

# CHAPTER 12 INTERMOLECULAR FORCES: LIQUIDS, SOLIDS, AND PHASE CHANGES

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## END-OF-CHAPTER PROBLEMS

- 12.1 The energy of attraction is a *potential* energy and denoted  $E_p$ . The energy of motion is *kinetic* energy and denoted  $E_k$ . The relative strength of  $E_p$  vs.  $E_k$  determines the phase of the substance. In the gas phase,  $E_p \ll E_k$  because gas particles experience little attraction for one another and the particles are moving very fast. In the solid phase,  $E_p \gg E_k$  because the particles are very close together and are only vibrating in place. Two properties that differ between a gas and a solid are the volume and density. The volume of a gas expands to fill the container it is in while the volume of a solid is constant no matter what container holds the solid. Density of a gas is much less than the density of a solid. The density of a gas also varies significantly with temperature and pressure changes. The density of a solid is only slightly altered by changes in temperature and pressure. Compressibility and ability to flow are other properties that differ between gases and solids.
- 12.2 a) Gases are more easily compressed than liquids because the distance between particles is much greater in a gas than in a liquid. Liquids have very little free space between particles and thus can be compressed (crowded together) only very slightly.  
b) Liquids have a greater ability to flow because the interparticle forces are weaker in the liquid phase than in the solid phase. The stronger interparticle forces in the solid phase fix the particles in place. Liquid particles have enough kinetic energy to move around.
- 12.3 a) **intermolecular**      b) **intermolecular**      c) **intermolecular**      d) **intramolecular**
- 12.4 a) Heat of fusion refers to the change between the solid and the liquid states and heat of vaporization refers to the change between liquid and gas states. In the change from solid to liquid, the kinetic energy of the molecules must increase only enough to partially offset the intermolecular attractions between molecules. In the change from liquid to gas, the kinetic energy of the molecules must increase enough to overcome the intermolecular forces. The energy to overcome the intermolecular forces for the molecules to move freely in the gaseous state is much greater than the amount of energy needed to allow the molecules to move more easily past each other but still stay very close together.  
b) The net force holding molecules together in the solid state is greater than that in the liquid state. Thus, to change solid molecules to gaseous molecules in sublimation requires more energy than to change liquid molecules to gaseous molecules in vaporization.  
c) At a given temperature and pressure, the magnitude of  $\Delta H_{\text{vap}}$  is the same as the magnitude of  $\Delta H_{\text{cond}}$ . The only difference is in the sign:  $\Delta H_{\text{vap}} = -\Delta H_{\text{cond}}$ .
- 12.5 a) **Condensation**      The water vapor in the air condenses to liquid when the temperature drops during the night.  
b) **Fusion** (melting)      Solid ice melts to liquid water.  
c) **Evaporation**      Liquid water on clothes evaporates to water vapor.
- 12.6 a) **deposition**      b) **sublimation**      c) **crystallization** (freezing)
- 12.7 The propane gas molecules slow down as the gas is compressed. Therefore, much of the **kinetic energy** lost by the propane molecules is released to the surroundings upon liquefaction.
- 12.8 **Sublimation and deposition**
- 12.9 The gaseous  $\text{PCl}_3$  molecules are moving faster and are farther apart than the liquid molecules. As they condense, the kinetic energy of the molecules is changed into potential energy stored in the dipole-dipole interactions between the molecules.

- 12.10 The two processes are the formation of solid from liquid and the formation of liquid from solid (at the macroscopic level). At the molecular level, the two processes are the removal of kinetic energy from the liquid molecules as they solidify and the overcoming of the dispersion forces between the molecules as they turn to liquid.
- 12.11 In closed containers, two processes, evaporation and condensation, occur simultaneously. Initially there are few molecules in the vapor phase, so more liquid molecules evaporate than gas molecules condense. Thus, the number of molecules in the gas phase increases, causing the vapor pressure of hexane to increase. Eventually, the number of molecules in the gas phase reaches a maximum where the number of liquid molecules evaporating equals the number of gas molecules condensing. In other words, the evaporation rate equals the condensation rate. At this point, there is no further change in the vapor pressure.
- 12.12 **Point 1 is depicted by C.** This is the equilibrium between melting and freezing.  
**Point 2 is depicted by A.** This is the equilibrium between vaporization and condensation.  
**Point 3 is depicted by D.** This is the equilibrium between sublimation and deposition.
- 12.13 **No**, at 1.1 atm, water boils at a temperature above 100°C, since it is more difficult for gas molecules to escape the liquid when the applied pressure is greater.
- 12.14 If the solid is more dense than the liquid, the solid-liquid line slopes to the right; if less dense, to the left.
- 12.15 Plan: The total heat required is the sum of three processes: warming the ice to 0.00°C, the melting point; melting the ice to liquid water; warming the water to 0.500°C. The equation  $q = c \times \text{mass} \times \Delta T$  is used to calculate the heat involved in changing the temperature of the ice and of the water; the heat of fusion is used to calculate the heat involved in the phase change of ice to water.  
Solution:  
 1) Warming the ice from -6.00°C to 0.00°C:  
 $q_1 = c \times \text{mass} \times \Delta T = (2.09 \text{ J/g}^\circ\text{C})(22.00 \text{ g})[0.0 - (-6.00)]^\circ\text{C} = 275.88 \text{ J}$   
 2) Phase change of ice at 0.00°C to water at 0.00°C:  
 $q_2 = n(\Delta H_{\text{fus}}^\circ) = (22.0 \text{ g})\left(\frac{1 \text{ mol}}{18.02 \text{ g}}\right)\left(\frac{6.02 \text{ kJ}}{\text{mol}}\right)\left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) = 7349.6115 \text{ J}$   
 3) Warming the liquid from 0.00°C to 0.500°C:  
 $q_3 = c \times \text{mass} \times \Delta T = (4.21 \text{ J/g}^\circ\text{C})(22.00 \text{ g})[0.500 - (0.0)]^\circ\text{C} = 46.31 \text{ J}$   
 The three heats are positive because each process takes heat from the surroundings (endothermic). The phase change requires much more energy than the two temperature change processes. The total heat is  
 $q_1 + q_2 + q_3 = (275.88 \text{ J} + 7349.6115 \text{ J} + 46.31 \text{ J}) = 7671.8015 = \mathbf{7.67 \times 10^3 \text{ J}}$
- 12.16  $0.333 \text{ mol} \times 46.07 \text{ g/mol} = 15.34131 \text{ g ethanol}$   
 Cooling vapor to boiling point:  
 $q_1 = c \times \text{mass} \times \Delta T = (1.43 \text{ J/g}^\circ\text{C})(15.34131 \text{ g})(78.5 - 300)^\circ\text{C} = -4859.28 \text{ J}$   
 Condensing vapor: (note  $\Delta H_{\text{cond}} = -\Delta H_{\text{vap}}$ )  
 $q_2 = n(\Delta H_{\text{cond}}^\circ) = (0.333 \text{ mol})(-38.6 \text{ kJ/mol})(10^3 \text{ J/kJ}) = -12,853.8 \text{ J}$   
 Cooling liquid to 25.0°C:  
 $q_3 = c \times \text{mass} \times \Delta T = (2.45 \text{ J/g}^\circ\text{C})(15.34131 \text{ g})(25.0 - 78.5)^\circ\text{C} = -2010.86 \text{ J}$   
 $q_{\text{total}} = q_1 + q_2 + q_3 = (-4859.28 \text{ J}) + (-12,853.8 \text{ J}) + (-2010.86 \text{ J}) = -19,723.94 = \mathbf{-1.97 \times 10^4 \text{ J}}$
- 12.17 Plan: The Clausius-Clapeyron equation gives the relationship between vapor pressure and temperature. We are given  $\Delta H_{\text{vap}}^\circ$ ,  $P_1$ ,  $T_1$ , and  $T_2$ ; these values are substituted into the equation to find the  $P_2$ , the vapor pressure.  
Solution:  
 $P_1 = 1.00 \text{ atm} \quad T_1 = 122^\circ\text{C} + 273 = 395 \text{ K}$   
 $P_2 = ? \quad T_2 = 113^\circ\text{C} + 273 = 386 \text{ K} \quad \Delta H_{\text{vap}}^\circ = 35.5 \text{ kJ/mol}$

