22} \frac{\text{g}}{\text{unit cell}}}{3.09823 \times 10^{-23} \frac{\text{cm}^3}{\text{unit cell}}} = 10.3 \frac{\text{g}}{\text{cm}^3}$$

**Check:** The units (pm and g/cm<sup>3</sup>) are correct. The magnitude (314 pm) makes sense because it must be larger than the radius of an atom. The magnitude (10 g/cm<sup>3</sup>) is reasonable for a metal density.

11.101

**Given:** rhodium, face-centered cubic structure,  $d = 12.41 \text{ g/cm}^3$  **Find:**  $r$  (Rh)

**Conceptual Plan:**  $M, \text{ FCC structure} \rightarrow m \text{ then } m, V \rightarrow d \text{ then } V(\text{cm}^3) \rightarrow l(\text{cm}) \rightarrow l(\text{pm}) \text{ then } l \rightarrow r$

$$m = \frac{4 \text{ atoms}}{\text{unit cell}} \times \frac{M}{N_A} \quad d = m/V \quad V = l^3 \quad \frac{10^{10} \text{ pm}}{1 \text{ cm}} \quad l = 2\sqrt{2}r$$

$$\text{Solution: } m = \frac{4 \text{ atoms}}{\text{unit cell}} \times \frac{M}{N_A} = \frac{4 \text{ atoms}}{\text{unit cell}} \times \frac{102.905 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} = 6.835271 \times 10^{-22} \frac{\text{g}}{\text{unit cell}}$$

$$\text{then } d = \frac{m}{V}. \text{ Rearrange to solve for } V. V = \frac{m}{d} = \frac{6.835271 \times 10^{-22} \frac{\text{g}}{\text{unit cell}}}{12.41 \frac{\text{g}}{\text{cm}^3}} = 5.507873 \times 10^{-23} \frac{\text{cm}^3}{\text{unit cell}}$$

then  $V = l^3$ . Rearrange to solve for  $l$ .

$$l = \sqrt[3]{V} = \sqrt[3]{5.507873 \times 10^{-23} \text{ cm}^3} = 3.804831 \times 10^{-8} \text{ cm} \times \frac{10^{10} \text{ pm}}{1 \text{ cm}} = 380.4831 \text{ pm then } l = 2\sqrt{2}r.$$

$$\text{Rearrange to solve for } r. r = \frac{l}{2\sqrt{2}} = \frac{380.4831 \text{ pm}}{2\sqrt{2}} = 134.5 \text{ pm.}$$

**Check:** The units (pm) are correct. The magnitude (135 pm) is consistent with an atomic diameter.

11.102

**Given:** barium, body-centered cubic structure,  $d = 3.59 \text{ g/cm}^3$  **Find:**  $r$  (Ba)

**Conceptual Plan:**  $M, \text{ BCC structure} \rightarrow m \text{ then } m, V \rightarrow d \text{ then } V(\text{cm}^3) \rightarrow l(\text{cm}) \rightarrow l(\text{pm}) \text{ then } l \rightarrow r$

$$m = \frac{2 \text{ atoms}}{\text{unit cell}} \times \frac{M}{N_A} \quad d = m/V \quad V = l^3 \quad \frac{10^{10} \text{ pm}}{1 \text{ cm}} \quad l = \frac{4r}{\sqrt{3}}$$

$$\text{Solution: } m = \frac{2 \text{ atoms}}{\text{unit cell}} \times \frac{M}{N_A} = \frac{2 \text{ atoms}}{\text{unit cell}} \times \frac{137.34 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} = 4.561275 \times 10^{-22} \frac{\text{g}}{\text{unit cell}} \text{ then}$$

$$d = \frac{m}{V}. \text{ Rearrange to solve for } V. V = \frac{m}{d} = \frac{4.561275 \times 10^{-22} \frac{\text{g}}{\text{unit cell}}}{3.59 \frac{\text{g}}{\text{cm}^3}} = 1.270550 \times 10^{-22} \frac{\text{cm}^3}{\text{unit cell}}$$

then  $V = l^3$ . Rearrange to solve for  $l$ .

$$l = \sqrt[3]{V} = \sqrt[3]{1.270550 \times 10^{-22} \text{ cm}^3} = 5.027336 \times 10^{-8} \text{ cm} \times \frac{10^{10} \text{ pm}}{1 \text{ cm}} = 502.7336 \text{ pm}$$

$$\text{then } l = \frac{4r}{\sqrt{3}}. \text{ Rearrange to solve for } r. r = \frac{l\sqrt{3}}{4} = \frac{502.7336 \text{ pm} \times \sqrt{3}}{4} = 217.7 \text{ pm.}$$

**Check:** The units (pm) are correct. The magnitude (218 pm) is consistent with an atomic diameter.

11.103

**Given:** polonium, simple cubic structure,  $d = 9.3 \text{ g/cm}^3$ ;  $r = 167 \text{ pm}$ ;  $M = 209 \text{ g/mol}$  **Find:** estimate  $N_A$

**Conceptual Plan:**  $r \rightarrow l \text{ and } l \rightarrow V(\text{pm}^3) \rightarrow V(\text{cm}^3) \text{ then } d, V \rightarrow m \text{ then } M, \text{ SC structure} \rightarrow m$

$$l = 2r \quad V = l^3 \quad \frac{(1 \text{ cm})^3}{(10^{10} \text{ pm})^3} \quad d = m/V \quad m = \frac{1 \text{ atom}}{\text{unit cell}} \times \frac{M}{N_A}$$

