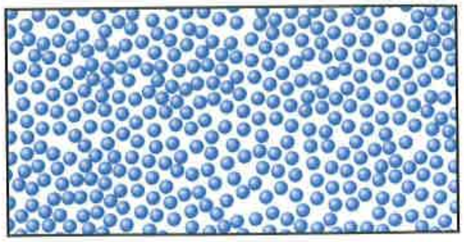
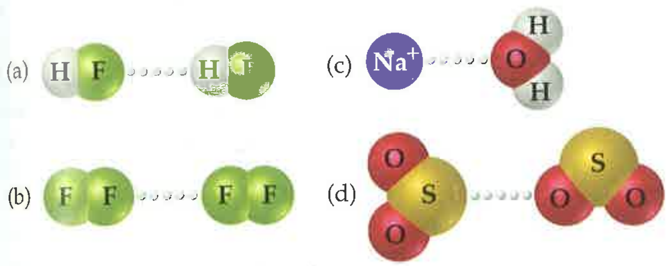
- Know the difference between crystalline and amorphous solids, and be able to explain the differences between primitive cubic, body-centered cubic, and face-centered cubic unit cells.
- Classify solids based on their bonding/intermolecular forces and understand how difference in bonding relates to physical properties.

VISUALIZING CONCEPTS

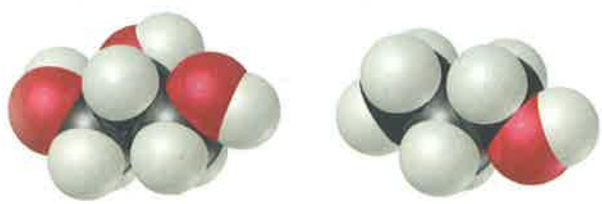
11.1 CQ Does the following diagram best describe a crystalline solid, liquid, or gas? Explain. [Section 11.1]



11.2 CQ **(a)** What kind of intermolecular attractive force is shown in each of the following cases? **(b)** Predict which two interactions are stronger than the other two. [Section 11.2]



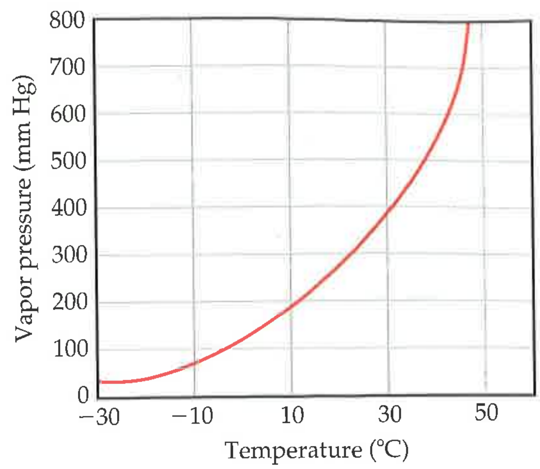
11.3 CQ The molecular models of glycerol and 1-propanol are given here.



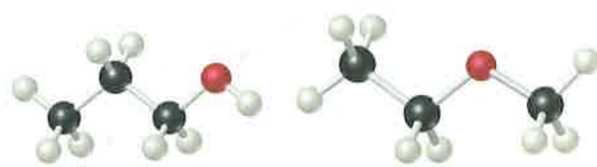
(a) Glycerol (b) 1-propanol

Do you expect the viscosity of glycerol to be larger or smaller than that of 1-propanol? Explain. [Section 11.3]

11.4 CQ Using the following graph of CS_2 data, determine **(a)** the approximate vapor pressure of CS_2 at 30 °C, **(b)** the temperature at which the vapor pressure equals 300 torr, **(c)** the normal boiling point of CS_2. [Section 11.5]

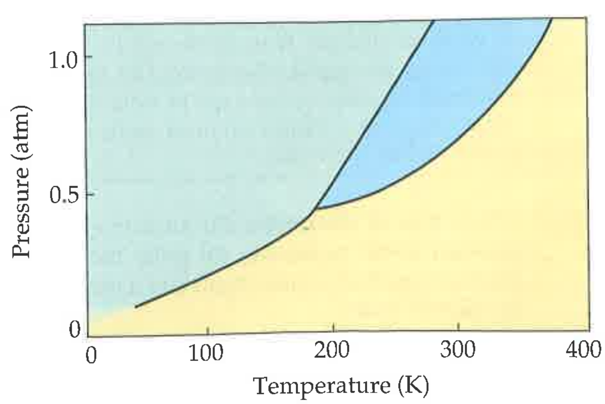


11.5 CQ The following molecules have the same molecular formula (C_3H_8O), yet they have different normal boiling points, as shown. Rationalize the difference in boiling points. [Sections 11.2 and 11.5]



(a) Propanol 97.2 °C (b) Ethyl methyl ether 10.8 °C

11.6 CQ The phase diagram of a hypothetical substance is shown below.

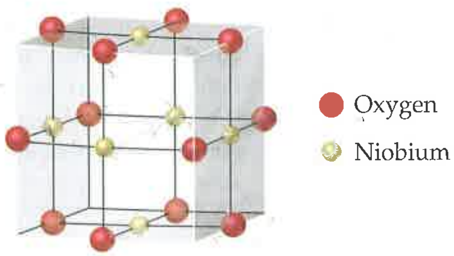


(a) Estimate the normal boiling point and freezing point of the substance.