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

$$\ln \frac{P_2}{1.00 \text{ atm}} = \frac{-35.5 \frac{\text{kJ}}{\text{mol}}}{8.314 \text{ J/mol}\cdot\text{K}} \left( \frac{1}{386 \text{ K}} - \frac{1}{395 \text{ K}} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -0.2520440$$

$$\frac{P_2}{1.00 \text{ atm}} = 0.7772105$$

$$P_2 = (0.7772105)(1.00 \text{ atm}) = 0.7772105 = \mathbf{0.777 \text{ atm}}$$

12.18 Plan: The Clausius-Clapeyron equation gives the relationship between vapor pressure and temperature. We are given  $P_1$ ,  $P_2$ ,  $T_1$ , and  $T_2$ ; these values are substituted into the equation to find  $\Delta H_{\text{vap}}^{\circ}$ . The pressure in torr must be converted to atm.

Solution:

$$P_1 = (621 \text{ torr}) \left( \frac{1 \text{ atm}}{760 \text{ torr}} \right) = 0.817105 \text{ atm} \quad T_1 = 85.2^{\circ}\text{C} + 273.2 = 358.4 \text{ K}$$

$$P_2 = 1 \text{ atm} \quad T_2 = 95.6^{\circ}\text{C} + 273.2 = 368.8 \text{ K} \quad \Delta H_{\text{vap}}^{\circ} = ?$$

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

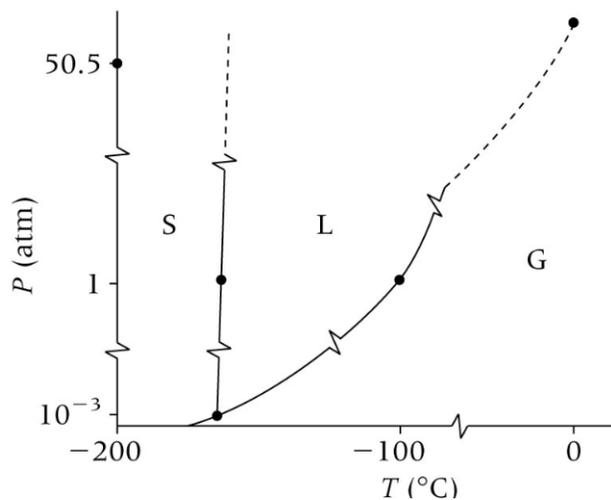
$$\ln \frac{1 \text{ atm}}{0.817105 \text{ atm}} = \frac{-\Delta H_{\text{vap}}^{\circ}}{8.314 \text{ J/mol}\cdot\text{K}} \left( \frac{1}{368.8 \text{ K}} - \frac{1}{358.4 \text{ K}} \right)$$

$$0.2019877 = -\Delta H_{\text{vap}}^{\circ} (-9.463775 \times 10^{-6}) \text{ J/mol}$$

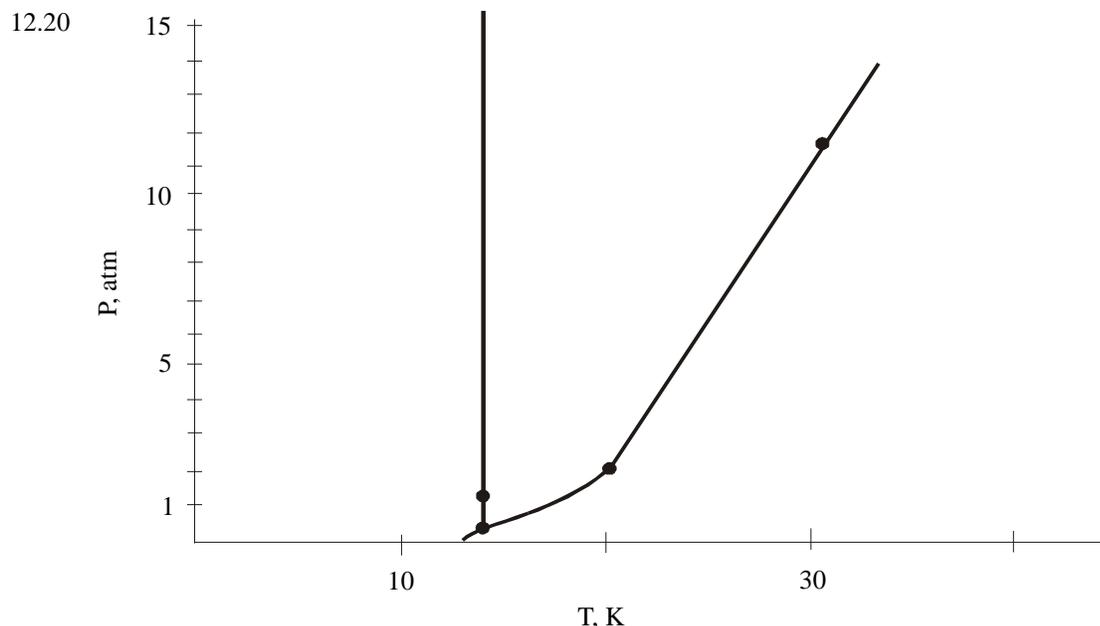
$$\Delta H_{\text{vap}}^{\circ} = 21,343.248 = \mathbf{2 \times 10^4 \text{ J/mol}}$$

(The significant figures in the answer are limited by the 1 atm in the problem.)

12.19



The pressure scale is distorted to represent the large range in pressures given in the problem, so the liquid-solid curve looks different from the one shown in the text. The important features of the graph include the distinction between the gas, liquid, and solid states, and the melting point  $T$ , which is located directly above the critical  $T$ . Solid ethylene is **more dense** than liquid ethylene since the solid-liquid line slopes to the right with increasing pressure.



Hydrogen does not sublime at 0.05 atm, since 0.05 atm is below the triple point pressure.