**Solution:**  $l = 2r = 2 \times 167 \text{ pm} = 334 \text{ pm}$  and  $V = l^3 = (334 \text{ pm})^3 \times \frac{(1 \text{ cm})^3}{(10^{10} \text{ pm})^3} = 3.72597 \times 10^{-23} \text{ cm}^3$  then

$$d = \frac{m}{V}. \text{ Rearrange to solve for } m. m = dV = 9.3 \frac{\text{g}}{\text{cm}^3} \times \frac{3.72597 \times 10^{-23} \text{ cm}^3}{\text{unit cell}} = 3.46515 \times 10^{-22} \frac{\text{g}}{\text{unit cell}}$$

then  $m = \frac{1 \text{ atom}}{\text{unit cell}} \times \frac{\mathcal{M}}{N_A}$ . Rearrange to solve for  $N_A$ .

$$N_A = \frac{1 \text{ atom}}{\text{unit cell}} \times \frac{\mathcal{M}}{m} = \frac{1 \text{ atom}}{\text{unit cell}} \times \frac{209 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ unit cell}}{3.46515 \times 10^{-22} \text{ g}} = 6.0 \times 10^{23} \frac{\text{atom}}{\text{mol}}$$

**Check:** The units (atoms/mol) are correct. The magnitude ( $6 \times 10^{23}$ ) is consistent with Avogadro's number.

11.104

**Given:** palladium, face-centered cubic structure,  $d = 12.0 \text{ g/cm}^3$ ;  $r = 138 \text{ pm}$ ;  $\mathcal{M} = 106.42 \text{ g/mol}$

**Find:** estimate  $N_A$

**Conceptual Plan:**  $r \rightarrow l$  and  $l \rightarrow V(\text{pm}^3) \rightarrow V(\text{cm}^3)$  then  $d, V \rightarrow m$  then  $\mathcal{M}, \text{FCC structure} \rightarrow m$

$$l = 2\sqrt{2}r \quad V = l^3 \quad \frac{(1 \text{ cm})^3}{(10^{10} \text{ pm})^3} \quad d = m/V \quad m = \frac{4 \text{ atoms}}{\text{unit cell}} \times \frac{\mathcal{M}}{N_A}$$

**Solution:**  $l = 2\sqrt{2}r = 2\sqrt{2} \times 138 \text{ pm} = 390.323 \text{ pm}$  and

$$V = l^3 = (390.323 \text{ pm})^3 \times \frac{(1 \text{ cm})^3}{(10^{10} \text{ pm})^3} = 5.94665 \times 10^{-23} \text{ cm}^3 \text{ then } d = \frac{m}{V}. \text{ Rearrange to solve for } m.$$

$$m = dV = 12.0 \frac{\text{g}}{\text{cm}^3} \times \frac{5.94665 \times 10^{-23} \text{ cm}^3}{\text{unit cell}} = 7.13598 \times 10^{-22} \frac{\text{g}}{\text{unit cell}} \text{ then } m = \frac{4 \text{ atoms}}{\text{unit cell}} \times \frac{\mathcal{M}}{N_A}$$

$$\text{Rearrange to solve for } N_A. N_A = \frac{4 \text{ atoms}}{\text{unit cell}} \times \frac{\mathcal{M}}{m} = \frac{4 \text{ atoms}}{\text{unit cell}} \times \frac{106.42 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ unit cell}}{7.13598 \times 10^{-22} \text{ g}} = 5.97 \times 10^{23} \frac{\text{atom}}{\text{mol}}$$

**Check:** The units (atoms/mol) are correct. The magnitude ( $6 \times 10^{23}$ ) is consistent with Avogadro's number.

- 11.105 (a) atomic, since Ar is an atom  
 (b) molecular, since water is a molecule  
 (c) ionic, since  $\text{K}_2\text{O}$  is an ionic solid  
 (d) atomic, since iron is an atom
- 11.106 (a) ionic, since  $\text{CaCl}_2$  is an ionic solid  
 (b) molecular, since  $\text{CO}_2$  is a molecule  
 (c) atomic, since nickel (Ni) is an atom  
 (d) molecular, since  $\text{I}_2$  is a molecule
- 11.107  $\text{LiCl}$  has the highest melting point since it is the only ionic solid in the group. The other three solids are held together by intermolecular forces, while  $\text{LiCl}$  is held together by stronger coulombic interactions between the cations and anions of the crystal lattice.
- 11.108 C (diamond) has the highest melting point ( $3800 \text{ }^\circ\text{C}$ ). Both covalent network solids and ionic solids have high melting points.  $\text{NaCl}$  has a melting point of  $801 \text{ }^\circ\text{C}$ . In diamond (Figure 11.57a), each carbon atom forms four covalent bonds to four other carbon atoms in a tetrahedral geometry. This structure extends throughout the entire crystal, so that a diamond crystal can be thought of as a giant molecule, held together by these covalent bonds. Since covalent bonds are very strong, covalent atomic solids have high melting points.
- 11.109 (a)  $\text{TiO}_2$  because it is an ionic solid  
 (b)  $\text{SiCl}_4$  because it has a higher molar mass and therefore has stronger dispersion forces  
 (c) Xe because it has a higher molar mass and therefore has stronger dispersion forces  
 (d)  $\text{CaO}$  because the ions have greater charge and therefore stronger dipole-dipole interactions