(b) What is the physical state of the substance under the following conditions?
(i) $T = 150$ K, $P = 0.2$ atm
(ii) $T = 100$ K, $P = 0.8$ atm
(iii) $T = 300$ K, $P = 1.0$ atm

(c) What is the triple point of the substance? [Section 11.6]

11.7 Niobium(II) oxide crystallizes in the following cubic
CQ unit cell.



(a) How many niobium atoms and how many oxygen atoms are within the unit cell?
(b) What is the empirical formula of niobium oxide?
(c) Is this a molecular, covalent-network, or ionic solid? [Sections 11.7 and 11.8]

11.8 **(a)** What kind of packing arrangement is seen in the ac-
CQ companying photo? **(b)** What is the coordination number of each orange in the interior of the stack? **(c)** If each orange represents an argon atom, what category of solid is represented? [Sections 11.7 and 11.8]

EXERCISES

Molecular Comparisons of Gases, Liquids, and Solids

11.9 List the three states of matter in order of **(a)** increasing molecular disorder and **(b)** increasing intermolecular attractions. **(c)** Which state of matter is most easily compressed?

11.10 **(a)** How does the average kinetic energy of molecules
CQ compare with the average energy of attraction between molecules in solids, liquids, and gases? **(b)** Why does increasing the temperature cause a solid substance to change in succession from a solid to a liquid to a gas? **(c)** What happens to a gas if you put it under extremely high pressure?

11.11 If you mix olive oil with water, the olive oil will float on
CQ top of the water. The density of water is 1.00 g/cm^3 at room temperature. **(a)** Is the density of olive oil more or less than 1.00 g/cm^3? **(b)** The density of olive oil in its liquid phase does vary with temperature. Do you think olive oil would be more dense or less dense at higher temperatures? Explain.

11.12 Benzoic acid, C_6H_5COOH, melts at 122 °C. The density
CQ in the liquid state at 130 °C is 1.08 g/cm^3. The density of solid benzoic acid at 15 °C is 1.266 g/cm^3. **(a)** In which of these two states is the average distance between molecules greater? **(b)** Explain the difference in densities at the two temperatures in terms of the relative kinetic energies of the molecules.

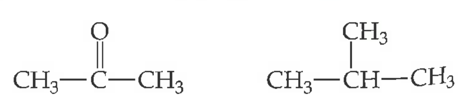
Intermolecular Forces

11.13 Which type of intermolecular attractive force operates between **(a)** all molecules, **(b)** polar molecules, **(c)** the hydrogen atom of a polar bond and a nearby small electronegative atom?

11.14 Based on what you have learned about intermolecular
CQ forces, would you say that matter is fundamentally attracted or repulsed by other matter?

11.15 Describe the intermolecular forces that must be over-
CQ come to convert each of the following from a liquid or solid to a gas: (a) I_2, (b) CH_3CH_2OH, (c) H_2Se.

11.16 What type of intermolecular force accounts for the fol-
CQ lowing differences in each case? **(a)** CH_3OH boils at 65 °C, CH_3SH boils at 6 °C. **(b)** Xe is liquid at atmospheric pressure and 120 K, whereas Ar is a gas. **(c)** Kr, atomic weight 84, boils at 120.9 K, whereas Cl_2, molecular weight about 71, boils at 238 K. **(d)** Acetone boils at 56 °C, whereas 2-methylpropane boils at −12 °C.



Acetone 2-Methylpropane

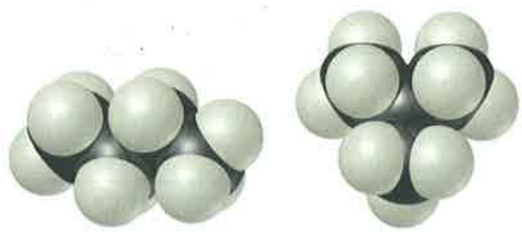
11.17 **(a)** What is meant by the term *polarizability*? **(b)** Which of the following atoms would you expect to be most polarizable: N, P, As, Sb? Explain. **(c)** Put the following molecules in order of increasing polarizability: $GeCl_4$, CH_4, $SiCl_4$, SiH_4, and $GeBr_4$. **(d)** Predict the order of boiling points of the substances in part (c).

11.18 True or false:
(a) The more polarizable the molecules, the stronger the dispersion forces between them.
(b) The boiling points of the noble gases decrease as you go down the column in the periodic table.
(c) In general, the smaller the molecule, the stronger the dispersion forces.
(d) All other factors being the same, dispersion forces between molecules increase with the number of electrons in the molecules.

11.19 Which member of the following pairs has the larger London dispersion forces: **(a)** H_2O or H_2S, **(b)** CO_2 or CO, **(c)** SiH_4 or GeH_4?

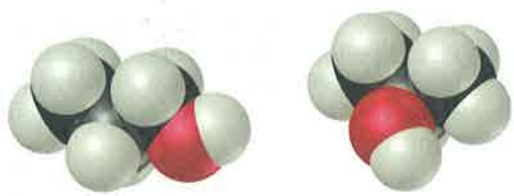
11.20 Which member of the following pairs has the stronger intermolecular dispersion forces: **(a)** Br_2 or O_2, **(b)** $CH_3CH_2CH_2CH_2SH$ or $CH_3CH_2CH_2CH_2CH_2SH$, **(c)** $CH_3CH_2CH_2Cl$ or $(CH_3)_2CHCl$?

11.21 CQ Butane and 2-methylpropane, whose space-filling models are shown, are both nonpolar and have the same molecular formula, yet butane has the higher boiling point (−0.5 °C compared to −11.7 °C). Explain.



(a) Butane (b) 2-Methylpropane

11.22 CQ Propyl alcohol ($CH_3CH_2CH_2OH$) and isopropyl alcohol [$(CH_3)_2CHOH$], whose space-filling models are shown, have boiling points of 97.2 °C and 82.5 °C, respectively. Explain why the boiling point of propyl alcohol is higher, even though both have the molecular formula of C_3H_8O.