- 12.21 **Plan:** The Clausius-Clapeyron equation gives the relationship between vapor pressure and temperature. We are given  $\Delta H_{\text{vap}}^{\circ}$ ,  $P_1$ ,  $T_1$ , and  $T_2$ ; these values are substituted into the equation to find  $P_2$ . Convert the temperatures from  $^{\circ}\text{C}$  to K and  $\Delta H_{\text{vap}}^{\circ}$  from kJ/mol to J/mol to allow cancellation with the units in  $R$ .

**Solution:**

$$P_1 = 2.3 \text{ atm} \quad T_1 = 25.0^{\circ}\text{C} + 273 = 298 \text{ K}$$

$$P_2 = ? \quad T_2 = 135^{\circ}\text{C} + 273 = 408 \text{ K} \quad \Delta H_{\text{vap}}^{\circ} = 24.3 \text{ kJ/mol}$$

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

$$\ln \frac{P_2}{2.3 \text{ atm}} = \frac{-24.3 \frac{\text{kJ}}{\text{mol}}}{8.314 \text{ J/mol}\cdot\text{K}} \left( \frac{1}{408 \text{ K}} - \frac{1}{298 \text{ K}} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right)$$

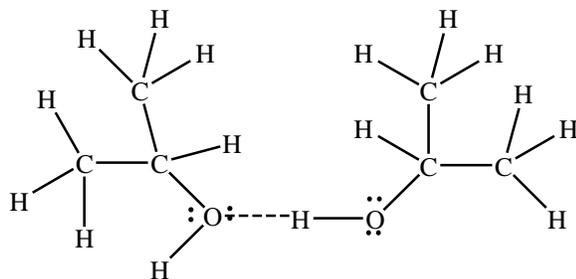
$$\ln \frac{P_2}{2.3 \text{ atm}} = 2.644311$$

$$\frac{P_2}{2.3 \text{ atm}} = 14.07374$$

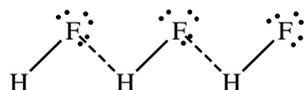
$$P_2 = (14.07374)(2.3 \text{ atm}) = 32.3696 = \mathbf{32 \text{ atm}}$$

- 12.22 a) At  $20^{\circ}\text{C}$  and  $40^{\circ}\text{C}$ , no liquid exists, only gas. At  $-40^{\circ}\text{C}$ , liquid exists. At  $-120^{\circ}\text{C}$ , no liquid exists, only solid.  
 b) **No**, at any pressure below the triple point pressure, the  $\text{CO}_2(s)$  will sublime.  
 c) **No**  
 d) **No**
- 12.23 Intermolecular forces involve interactions of lower (partial) charges at relatively larger distances than in covalent bonds.
- 12.24 Even though molecules are neutral, many of them are polar. These polar molecules will orient themselves so that their partial charges will result in dipole-dipole interactions. The partially positive pole of one molecule attracts the partially negative pole of another.

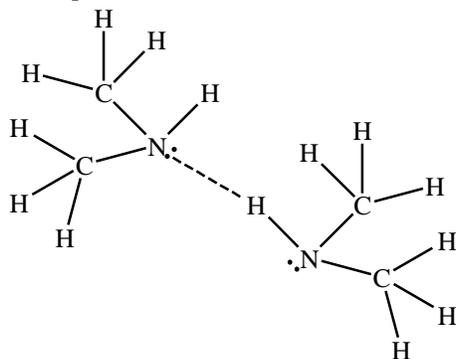
- 12.25 a) Scene A: dipole-dipole forces; Scene B: dipole-dipole forces; Scene C: ion-dipole forces; Scene D: hydrogen bonds  
b) dipole-dipole forces < hydrogen bonds < ion-dipole
- 12.26 To form hydrogen bonds, the atom bonded to hydrogen must have two characteristics: small size and high electronegativity (so that the atom has a very high electron density). With this high electron density, the attraction for a hydrogen on another molecule is very strong. Selenium is much larger than oxygen (atomic radius of 119 pm vs. 73 pm) and less electronegative than oxygen (2.4 for Se and 3.5 for O) resulting in an electron density on Se in H<sub>2</sub>Se that is too small to form hydrogen bonds.
- 12.27 All particles (atoms and molecules) exhibit dispersion forces, but these are the weakest of intermolecular forces. The dipole-dipole forces in polar molecules dominate the dispersion forces.
- 12.28 Polarity refers to a permanent imbalance in the distribution of electrons in the molecule. Polarizability refers to the ability of the electron distribution in a molecule to change temporarily. The polarity affects dipole-dipole interactions, while the polarizability affects dispersion forces.
- 12.29 If the electron distribution in one molecule is not symmetrical (permanent or temporary), that can induce a temporary dipole in an adjacent molecule by causing the electrons in that molecule to shift for some (often short) time.
- 12.30 Plan: Dispersion forces are the only forces between nonpolar substances; dipole-dipole forces exist between polar substances. Hydrogen bonds only occur in substances in which hydrogen is directly bonded to either oxygen, nitrogen, or fluorine.  
Solution:  
a) **Hydrogen bonding** will be the strongest force between methanol molecules since they contain O–H bonds. Dipole-dipole and dispersion forces also exist.  
b) **Dispersion forces** are the only forces between nonpolar carbon tetrachloride molecules and, thus, are the strongest forces.  
c) **Dispersion forces** are the only forces between nonpolar chlorine molecules and, thus, are the strongest forces.
- 12.31 a) **Hydrogen bonding**   b) **Dipole-dipole**   c) **Ionic bonds**
- 12.32 Plan: Dispersion forces are the only forces between nonpolar substances; dipole-dipole forces exist between polar substances. Hydrogen bonds only occur in substances in which hydrogen is directly bonded to either oxygen, nitrogen, or fluorine.  
Solution:  
a) **Dipole-dipole** interactions will be the strongest forces between methyl chloride molecules because the C–Cl bond has a dipole moment.  
b) **Dispersion** forces dominate because CH<sub>3</sub>CH<sub>3</sub> (ethane) is a symmetrical nonpolar molecule.  
c) **Hydrogen bonding** dominates because hydrogen is bonded to nitrogen, which is one of the three atoms (N, O, or F) that participate in hydrogen bonding.
- 12.33 a) **Dispersion**   b) **Dipole-dipole**   c) **Hydrogen bonding**
- 12.34 Plan: Hydrogen bonds are formed when a hydrogen atom is bonded to N, O, or F.  
Solution:  
a) The presence of an OH group leads to the formation of hydrogen bonds in **CH<sub>3</sub>CH(OH)CH<sub>3</sub>**. There are no hydrogen bonds in CH<sub>3</sub>SCH<sub>3</sub>.



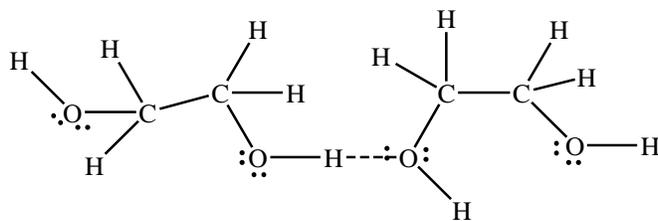
b) The presence of H attached to F in **HF** leads to the formation of hydrogen bonds. There are no hydrogen bonds in **HBr**.



12.35 a) The presence of H directly attached to the N in **(CH<sub>3</sub>)<sub>2</sub>NH** leads to hydrogen bonding. More than one arrangement is possible.



b) Each of the hydrogen atoms directly attached to oxygen atoms in **HOCH<sub>2</sub>CH<sub>2</sub>OH** leads to hydrogen bonding. More than one arrangement is possible. In **FCH<sub>2</sub>CH<sub>2</sub>F**, the H atoms are bonded to C so there is no hydrogen bonding.



12.36 Plan: Polarizability increases down a group and decreases from left to right because as atomic size increases, polarizability increases.

Solution:

a) **Iodide ion** has greater polarizability than the bromide ion because the iodide ion is larger. The electrons can be polarized over a larger volume in a larger atom or ion.

b) **Ethene (CH<sub>2</sub>=CH<sub>2</sub>)** has greater polarizability than ethane (CH<sub>3</sub>CH<sub>3</sub>) because the electrons involved in  $\pi$  bonds are more easily polarized than electrons involved in  $\sigma$  bonds.

c) **H<sub>2</sub>Se** has greater polarizability than water because the selenium atom is larger than the oxygen atom.

12.37 a) **Ca** b) **CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>** c) **CCl<sub>4</sub>**

In all cases, the larger molecule (i.e., the one with more electrons) has the higher polarizability.

12.38 Plan: Weaker attractive forces result in a higher vapor pressure because the molecules have a smaller energy barrier in order to escape the liquid and go into the gas phase. Decide which of the two substances in each pair has the weaker interparticle force. Dispersion forces are weaker than dipole-dipole forces, which are weaker than hydrogen bonds.

Solution:

- a)  $\text{C}_2\text{H}_6$   $\text{C}_2\text{H}_6$  is a smaller molecule exhibiting weaker dispersion forces than  $\text{C}_4\text{H}_{10}$ .  
b)  $\text{CH}_3\text{CH}_2\text{F}$   $\text{CH}_3\text{CH}_2\text{F}$  has no H–F bonds (F is bonded to C, not to H), so it only exhibits dipole-dipole forces, which are weaker than the hydrogen bonding in  $\text{CH}_3\text{CH}_2\text{OH}$ .  
c)  $\text{PH}_3$   $\text{PH}_3$  has weaker intermolecular forces (dipole-dipole) than  $\text{NH}_3$  (hydrogen bonding).

- 12.39 a)  $\text{HOCH}_2\text{CH}_2\text{OH}$  has a stronger intermolecular force, because there are more –OH groups to hydrogen bond.  
b)  $\text{CH}_3\text{COOH}$  has a stronger intermolecular force, because hydrogen bonding is stronger than dipole-dipole forces.  
c)  $\text{HF}$  has a stronger intermolecular force, because hydrogen bonding is stronger than dipole-dipole forces.

12.40 Plan: The weaker the interparticle forces, the lower the boiling point. Decide which of the two substances in each pair has the weaker interparticle force. Dispersion forces are weaker than dipole-dipole forces, which are weaker than hydrogen bonds, which are weaker than ionic forces.

Solution:

- a)  $\text{HCl}$  would have a lower boiling point than  $\text{LiCl}$  because the dipole-dipole intermolecular forces between hydrogen chloride molecules in the liquid phase are weaker than the significantly stronger ionic forces holding the ions in lithium chloride together.  
b)  $\text{PH}_3$  would have a lower boiling point than  $\text{NH}_3$  because the intermolecular forces in  $\text{PH}_3$  are weaker than those in  $\text{NH}_3$ . Hydrogen bonding exists between  $\text{NH}_3$  molecules but weaker dipole-dipole forces hold  $\text{PH}_3$  molecules together.  
c)  $\text{Xe}$  would have a lower boiling point than iodine. Both are nonpolar with dispersion forces, but the forces between xenon atoms would be weaker than those between iodine molecules since the iodine molecules are more polarizable because of their larger size.

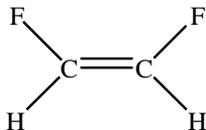
- 12.41 a)  $\text{CH}_3\text{CH}_2\text{OH}$ , hydrogen bonding ( $\text{CH}_3\text{CH}_2\text{OH}$ ) vs. dispersion ( $\text{CH}_3\text{CH}_2\text{CH}_3$ )  
b)  $\text{NO}$ , dipole-dipole ( $\text{NO}$ ) vs. dispersion ( $\text{N}_2$ )  
c)  $\text{H}_2\text{Te}$ , the larger molecule has larger dispersion forces

12.42 Plan: The weaker the intermolecular forces, the lower the boiling point. Decide which of the two substances in each pair has the weaker intermolecular force. Dispersion forces are weaker than dipole-dipole forces, which are weaker than hydrogen bonds, which are weaker than ionic forces.

Solution:

- a)  $\text{C}_4\text{H}_8$ , the cyclic molecule, cyclobutane, has less surface area exposed, so its dispersion forces are weaker than the straight chain molecule,  $\text{C}_4\text{H}_{10}$ .  
b)  $\text{PBr}_3$ , the dipole-dipole forces of phosphorous tribromide are weaker than the ionic forces of sodium bromide.  
c)  $\text{HBr}$ , the dipole-dipole forces of hydrogen bromide are weaker than the hydrogen bonding forces of water.

- 12.43 a)  $\text{CH}_3\text{OH}$ , hydrogen bonding ( $\text{CH}_3\text{OH}$ ) vs. dispersion forces ( $\text{CH}_3\text{CH}_3$ ).  
b)  $\text{FNO}$ , greater polarity in  $\text{FNO}$  vs.  $\text{ClNO}$   
c)



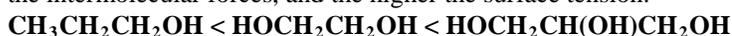
This molecule has dipole-dipole forces since the two C–F bonds do not cancel and the molecule is polar. The other molecule has only dispersion forces since the two C–F bonds do cancel, so that the molecule is nonpolar.

- 12.44 The molecules of motor oil are long chains of  $\text{CH}_2$  units. The high molar mass results in stronger dispersion forces and leads to a high boiling point. In addition, these chains can become tangled in one another and restrict each other's motions and ease of vaporization.
- 12.45 The ethylene glycol molecules have two sites (two  $-\text{OH}$  groups) which can hydrogen bond; the propanol has only one  $-\text{OH}$  group.
- 12.46 The molecules at the surface are attracted to one another and to those molecules in the bulk of the liquid. Since this force is directed downwards and sideways, it tends to "tighten the skin."
- 12.47 The shape of the drop depends upon the competing cohesive forces (attraction of molecules within the drop itself) and adhesive forces (attraction between molecules in the drop and the molecules of the waxed floor). If the cohesive forces are strong and outweigh the adhesive forces, the drop will be as spherical as gravity will allow. If, on the other hand, the adhesive forces are significant, the drop will spread out. Both water (hydrogen bonding) and mercury (metallic bonds) have strong cohesive forces, whereas cohesive forces in oil (dispersion) are relatively weak. Neither water nor mercury will have significant adhesive forces to the nonpolar wax molecules, so these drops will remain nearly spherical. The adhesive forces between the oil and wax can compete with the weak, cohesive forces of the oil (dispersion) and so the oil drop spreads out.
- 12.48 The strength of the intermolecular forces does not change when the liquid is heated, but the molecules have greater kinetic energy and can overcome these forces more easily as they are heated. The molecules have more energy at higher temperatures, so they can break the intermolecular forces and can move more easily past their neighbors; thus, viscosity decreases.