(a) Propyl alcohol (b) Isopropyl alcohol

11.23 **(a)** What atoms must a molecule contain to participate in hydrogen bonding with other molecules of the same kind? **(b)** Which of the following molecules can form hydrogen bonds with other molecules of the same kind: CH_3F, CH_3NH_2, CH_3OH, CH_3Br?

11.24 CQ Rationalize the difference in boiling points between the members of the following pairs of substances: **(a)** HF (20 °C) and HCl (−85 °C), **(b)** $CHCl_3$ (61 °C) and $CHBr_3$ (150 °C), **(c)** Br_2 (59 °C) and ICl (97 °C).

11.25 Ethylene glycol ($HOCH_2CH_2OH$), the major substance in antifreeze, has a normal boiling point of 198 °C. By comparison, ethyl alcohol (CH_3CH_2OH) boils at 78 °C at atmospheric pressure. Ethylene glycol dimethyl ether ($CH_3OCH_2CH_2OCH_3$) has a normal boiling point of 83 °C, and ethyl methyl ether ($CH_3CH_2OCH_3$) has a normal boiling point of 11 °C. **(a)** Explain why replacement of a hydrogen on the oxygen by CH_3 generally results in a lower boiling point. **(b)** What are the major factors responsible for the difference in boiling points of the two ethers?

11.26 Identify the types of intermolecular forces present in each of the following substances, and select the substance in each pair that has the higher boiling point: **(a)** C_6H_{14} or C_8H_{18}, **(b)** C_3H_8 or CH_3OCH_3, **(c)** HOOH or HSSH, **(d)** NH_2NH_2 or CH_3CH_3.

11.27 CQ Look up and compare the normal boiling points and normal melting points of H_2O and H_2S. **(a)** Based on these physical properties, which substance has stronger intermolecular forces? What kind of intermolecular forces exist for each molecule? **(b)** Predict whether solid H_2S is more or less dense than liquid H_2S. How does this compare to H_2O? Explain. **(c)** Water has an unusually high specific heat. Is this related to its intermolecular forces? Explain.

11.28 CQ The following quote about ammonia (NH_3) is from a textbook of inorganic chemistry: "It is estimated that 26% of the hydrogen bonding in NH_3 breaks down on melting, 7% on warming from the melting to the boiling point, and the final 67% on transfer to the gas phase at the boiling point." From the standpoint of the kinetic energy of the molecules, explain **(a)** why there is a decrease of hydrogen-bonding energy on melting and **(b)** why most of the loss in hydrogen bonding occurs in the transition from the liquid to the vapor state.

Viscosity and Surface Tension

11.29 CQ **(a)** Explain why surface tension and viscosity decrease with increasing temperature. **(b)** Why do substances with high surface tensions also tend to have high viscosities?

11.30 CQ **(a)** Distinguish between adhesive forces and cohesive forces. **(b)** What adhesive and cohesive forces are involved when a paper towel absorbs water? **(c)** Explain the cause for the U-shaped meniscus formed when water is in a glass tube.

11.31 CQ Explain the following observations: **(a)** The surface tension of $CHBr_3$ is greater than that of $CHCl_3$. **(b)** As temperature increases, oil flows faster through a narrow tube. **(c)** Raindrops that collect on a waxed automobile hood take on a nearly spherical shape. **(d)** Oil droplets that collect on a waxed automobile hood take on a flat shape.

11.32 CQ Hydrazine (H_2NNH_2), hydrogen peroxide (HOOH), and water (H_2O) all have exceptionally high surface tensions compared with other substances of comparable molecular weights. **(a)** Draw the Lewis structures for these three compounds. **(b)** What structural property do these substances have in common, and how might that account for the high surface tensions?

Phase Changes

11.33 Name the phase transition in each of the following situations, and indicate whether it is exothermic or endothermic: **(a)** When ice is heated, it turns to water. **(b)** Wet clothes dry on a warm summer day. **(c)** Frost appears on a window on a cold winter day. **(d)** Droplets of water appear on a cold glass of beer.

11.34 Name the phase transition in each of the following situations, and indicate whether it is exothermic or endothermic: **(a)** Bromine vapor turns to bromine liquid as it is cooled. **(b)** Crystals of iodine disappear from an evaporating dish as they stand in a fume hood. **(c)** Rubbing alcohol in an open container slowly disappears. **(d)** Molten lava from a volcano turns into solid rock.

11.35 CQ Explain why the heat of fusion of any substance is generally lower than its heat of vaporization.

11.36 CQ Ethyl chloride (C_2H_5Cl) boils at 12 °C. When liquid C_2H_5Cl under pressure is sprayed on a room-temperature (25 °C) surface in air, the surface is cooled considerably. **(a)** What does this observation tell us about the specific heat of $C_2H_5Cl(g)$ as compared with $C_2H_5Cl(l)$? **(b)** Assume that the heat lost by the surface is gained by ethyl chloride. What enthalpies must you consider if you were to calculate the final temperature of the surface?

11.37 For many years drinking water has been cooled in hot climates by evaporating it from the surfaces of canvas bags or porous clay pots. How many grams of water can be cooled from 35 °C to 20 °C by the evaporation of 60 g of water? (The heat of vaporization of water in this temperature range is 2.4 kJ/g. The specific heat of water is 4.18 J/g-K.)

11.38 Compounds like CCl_2F_2 are known as chlorofluorocarbons, or CFCs. These compounds were once widely used as refrigerants but are now being replaced by compounds that are believed to be less harmful to the environment. The heat of vaporization of CCl_2F_2 is 289 J/g. What mass of this substance must evaporate to freeze 200 g of water initially at 15 °C? (The heat of fusion of water is 334 J/g; the specific heat of water is 4.18 J/g-K.)