- 12.49 **Plan:** The stronger the intermolecular force, the greater the surface tension. Decide which of the substances has the weakest intermolecular force and which has the strongest. Dispersion forces are weaker than dipole-dipole forces, which are weaker than hydrogen bonds, which are weaker than ionic forces.

**Solution:**

All three molecules exhibit hydrogen bonding (H is bonded to O), but the extent of hydrogen bonding increases with the number of O–H bonds present in each molecule.  $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$  with three O–H groups can form more hydrogen bonds than  $\text{HOCH}_2\text{CH}_2\text{OH}$  with two O–H groups, which in turn can form more hydrogen bonds than  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  with only one O–H group. The greater the number of hydrogen bonds, the stronger the intermolecular forces, and the higher the surface tension.



- 12.50  **$\text{CH}_3\text{OH} > \text{H}_2\text{CO} > \text{CH}_3\text{CH}_3$**   
The intermolecular forces would decrease as shown (hydrogen bonding > dipole-dipole > dispersion), as would the surface tension.

- 12.51 a) Calculate the energies involved using the heats of fusion.

$$q_{\text{Hg}} = n(\Delta H_{\text{fus}}^\circ) = (12.0 \text{ g Hg}) \left( \frac{1 \text{ mol Hg}}{200.6 \text{ g Hg}} \right) \left( \frac{23.4 \text{ kJ}}{1 \text{ mol Hg}} \right) = 1.3998 = 1.40 \text{ kJ}$$

$$q_{\text{methane}} = n(\Delta H_{\text{fus}}^\circ) = (12.0 \text{ g CH}_4) \left( \frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4} \right) \left( \frac{0.94 \text{ kJ}}{1 \text{ mol CH}_4} \right) = 0.70324 = 0.70 \text{ kJ}$$

**Mercury** takes more energy.

- b) Calculate the energies involved using the heats of vaporization.

$$q_{\text{Hg}} = n(\Delta H_{\text{vap}}^\circ) = (12.0 \text{ g Hg}) \left( \frac{1 \text{ mol Hg}}{200.6 \text{ g Hg}} \right) \left( \frac{59 \text{ kJ}}{1 \text{ mol Hg}} \right) = 3.5294 = 3.5 \text{ kJ}$$

$$q_{\text{methane}} = n(\Delta H_{\text{vap}}^\circ) = (12.0 \text{ g CH}_4) \left( \frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4} \right) \left( \frac{8.9 \text{ kJ}}{1 \text{ mol CH}_4} \right) = 6.65835 = 6.6 \text{ kJ}$$

**Methane** takes more energy.

- c) Mercury involves **metallic bonding** and methane involves **dispersion forces**.

- 12.52 The pentanol has stronger intermolecular forces (hydrogen bonds) than the hexane (dispersion forces).
- 12.53 Water is a good solvent for polar and ionic substances and a poor solvent for nonpolar substances. Water is a polar molecule and dissolves polar substances because their intermolecular forces are of similar strength. Water is also able to dissolve ionic compounds and keep ions separated in solution through ion-dipole interactions. Nonpolar substances will not be very soluble in water since their dispersion forces are much weaker than the hydrogen bonds in water. A solute whose intermolecular attraction to a solvent molecule is less than the attraction between two solvent molecules will not dissolve because its attraction cannot replace the attraction between solvent molecules.
- 12.54 A single water molecule can form four hydrogen bonds. The two hydrogen atoms form a hydrogen bond each to oxygen atoms on neighboring water molecules. The two lone pairs on the oxygen atom form hydrogen bonds with hydrogen atoms on neighboring molecules.
- 12.55 The heat capacity of water is quite high, meaning that a large amount of heat is needed to change the temperature of a quantity of water by even a small amount.
- 12.56 Water exhibits strong capillary action, which allows it to be easily absorbed by the plant's roots and transported to the leaves.
- 12.57 In ice, water molecules pack in a very specific, ordered way. When it melts, the molecular order is disrupted and the molecules pack more closely. This makes liquid water (at least below 4°C) denser than ice and allows ice to float.
- 12.58 As the temperature of the ice increases, the water molecules move more vigorously about their fixed positions until at some temperature, the increasing kinetic energy of the water molecules at last overcomes the attractions (hydrogen bonding) between them, allowing the water molecules to move freely through the liquid.
- 12.59 An amorphous solid has little order on the molecular level and has no characteristic crystal shape on the macroscopic level. An example would be rubber. A crystalline solid has a great deal of order on the molecular level and forms regularly shaped forms bounded by flat faces on the macroscopic level. An example would be NaCl.
- 12.60 When the unit cell is repeated infinitely in all directions, the crystal lattice is formed.
- 12.61 The simple, body-centered, and face-centered cubic unit cells contain one, two, and four atoms, respectively. Atoms in the body of a cell are in that cell only; atoms on faces are shared by two cells; atoms at corners are shared by eight cells. All of the cells have eight corner atoms;  $8 \text{ atoms} \times \frac{1}{8} \text{ atom per cell} = 1 \text{ atom}$ . In addition, the body-centered cell has an atom in the center, for a total of two atoms. The face-centered cell has six atoms in the faces;  $6 \text{ atoms} \times \frac{1}{2} \text{ atom per cell} = 3 \text{ atoms}$ , for a total of 4 in the cell (corner + face).
- 12.62 A solid metal is a shiny solid that conducts heat, is malleable, and melts at high temperatures. (Other answers include relatively high boiling point and good conductor of electricity.)
- 12.63 a) Potassium is a larger atom than sodium, so its electrons are held more loosely and thus its metallic bond strength is weaker.  
b) Be has two valence electrons per atom compared with Li, which has one. The metallic bond strength is stronger for the Be.  
c) The boiling point is high due to the large amount of energy needed to separate the metal ions from each other in the electron sea.
- 12.64 When metallic magnesium is deformed, the atoms are displaced and pass over one another while still being tightly held by the attraction of the "sea of electrons." When ionic  $\text{MgF}_2$  is deformed, the ions are displaced so that repulsive forces between neighboring ions of like charge cause shattering of the crystals.

- 12.65 The energy gap is the energy difference between the highest filled energy level (valence band) and the lowest unfilled energy level (conduction band). In conductors and superconductors, the energy gap is zero because the valence band overlaps the conduction band. In semiconductors, the energy gap is small but greater than zero. In insulators, the energy gap is large and thus insulators do not conduct electricity.
- 12.66 Plan: The simple cubic structure unit cell contains one atom since the atoms at the eight corners are shared by eight cells for a total of  $8 \text{ atoms} \times 1/8 \text{ atom per cell} = 1 \text{ atom}$ ; the body-centered cell also has an atom in the center, for a total of two atoms; the face-centered cell has six atoms in the faces which are shared by two cells:  $6 \text{ atoms} \times 1/2 \text{ atom per cell} = 3 \text{ atoms}$  plus another atom from the eight corners for a total of four atoms.  
Solution:  
a) Ni is **face-centered cubic** since there are four atoms/unit cell.  
b) Cr is **body-centered cubic** since there are two atoms/unit cell.  
c) Ca is **face-centered cubic** since there are four atoms/unit cell.
- 12.67 a) **one** b) **two** c) **four**
- 12.68 a) There is a change in unit cell from CdO in a sodium chloride structure to CdSe in a zinc blende structure.  
b) **Yes**, the coordination number of Cd does change from six in the CdO unit cell to four in the CdSe unit cell.
- 12.69 a) The unit cell of Fe changes from a face-centered cubic unit cell at 1674 K to a body-centered cubic unit cell below 1181 K.  
b) The face-centered cubic cell has the greater packing efficiency.
- 12.70 Plan: Substances composed of individual atoms are atomic solids; molecular substances composed of covalent molecules form molecular solids; ionic compounds form ionic solids; metal elements form metallic solids; certain substances that form covalent bonds between atoms or molecules form network covalent solids.  
Solution:  
a) Nickel forms a **metallic solid** since nickel is a metal whose atoms are held together by metallic bonds.  
b) Fluorine forms a **molecular solid** since the  $F_2$  molecules have covalent bonds and the molecules are held to each other by dispersion forces.  
c) Methanol forms a **molecular solid** since the covalently bonded  $CH_3OH$  molecules are held to each other by hydrogen bonds.  
d) Tin forms a **metallic solid** since tin is a metal whose atoms are held together by metallic bonds.  
e) Silicon is in the same group as carbon, so it exhibits similar bonding properties. Since diamond and graphite are both **network covalent** solids, it makes sense that Si forms the same type of bonds.  
f) Xe is an **atomic** solid since individual atoms are held together by dispersion forces.
- 12.71 a) **Network covalent**, since this is similar to diamond.  
b) **Ionic**, since it consists of ions.  
c) **Molecular**, since this is a molecule.  
d) **Molecular**, since this is a molecule.  
e) **Ionic**, since it is an ionic compound.  
f) **Network covalent**, since this substance is isoelectronic with C (diamond).
- 12.72 Figure P12.73 shows the face-centered cubic array of zinc blende, ZnS. Both ZnS and ZnO have a 1:1 ion ratio, so the ZnO unit cell will also contain **four**  $Zn^{2+}$  ions.
- 12.73 Figure P12.73 shows the face-centered cubic array of calcium sulfide, CaS. Both CaS and NaCl have a 1:1 ion ratio, so the CaS unit cell will also contain **four**  $S^{2-}$  ions.
- 12.74 Plan: To determine the number of  $Zn^{2+}$  ions and  $Se^{2-}$  ions in each unit cell count the number of ions at the corners, faces, and center of the unit cell. Atoms at the eight corners are shared by eight cells for a total of  $8 \text{ atoms} \times 1/8 \text{ atom per cell} = 1 \text{ atom}$ ; atoms in the body of a cell are in that cell only; atoms at the faces are shared by two cells:  $6 \text{ atoms} \times 1/2 \text{ atom per cell} = 3 \text{ atoms}$ . Add the masses of the total number of atoms in the cell to find the mass of the cell. Given the mass of one unit cell and the ratio of mass to volume (density) divide the mass, converted to grams (conversion factor is  $1 \text{ amu} = 1.66054 \times 10^{-24} \text{ g}$ ), by the density to find the volume of the

unit cell. Since the volume of a cube is length x width x height, the edge length is found by taking the cube root of the cell volume.

Solution:

a) Looking at selenide ions, there is one ion at each corner and one ion on each face. The total number of selenide ions is  $1/8$  (8 corner ions) +  $1/2$  (6 face ions) = **4 Se<sup>2-</sup> ions**. There are also **4 Zn<sup>2+</sup> ions** due to the 1:1 ratio of Se ions to Zn ions.

b) Mass of unit cell = (4 x mass of Zn atom) + (4 x mass of Se atom)  
 = (4 x 65.41 amu) + (4 x 78.96 amu) = **577.48 amu**

c) Volume (cm<sup>3</sup>) = (577.48 amu)  $\left(\frac{1.66054 \times 10^{-24} \text{ g}}{1 \text{ amu}}\right) \left(\frac{\text{cm}^3}{5.42 \text{ g}}\right)$  =  $1.76924 \times 10^{-22}$  = **1.77 x 10<sup>-22</sup> cm<sup>3</sup>**

d) The volume of a cube equals (length of edge)<sup>3</sup>.

Edge length (cm) =  $\sqrt[3]{1.76924 \times 10^{-22} \text{ cm}^3}$  =  $5.6139 \times 10^{-8}$  = **5.61 x 10<sup>-8</sup> cm**

12.75 a) A face-centered cubic unit cell contains **four atoms**.

b) Volume =  $(4.52 \times 10^{-8} \text{ cm})^3$  =  $9.23454 \times 10^{-23}$  = **9.23 x 10<sup>-23</sup> cm<sup>3</sup>**

c) Mass of unit cell =  $(1.45 \text{ g/cm}^3)(9.23454 \times 10^{-23} \text{ cm}^3)$  =  $1.3390 \times 10^{-22}$  = **1.34 x 10<sup>-22</sup> g**

d) Mass of atom =  $\left(\frac{1.3390 \times 10^{-22} \text{ g}}{1 \text{ unit cell}}\right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}}\right) \left(\frac{1 \text{ amu}}{1.66054 \times 10^{-27} \text{ kg}}\right) \left(\frac{1 \text{ unit cell}}{4 \text{ atoms}}\right)$   
 = 20.1592 = **20.2 amu/atom**

12.76 Plan: To classify a substance according to its electrical conductivity, first locate it on the periodic table as a metal, metalloid, or nonmetal. In general, metals are conductors, metalloids are semiconductors, and nonmetals are insulators.

Solution:

a) Phosphorous is a nonmetal and an **insulator**.

b) Mercury is a metal and a **conductor**.

c) Germanium is a metalloid in Group 4A(14) and is beneath carbon and silicon in the periodic table. Pure germanium crystals are **semiconductors** and are used to detect gamma rays emitted by radioactive materials. Germanium can also be doped with phosphorous (similar to the doping of silicon) to form an n-type semiconductor or be doped with lithium to form a p-type semiconductor.

12.77 Plan: First, classify the substance as an insulator, conductor, or semiconductor. The electrical conductivity of conductors decreases with increasing temperature, whereas that of semiconductors increases with temperature. Temperature increases have little impact on the electrical conductivity of insulators.

Solution:

a) Antimony, Sb, is a metalloid, so it is a semiconductor. Its electrical conductivity **increases** as the temperature increases.

b) Tellurium, Te, is a metalloid, so it is a semiconductor. Its electrical conductivity **increases** as temperature increases.

c) Bismuth, Bi, is a metal, so it is a conductor. Its electrical conductivity **decreases** as temperature increases.