11.39 Ethanol (C_2H_5OH) melts at −114 °C and boils at 78 °C. Its density is 0.789 g/mL. The enthalpy of fusion of ethanol is 5.02 kJ/mol, and its enthalpy of vaporization is 38.56 kJ/mol. The specific heats of solid and liquid ethanol are 0.97 J/g-K and 2.3 J/g-K, respectively. **(a)** How much heat is required to convert 25.0 g of ethanol at 25 °C to the vapor phase at 78 °C? **(b)** How much heat is required to convert 5.00 L of ethanol at −140 °C to the vapor phase at 78 °C?

11.40 The fluorocarbon compound $C_2Cl_3F_3$ has a normal boiling point of 47.6 °C. The specific heats of $C_2Cl_3F_3(l)$ and $C_2Cl_3F_3(g)$ are 0.91 J/g-K and 0.67 J/g-K, respectively. The heat of vaporization for the compound is 27.49 kJ/mol. Calculate the heat required to convert 50.0 g of $C_2Cl_3F_3$ from a liquid at 10.00 °C to a gas at 85.00 °C.

11.41 CQ **(a)** What is the significance of the critical pressure of a substance? **(b)** What happens to the critical temperature of a series of compounds as the force of attraction between molecules increases? **(c)** Which of the substances listed in Table 11.5 can be liquefied at the temperature of liquid nitrogen (−196 °C)?

11.42 CQ The critical temperatures (K) and pressures (atm) of a series of halogenated methanes are as follows:

Compound	CCl_3F	CCl_2F_2	$CClF_3$	CF_4
Critical Temperature	471	385	302	227
Critical Pressure	43.5	40.6	38.2	37.0

(a) List the intermolecular forces that occur for each compound. **(b)** Predict the order of increasing intermolecular attraction, from least to most, for this series of compounds. **(c)** Predict the critical temperature and pressure for CCl_4 based on the trends in this table. Look up the experimentally determined critical temperatures and pressures for CCl_4, using a source such as the *CRC Handbook of Chemistry and Physics*, and suggest a reason for any discrepancies.

Vapor Pressure and Boiling Point

11.43 CQ Explain how each of the following affects the vapor pressure of a liquid: **(a)** volume of the liquid, **(b)** surface area, **(c)** intermolecular attractive forces, **(d)** temperature, **(e)** density of the liquid.

11.44 CQ A liquid that has an equilibrium vapor pressure of 130 torr at 25 °C is placed into a 1-L vessel like that shown in Figure 11.22. What is the pressure difference shown on the manometer, and what is the composition of the gas in the vessel, under each of the following conditions: **(a)** Two hundred mL of the liquid is introduced into the vessel and frozen at the bottom. The vessel is evacuated and sealed, and the liquid is allowed to warm to 25 °C. **(b)** Two hundred milliliters of the liquid is added to the vessel at 25 °C under atmospheric pressure, and after a few minutes the vessel is closed off. **(c)** A few mL of the liquid is introduced into the vessel at 25 °C while it has a pressure of 1 atm of air in it, without allowing any of the air to escape. After a few minutes a few drops of liquid remain in the vessel.

11.45 **(a)** Place the following substances in order of increasing volatility: CH_4, CBr_4, CH_2Cl_2, CH_3Cl, $CHBr_3$, and CH_2Br_2. Explain. **(b)** How do the boiling points vary through this series?

11.46 True or false:

(a) CBr_4 is more volatile than CCl_4.
(b) CBr_4 has a higher boiling point than CCl_4.
(c) CBr_4 has weaker intermolecular forces than CCl_4.
(d) CBr_4 has a higher vapor pressure at the same temperature than CCl_4.

11.47 **(a)** Two pans of water are on different burners of a stove.
CQ One pan of water is boiling vigorously, while the other is boiling gently. What can be said about the temperature of the water in the two pans? **(b)** A large container of water and a small one are at the same temperature. What can be said about the relative vapor pressures of the water in the two containers?

11.48 Explain the following observations: **(a)** Water evapo-
CQ rates more quickly on a hot, dry day than on a hot, humid day. **(b)** It takes longer to boil water for tea at high altitudes than at lower altitudes.

11.49 Using the vapor-pressure curves in Figure 11.24, **(a)** estimate the boiling point of ethanol at an external pressure of 200 torr; **(b)** estimate the external pressure at which ethanol will boil at 60 °C; **(c)** estimate the boiling point of diethyl ether at 400 torr; **(d)** estimate the external pressure at which diethyl ether will boil at 40 °C.

11.50 Appendix B lists the vapor pressure of water at various external pressures.

(a) Plot the data in Appendix B, vapor pressure (torr) vs. temperature (°C). From your plot, estimate the vapor pressure of water at body temperature, 37 °C.

(b) Explain the significance of the data point at 760.0 torr, 100 °C.

(c) A city at an altitude of 5000 ft above sea level has a barometric pressure of 633 torr. To what temperature would you have to heat water to boil it in this city?

(d) A city at an altitude of 500 ft below sea level would have a barometric pressure of 774 torr. To what temperature would you have to heat water to boil it in this city?

(e) For the two cities in parts (c) and (d), compare the average kinetic energies of the water molecules at their boiling points. Are the kinetic energies the same or different? Explain.

Phase Diagrams

11.51 **(a)** What is the significance of the critical point in a
CQ phase diagram? **(b)** Why does the line that separates the gas and liquid phases end at the critical point?

11.52 **(a)** What is the significance of the triple point in a phase diagram? **(b)** Could you measure the triple point of water by measuring the temperature in a vessel in which water vapor, liquid water, and ice are in equilibrium under one atmosphere of air? Explain.