12.78 Rb ([Kr]5s<sup>1</sup>) has one valence electron, so the metallic bonding would be fairly weak, resulting in a soft, low-melting material. Cd ([Kr]5s<sup>2</sup>4d<sup>10</sup>) has two valence electrons so the metallic bonding is stronger. V ([Ar]4s<sup>2</sup>3d<sup>3</sup>) has five valence electrons, so its metallic bonding is the strongest, that is, its hardness, melting point, and other metallic properties would be greatest.

12.79 a) Edge of unit cell =  $\sqrt[3]{\left(\frac{95.94 \text{ g Mo}}{1 \text{ mol Mo}}\right) \left(\frac{\text{cm}^3}{10.28 \text{ g}}\right) \left(\frac{1 \text{ mol Mo}}{6.022 \times 10^{23} \text{ Mo atoms}}\right) (2 \text{ Mo atoms})}$   
 =  $3.1412218 \times 10^{-8}$  = **3.141 x 10<sup>-8</sup> cm**

b) The body-diagonal of a body-centered cubic unit cell is equal to four times the radius of the Mo atom. The body-diagonal is also =  $\sqrt{3}$  times the length of the unit cell edge.

$$4r = \sqrt{3}(3.1412218 \times 10^{-8} \text{ cm}) = 5.4407559 \times 10^{-8} \text{ cm}$$

$$r = 1.360189 \times 10^{-8} = \mathbf{1.360 \times 10^{-8} \text{ cm}}$$

12.80 Volume =  $\left(\frac{\text{cm}^3}{3.62 \text{ g}}\right)\left(\frac{137.3 \text{ g}}{1 \text{ mol Ba}}\right) = 37.9281768 \text{ cm}^3/\text{mol Ba}$

Volume/mol of Ba atoms = volume/mol Ba x packing efficiency

The packing efficiency in the body-centered cubic unit cell is 68%.

$$\text{Volume/mol of Ba atoms} = 37.9281768 \text{ cm}^3/\text{mol Ba} \times 0.68 = 25.791116 \text{ cm}^3/\text{mol Ba atoms}$$

$$\text{Volume of one Ba atom} = \left(\frac{25.791116 \text{ cm}^3}{1 \text{ mol Ba atoms}}\right)\left(\frac{1 \text{ mol Ba atoms}}{6.022 \times 10^{23} \text{ Ba atoms}}\right) = 4.28282 \times 10^{-23} \text{ cm}^3/\text{atom}$$

Use the volume of a sphere to find the radius of the Ba atom:

$$V = \frac{4}{3}\pi r^3$$

$$r = \sqrt[3]{\frac{3V}{4\pi}} = \sqrt[3]{\frac{3(4.28282 \times 10^{-23} \text{ cm}^3)}{4\pi}} = 2.17044 \times 10^{-8} = \mathbf{2.17 \times 10^{-8} \text{ cm}}$$

- 12.81 a) I, II, III, V  
 b) IV  
 c) V → IV → liquid → I  
 d) Triple point: I, II, liquid  
 Triple point: II, IV, liquid  
 Triple point: II, III, IV  
 Triple point: III, IV, V  
 Triple point: IV, V, liquid

- 12.82 Plan: The Clausius-Clapeyron equation gives the relationship between vapor pressure and temperature. We are given  $P_1$ ,  $P_2$ ,  $T_1$ , and  $\Delta H_{\text{vap}}^\circ$ ; these values are substituted into the equation to find  $T_2$ .

Solution:

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{\text{vap}}^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad P_1 = 1.20 \times 10^{-3} \text{ torr} \quad T_1 = 20.0^\circ\text{C} + 273 = 293 \text{ K}$$

$$P_2 = 5.0 \times 10^{-5} \text{ torr} \quad T_2 = ? \quad \Delta H_{\text{vap}}^\circ = 59.1 \text{ kJ/mol}$$

$$\ln \frac{5.0 \times 10^{-5} \text{ torr}}{1.20 \times 10^{-3} \text{ torr}} = \frac{-59.1 \text{ kJ/mol}}{8.314 \text{ J/mol}\cdot\text{K}} \left( \frac{1}{T_2} - \frac{1}{293 \text{ K}} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right)$$

$$-3.178054 = -7108.492 \left( \frac{1}{T_2} - \frac{1}{293 \text{ K}} \right)$$

$$(-3.17805)/(-7108.49) = 4.47078 \times 10^{-4} = \left( \frac{1}{T_2} - \frac{1}{293 \text{ K}} \right)$$

$$4.47078 \times 10^{-4} + 1/293 = 1/T_2$$

$$T_2 = 259.064 = \mathbf{259 \text{ K}}$$

- 12.83 a) A: solid      E: solid + liquid      F: liquid + gas  
 H: liquid      B: liquid + solid + gas      C: gas  
 b) Critical point: D      Triple point: B  
 c) BG  
 d) The substance is a solid, which would melt and then boil.

- e) The substance is a liquid, which would vaporize.  
 f) The liquid is denser than the solid.

12.84 **Plan:** Add up the number of atoms in the unit cell. An atom at a corner counts 1/8 of an atom, an atom in the center counts as one atom, and an atom on an edge counts as 1/4 of an atom. Use the edge length of the cell to calculate the volume of the cell; the mass of the cell divided by the volume gives the density.

**Solution:**

a) The cell contents are one Ca,  $8 \times (1/8) = 1$  Ti, and  $12 \times (1/4) = 3$  O, or one  $\text{CaTiO}_3$  formula unit. The presence of one formula unit per unit cell indicates a **simple cubic** unit cell.

$$\text{b) Mass (g) of the unit cell} = \left( \frac{1 \text{ CaTiO}_3}{\text{unit cell}} \right) \left( \frac{1 \text{ mol CaTiO}_3}{6.022 \times 10^{23} \text{ CaTiO}_3} \right) \left( \frac{135.96 \text{ g CaTiO}_3}{1 \text{ mol CaTiO}_3} \right) = 2.257722 \times 10^{-22} \text{ g}$$

$$\text{Volume (cm}^3\text{) of the unit cell} = \left( \frac{(3.84 \text{ \AA})^3}{\text{unit cell}} \right) \left( \frac{10^{-8} \text{ cm}}{1 \text{ \AA}} \right)^3 = 5.6623 \times 10^{-23} \text{ cm}^3$$

$$\text{Density} = \frac{2.257722 \times 10^{-22} \text{ g}}{5.6623 \times 10^{-23} \text{ cm}^3} = 3.98729 = \mathbf{3.99 \text{ g/cm}^3}$$

12.85 The density of Fe is  $7.874 \text{ g/cm}^3$ , but Fe atoms occupy only 68% of the volume in a body-centered cubic cell. Calculate the volume/mole Fe ratio, and multiply by 0.68 to determine the volume/mol Fe atoms ratio. Dividing by the volume of a single Fe will yield the units of atoms/mol, which is Avogadro's number.

$$\text{Molar volume of Fe} = (55.85 \text{ g/mol}) / (7.874 \text{ g/cm}^3) = 7.09296 \text{ cm}^3/\text{mol Fe}$$

The volume of just the atoms (not including the empty spaces between atoms) is:

$$\text{Volume/mole Fe atoms} = (7.09296 \text{ cm}^3/\text{mol Fe})(68\% / 100\%) = 4.82321 \text{ cm}^3/\text{mol Fe atoms}$$

The number of atoms in one mole of Fe is obtained by dividing by the volume of one Fe atom:

$$\begin{aligned} \text{Atoms/mol} &= (4.82321 \text{ cm}^3/\text{mol Fe atoms})(1 \text{ Fe atom}/8.38 \times 10^{-24} \text{ cm}^3) \\ &= 5.7556 \times 10^{23} = \mathbf{5.8 \times 10^{23} \text{ atoms/mol}} \end{aligned}$$

12.86 The number of anions that can fit around a cation depends on the relative sizes of the two ions, or the ratio  $r_+/r_-$ . The large size of the  $\text{Cs}^+$  ion allows for eight anions ( $\text{CN} = 8$ ) to fit around the cation in a cubic arrangement, while the smaller size  $\text{Na}^+$  ion can only fit six anions ( $\text{CN} = 6$ ). With this additional contact, the high polarizability of the large ions allows for strong dispersion forces, which favor the  $\text{CsCl}$  structure.