11.53 Refer to Figure 11.27(a), and describe all the phase changes that would occur in each of the following cases: **(a)** Water vapor originally at 0.005 atm and −0.5 °C is slowly compressed at constant temperature until the final pressure is 20 atm. **(b)** Water originally at 100.0 °C and 0.50 atm is cooled at constant pressure until the temperature is −10 °C.

11.54 Refer to Figure 11.27(b), and describe the phase changes (and the temperatures at which they occur) when CO_2 is heated from −80 °C to −20 °C at **(a)** a constant pressure of 3 atm, **(b)** a constant pressure of 6 atm.

11.55 Sketch a generic phase diagram for a substance that has a more dense solid phase than a liquid phase. Label all regions, lines, and points.

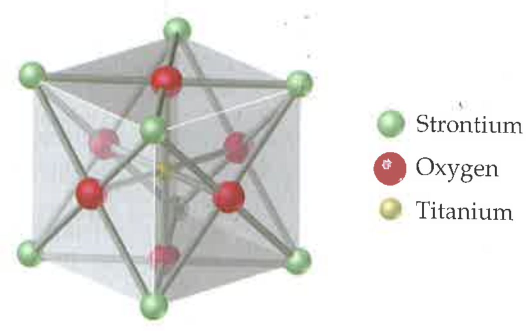
11.56 The normal melting and boiling points of O_2 are −218 °C and −183 °C respectively. Its triple point is at −219 °C and 1.14 torr, and its critical point is at −119 °C and 49.8 atm. **(a)** Sketch the phase diagram for O_2, showing the four points given and indicating the area in which each phase is stable. **(b)** Will $O_2(s)$ float on $O_2(l)$? Explain. **(c)** As it is heated, will solid O_2 sublime or melt under a pressure of 1 atm?

Structures of Solids

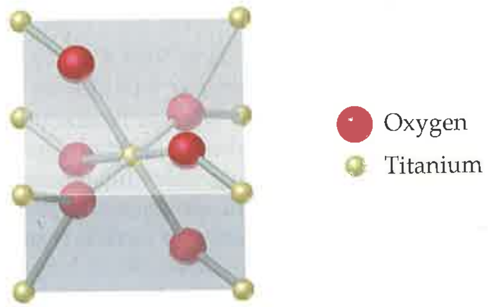
11.57 **(a)** Draw a picture that represents a crystalline solid at
CQ the atomic level. **(b)** Now draw a picture that represents an amorphous solid at the atomic level.

11.58 Amorphous silica has a density of about 2.2 g/cm^3,
CQ whereas the density of crystalline quartz is 2.65 g/cm^3. Account for this difference in densities.

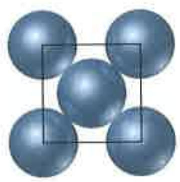
11.59 Tausonite, a mineral composed of Sr, O, and Ti, has the cubic unit cell shown in the drawing. **(a)** What is the chemical formula of this mineral? **(b)** It is easy to see that Ti is coordinated by six oxygen atoms, because the Ti atom is located at the center of the unit cell. To see the full coordination environment of the other ions, we have to consider neighboring unit cells. How many oxygens are coordinated to strontium?



11.60 Rutile is a mineral composed of Ti and O. Its unit cell, shown in the drawing, contains Ti atoms at each corner and a Ti atom at the center of the cell. Four O atoms are on the opposite faces of the cell, and two are entirely within the cell. **(a)** What is the chemical formula of this mineral? **(b)** What is the nature of the bonding that holds the solid together? **(c)** What is the coordination number of each atom?



11.61 Iridium crystallizes in a face-centered cubic unit cell that has an edge length of 3.833 Å. The atom in the center of the face is in contact with the corner atoms, as shown in the drawing. **(a)** Calculate the atomic radius of an iridium atom. **(b)** Calculate the density of iridium metal.



11.62 Aluminum metal crystallizes in a cubic close-packed structure (face-centered cubic cell, Figure 11.34). **(a)** How many aluminum atoms are in a unit cell? **(b)** What is the coordination number of each aluminum atom? **(c)** Assume that the aluminum atoms can be represented as spheres, as shown in the drawing for Exercise 11.61. If each Al atom has a radius of 1.43 Å, what is the length of a side of the unit cell? **(d)** Calculate the density of aluminum metal.

11.63 An element crystallizes in a body-centered cubic lattice. The edge of the unit cell is 2.86 Å, and the density of the crystal is 7.92 g/cm^3. Calculate the atomic weight of the element.

11.64 KCl has the same structure as NaCl. The length of the unit cell is 628 pm. The density of KCl is 1.984 g/cm^3, and its formula mass is 74.55 amu. Using this information, calculate Avogadro's number.

11.65 NaF has the same structure as NaCl. **(a)** Use ionic radii from Chapter 7 to estimate the length of the unit cell edge for NaF. **(b)** Use the unit cell size calculated in part (a) to estimate the density of NaF.

11.66 What is the coordination number of **(a)** Na^+ in the NaCl structure, Figure 11.35; **(b)** Zn^{2+} in the ZnS unit cell, Figure 11.42(b); **(c)** Ca^{2+} in the CaF_2 unit cell, Figure 11.42(c)?

11.67 Clausthalite is a mineral composed of lead selenide (PbSe). The mineral adopts a NaCl-type structure. The density of PbSe at 25 °C is 8.27 g/cm^3. Calculate the length of an edge of the PbSe unit cell.

11.68 A particular form of cinnabar (HgS) adopts the zinc blende structure, Figure 11.42(b). The length of the unit cell side is 5.852 Å. **(a)** Calculate the density of HgS in this form. **(b)** The mineral tiemmanite (HgSe) also forms a solid phase with the zinc blende structure. The length of the unit cell side in this mineral is 6.085 Å. What accounts for the larger unit cell length in tiemmanite? **(c)** Which of the two substances has the higher density? How do you account for the difference in densities?

Bonding in Solids

11.69 CQ It is possible to change the temperature and pressure of a vessel containing argon gas so that the gas solidifies. **(a)** What intermolecular forces exist between argon atoms? **(b)** Is the solid argon a "covalent network solid"? Why or why not?

11.70 CQ **(a)** Silicon is the fundamental component of integrated circuits. Si has the same structure as diamond. Is Si a molecular, metallic, ionic, or covalent-network solid? **(b)** Silica is SiO_2. What type of solid would you expect silica to form?

11.71 What kinds of attractive forces exist between particles in **(a)** molecular crystals, **(b)** covalent-network crystals, **(c)** ionic crystals, **(d)** metallic crystals?

11.72 Indicate the type of crystal (molecular, metallic, covalent-network, or ionic) each of the following would form upon solidification: **(a)** $CaCO_3$, **(b)** Pt, **(c)** ZrO_2 (melting point, 2677 °C), **(d)** table sugar ($C_{12}H_{22}O_{11}$), **(e)** benzene, **(f)** I_2.

11.73 CQ Covalent bonding occurs in both molecular and covalent-network solids. Why do these two kinds of solids differ so greatly in their hardness and melting points?

11.74 Which type (or types) of crystalline solid is characterized by each of the following: **(a)** high mobility of electrons throughout the solid; **(b)** softness, relatively low melting point; **(c)** high melting point and poor electrical conductivity; **(d)** network of covalent bonds; **(e)** charged particles throughout the solid.

11.75 A white substance melts with some decomposition at 730 °C. As a solid, it does not conduct electricity, but it dissolves in water to form a conducting solution. Which type of solid (Table 11.7) might the substance be?

11.76 You are given a white substance that sublimes at 3000 °C; the solid is a nonconductor of electricity and is insoluble in water. Which type of solid (Table 11.7) might this substance be?

11.77 For each of the following pairs of substances, predict which will have the higher melting point and indicate why: **(a)** Ar, Xe; **(b)** SiO_2, CO_2; **(c)** KBr, Br_2; **(d)** C_6Cl_6, C_6H_6.

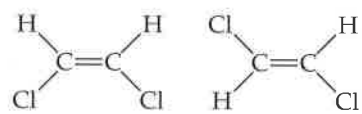
11.78 For each of the following pairs of substances, predict which will have the higher melting point, and indicate why: **(a)** HF, HCl; **(b)** C (graphite), CH_4; **(c)** KCl, Cl_2; **(d)** LiF, MgF_2.

ADDITIONAL EXERCISES

11.79 CQ As the intermolecular attractive forces between molecules increase in magnitude, do you expect each of the following to increase or decrease in magnitude? **(a)** vapor pressure, **(b)** heat of vaporization, **(c)** boiling point, **(d)** freezing point, **(e)** viscosity, **(f)** surface tension, **(g)** critical temperature.

11.80 Suppose you have two colorless molecular liquids, one boiling at −84 °C, the other at 34 °C, and both at atmospheric pressure. Which of the following statements is correct? For those that are not correct, modify the statement so that it is correct. **(a)** The higher-boiling liquid has greater total intermolecular forces than the other. **(b)** The lower boiling liquid must consist of nonpolar molecules. **(c)** The lower-boiling liquid has a lower molecular weight than the higher-boiling liquid. **(d)** The two liquids have identical vapor pressures at their normal boiling points. **(e)** At 34 °C both liquids have vapor pressures of 760 mm Hg.

11.81 Two isomers of the planar compound 1,2-dichloroethylene are shown here, along with their melting and boiling points.



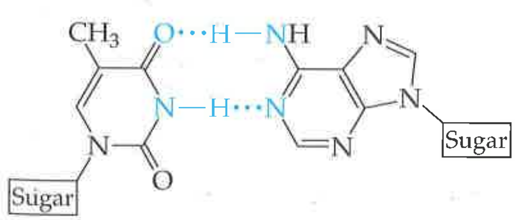
	cis isomer	trans isomer
Melting point (°C)	−80.5	−49.8
Boiling point (°C)	60.3	47.5

(a) Which of the two isomers will have the stronger dipole–dipole forces? Is this prediction borne out by the data presented here? **(b)** Based on the data presented here, which isomer packs more efficiently in the solid phase?

11.82 In dichloromethane, CH_2Cl_2 ($\mu = 1.60$ D), the dispersion force contribution to the intermolecular attractive forces is about five times larger than the dipole–dipole contribution. Would you expect the relative importance of the two kinds of intermolecular attractive forces to differ **(a)** in dibromomethane ($\mu = 1.43$ D), **(b)** in difluoromethane ($\mu = 1.93$ D)? Explain.

11.83 When an atom or group of atoms is substituted for an H atom in benzene (C_6H_6), the boiling point changes. Explain the order of the following boiling points: C_6H_6 (80 °C), C_6H_5Cl (132 °C), C_6H_5Br (156 °C), C_6H_5OH (182 °C).

11.84 The DNA double helix (Figure 25.40) at the atomic level looks like a twisted ladder, where the "rungs" of the ladder consist of molecules that are hydrogen-bonded together. Sugar and phosphate groups make up the sides of the ladder. Shown are the structures of the adenine-thymine (AT) "base pair" and the guanine-cytosine (GC) base pair:



Thymine Adenine

Cytosine Guanine

You can see that AT base pairs are held together by two hydrogen bonds, and the GC base pairs are held together by three hydrogen bonds. Which base pair is more stable to heating?

11.85 Ethylene glycol [$CH_2(OH)CH_2(OH)$] is the major component of antifreeze. It is a slightly viscous liquid, not very volatile at room temperature, with a boiling point of 198 °C. Pentane (C_5H_{12}), which has about the same molecular weight, is a nonviscous liquid that is highly volatile at room temperature and whose boiling point is 36.1 °C. Explain the differences in the physical properties of the two substances.

11.86 CQ Using the following list of normal boiling points for a series of hydrocarbons, estimate the normal boiling point for octane, C_8H_{18}: propane (C_3H_8, −42.1 °C), butane (C_4H_{10}, −0.5 °C), pentane (C_5H_{12}, 36.1 °C), hexane (C_6H_{14}, 68.7 °C), heptane (C_7H_{16}, 98.4 °C). Explain the trend in the boiling points.

[11.87] CQ Notice in Figure 11.21 that there is a pressure-reduction valve in the line just before the supercritical CO_2 and dissolved caffeine enter the separator. Suggest an explanation for the function of this valve in the overall process.

11.88 **(a)** When you exercise vigorously, you sweat. How does this help your body cool? **(b)** A flask of water is connected to a vacuum pump. A few moments after the pump is turned on, the water begins to boil. After a few minutes, the water begins to freeze. Explain why these processes occur.

[11.89] The following table gives the vapor pressure of hexafluorobenzene (C_6F_6) as a function of temperature:

Temperature (K)	Vapor Pressure (torr)
280.0	32.42
300.0	92.47
320.0	225.1
330.0	334.4
340.0	482.9

(a) By plotting these data in a suitable fashion, determine whether the Clausius–Clapeyron equation is obeyed. If it is obeyed, use your plot to determine ΔH_{vap} for C_6F_6. **(b)** Use these data to determine the boiling point of the compound.

[11.90] Suppose the vapor pressure of a substance is measured at two different temperatures. **(a)** By using the Clausius–Clapeyron equation, Equation 11.1, derive the following relationship between the vapor pressures, P_1 and P_2, and the absolute temperatures at which they were measured, T_1 and T_2:

$$\ln \frac{P_1}{P_2} = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

(b) Gasoline is a mixture of hydrocarbons, a major component of which is octane, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$. Octane has a vapor pressure of 13.95 torr at 25 °C and a vapor pressure of 144.78 torr at 75 °C. Use these data and the equation in part (a) to calculate the heat of vaporization of octane. **(c)** By using the equation in part (a) and the data given in part (b), calculate the normal boiling point of octane. Compare your answer to the one you obtained from Exercise 11.86. **(d)** Calculate the vapor pressure of octane at −30 °C.

[11.91] CQ The following data present the temperatures at which certain vapor pressures are achieved for dichloromethane (CH_2Cl_2) and methyl iodide (CH_3I):

Vapor Pressure (torr):	10.0	40.0	100.0	400.0
T for CH_2Cl_2 (°C):	−43.3	−22.3	−6.3	24.1
T for CH_3I (°C):	−45.8	−24.2	−7.0	25.3

(a) Which of the two substances is expected to have the greater dipole–dipole forces? Which is expected to have the greater London dispersion forces? Based on your answers, explain why it is difficult to predict which compound would be more volatile. **(b)** Which compound would you expect to have the higher boiling point? Check your answer in a reference book such as the *CRC Handbook of Chemistry and Physics*. **(c)** The order of volatility of these two substances changes as the temperature is increased. What quantity must be different for the two substances in order for this phenomenon to occur? **(d)** Substantiate your answer for part (c) by drawing an appropriate graph.

11.92 The elements xenon and gold both have solid-state structures with face-centered cubic unit cells, yet Xe melts at −112 °C and gold melts at 1064 °C. Account for these greatly different melting points.

11.93 In Chapter 7 we saw that Li reacts with oxygen to form lithium oxide, Li_2O, while the larger alkali metals react with oxygen to form peroxides (such as Na_2O_2, K_2O_2, etc.). The origin of this curious pattern of reactivity is related to the relative sizes of the cation and anion and the overall stoichiometry. Li_2O crystallizes with a structure called the antifluorite structure. This structure is identical to the fluorite structure shown in Figure 11.42(c), but the cations and anions have been switched. **(a)** In Li_2O, what are the coordination numbers for each ion? **(b)** As the cation radius increases, would you expect the coordination number to increase or decrease (assuming the anion size does not change)? **(c)** Why do you think the antifluorite structure becomes unstable for A_2O (A = Li, Na, K, Rb, Cs) compounds of the heavier alkali metal ions?

11.94 Gold crystallizes in a face-centered cubic unit cell that has an edge length of 4.078 Å. The atom in the center of the face is in contact with the corner atoms, as shown in the drawing for Exercise 11.61. **(a)** Calculate the apparent radius of a gold atom in this structure. **(b)** Calculate the density of gold metal.

11.95 **(a)** Explain why X-rays can be used to measure atomic distances in crystals but visible light cannot. **(b)** Why can't $CaCl_2$ have the same crystal structure as NaCl?

11.96 In their study of X-ray diffraction, William and Lawrence Bragg determined that the relationship among the wavelength of the radiation (λ), the angle at which the radiation is diffracted (θ), and the distance between the layers of atoms in the crystal that cause the diffraction (d) is given by $n\lambda = 2d \sin\theta$. **(a)** X-rays from a copper X-ray tube that have a wavelength of 1.54 Å are diffracted at an angle of 14.22 degrees by crystalline silicon. Using the Bragg equation, calculate the interplanar spacing in the crystal, assuming $n = 1$ (first-order diffraction). **(b)** Repeat the calculation of part (a) but for the $n = 2$ case (second-order diffraction).

[11.97] CQ **(a)** The density of diamond [Figure 11.41(a)] is 3.5 g/cm^3, and that of graphite [Figure 11.41(b)] is 2.3 g/cm^3. Based on the structure of buckminsterfullerene (Figure 11.43), what would you expect its density to be relative to these other forms of carbon? **(b)** X-ray diffraction studies of buckminsterfullerene show that it has a face-centered cubic lattice of C_{60} molecules. The length of a side of the unit cell is 14.2 Å. Calculate the density of buckminsterfullerene.

INTEGRATIVE EXERCISES

11.98 Spinel is a mineral that contains 37.9% Al, 17.1% Mg, and 45.0% O, by mass, and has a density of 3.57 g/cm^3. The unit cell is cubic, with an edge length of 809 pm. How many atoms of each type are in the unit cell?

11.99 CQ **(a)** At the molecular level, what factor is responsible for the steady increase in viscosity with increasing molecular weight in the hydrocarbon series shown in Table 11.4? **(b)** Although the viscosity varies over a factor of more than two in the series from hexane to nonane, the surface tension at 25 °C increases by only about 20% in the same series. How do you account for this? **(c)** n-Octyl alcohol, $CH_3(CH_2)_7OH$, has a viscosity of 1.01×10^{-2} kg m^{-1}s^{-1}, much higher than nonane, which has about the same molecular weight. What accounts for this difference? How does your answer relate to the difference in normal boiling points for these two substances?

11.100 Acetone, $(CH_3)_2CO$, is widely used as an industrial solvent. **(a)** Draw the Lewis structure for the acetone molecule, and predict the geometry around each carbon atom. **(b)** Is the acetone molecule polar or nonpolar? **(c)** What kinds of intermolecular attractive forces exist between acetone molecules? **(d)** 1-Propanol, $CH_3CH_2CH_2OH$, has a molecular weight that is very similar to that of acetone, yet acetone boils at 56.5 °C and 1-propanol boils at 97.2 °C. Explain the difference.

11.101 CQ The table shown here lists the molar heats of vaporization for several organic compounds. Use specific examples from this list to illustrate how the heat of vaporization varies with **(a)** molar mass, **(b)** molecular shape, **(c)** molecular polarity, **(d)** hydrogen-bonding interactions. Explain these comparisons in terms of the nature of the intermolecular forces at work. (You may find it helpful to draw out the structural formula for each compound.)

Compound	**Heat of Vaporization (kJ/mol)**
$CH_3CH_2CH_3$	19.0
$CH_3CH_2CH_2CH_2CH_3$	27.6
$CH_3CHBrCH_3$	31.8
CH_3COCH_3	32.0
$CH_3CH_2CH_2Br$	33.6
$CH_3CH_2CH_2OH$	47.3

11.102 CQ Liquid butane, C_4H_{10}, is stored in cylinders, to be used as a fuel. The normal boiling point of butane is listed as −0.5 °C. **(a)** Suppose the tank is standing in the sun and reaches a temperature of 35 °C. Would you expect the pressure in the tank to be greater or less than atmospheric pressure? How does the pressure within the tank depend on how much liquid butane is in it? **(b)** Suppose the valve to the tank is opened and a few liters of butane are allowed to escape rapidly. What do you expect would happen to the temperature of the remaining liquid butane in the tank? Explain. **(c)** How much heat must be added to vaporize 250 g of butane if its heat of vaporization is 21.3 kJ/mol? What volume does this much butane occupy at 755 torr and 35 °C?

[11.103] Using information in Appendices B and C, calculate the minimum number of grams of propane, $C_3H_8(g)$, that must be combusted to provide the energy necessary to convert 5.50 kg of ice at −20 °C to liquid water at 75 °C.

11.104 CQ In a certain type of nuclear reactor, liquid sodium metal is employed as a circulating coolant in a closed system, protected from contact with air or water. Much like the coolant that circulates in an automobile engine, the liquid sodium carries heat from the hot reactor core to heat exchangers. **(a)** What properties of the liquid sodium are of special importance in this application? **(b)** The viscosity of liquid sodium varies with temperature as follows:

Temperature (°C)	**Viscosity ($kg\ m^{-1}\ s^{-1}$)**
100	7.05×10^{-4}
200	4.50×10^{-4}
300	3.45×10^{-4}
600	2.10×10^{-4}

What forces within the liquid sodium are likely to be the major contributors to the viscosity? Why does viscosity decrease with increasing temperature?

11.105 The vapor pressure of a volatile liquid can be determined by slowly bubbling a known volume of gas through it at a known temperature and pressure. In an experiment, 5.00 L of N_2 gas is passed through 7.2146 g of liquid benzene, C_6H_6, at 26.0 °C. The liquid remaining after the experiment weighs 5.1493 g. Assuming that the gas becomes saturated with benzene vapor and that the total gas volume and temperature remain constant, what is the vapor pressure of the benzene in torr?

11.106 The relative humidity of air equals the ratio of the partial pressure of water in the air to the equilibrium vapor pressure of water at the same temperature, times 100%. If the relative humidity of the air is 58% and its temperature is 68 °F, how many molecules of water are present in a room measuring 12 ft × 10 ft × 8 ft?

11.107 Use a reference source such as the *CRC Handbook of Chemistry and Physics* to compare the melting and boiling points of the following pairs of inorganic substances: **(a)** W and WF_6, **(b)** SO_2 and SF_4, **(c)** SiO_2 and $SiCl_4$. Account for the major differences observed in terms of likely structures and bonding.