12.87 The formulas are **TaN** and **TaC**.

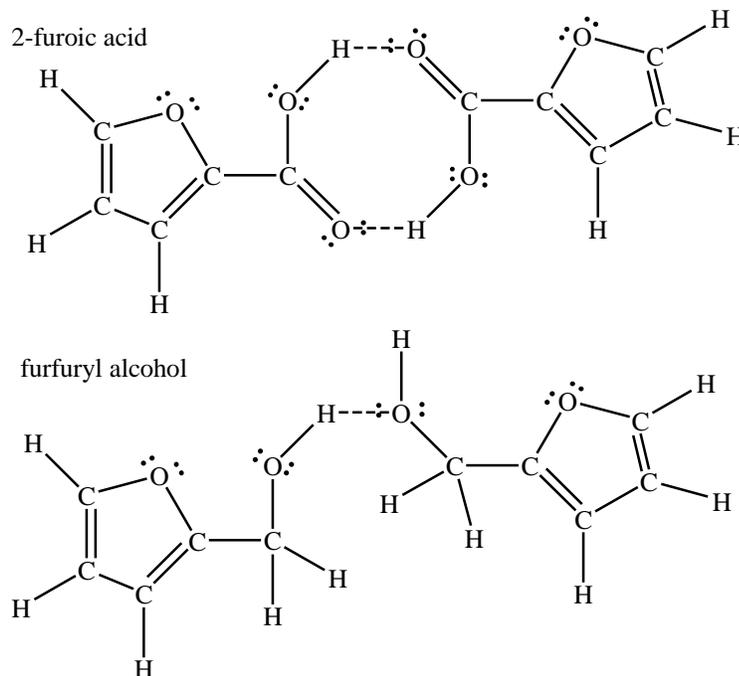
12.88 In the  $\text{NaCl}$  type lattice, there are four ions of each type.

$$\begin{aligned} \text{Density of KF} &= \left( \frac{4 \text{ KF}}{\text{unit cell}} \right) \left( \frac{1 \text{ mol KF}}{6.022 \times 10^{23} \text{ KF}} \right) \left( \frac{58.10 \text{ g KF}}{1 \text{ mol KF}} \right) \left( \frac{\text{unit cell}}{(5.39 \text{ \AA})^3} \right) \left( \frac{1 \text{ \AA}}{10^{-8} \text{ cm}} \right)^3 \\ &= 2.46450 = \mathbf{2.46 \text{ g/cm}^3} \end{aligned}$$

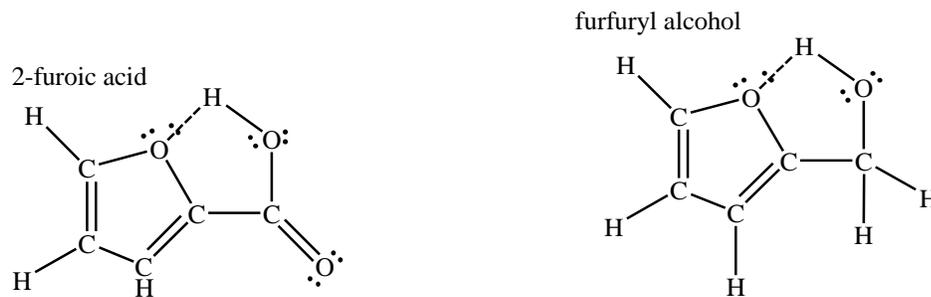
12.89 **Plan:** Hydrogen bonds only occur in substances in which hydrogen is directly bonded to either oxygen, nitrogen, or fluorine.

**Solution:**

a) Both **furfuryl alcohol** and 2-furoic acid can form hydrogen bonds since these two molecules have hydrogen directly bonded to oxygen.



b) Both **furfuryl alcohol** and **2-furoic acid** can form internal hydrogen bonds by forming a hydrogen bond between the O–H and the O in the ring.



- 12.90 The eight atoms of A are each 1/8 in the cell (i.e., shared by eight cells), so there is a net of one A atom. The six atoms of Z are each 1/2 in the cell (i.e., shared by two cells), so there are three net Z atoms. The compound is **AZ<sub>3</sub>**.
- 12.91 **No**, filling all the available holes (8) in the face-centered cubic lattice leads to a stoichiometry of 2:1 (8 holes/4 atoms).
- 12.92 a) Determine the vapor pressure of ethanol in the bottle at  $-11^{\circ}\text{C}$  by applying the Clausius-Clapeyron equation. The boiling point of ethanol is  $78.5^{\circ}\text{C}$  at a pressure of 1 atm (760 torr).  $\Delta H_{\text{vap}}^{\circ}$  (38.6 kJ/mol) is given in Figure 12.1.

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

$$P_1 = ? \quad T_1 = (273 + (-11^{\circ}\text{C})) = 262 \text{ K}$$

$$P_2 = 760. \text{ torr} \quad T_2 = (273.15 + 78.5^{\circ}\text{C}) = 351.6 \text{ K}$$

$$\Delta H_{\text{vap}}^{\circ} = 38.6 \text{ kJ/mol}$$

$$\ln \frac{760. \text{ torr}}{P_1} = \frac{-38.6 \text{ kJ/mol}}{8.314 \text{ J/mol}\cdot\text{K}} \left( \frac{1}{351.6 \text{ K}} - \frac{1}{262 \text{ K}} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 4.515804546$$

$$\frac{760. \text{ torr}}{P_1} = 91.45111307$$

$$P_1 = 8.31045 \text{ torr}$$

Note: The pressure should be small because not many ethanol molecules escape the liquid surface at such a cold temperature.

Determine the number of moles by substituting  $P$ ,  $V$ , and  $T$  into the ideal gas equation. Assume that the volume the liquid takes up in the 4.7 L space is negligible.

$$n = \frac{PV}{RT} = \frac{(8.31045 \text{ torr})(4.7 \text{ L})}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(262 \text{ K})} \left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) = 0.0023892652 \text{ mol C}_2\text{H}_6\text{O}$$

Convert moles of ethanol to mass of ethanol using the molar mass ( $\mathcal{M} = 46.07 \text{ g/mol}$ ).

$$\text{Mass (g) of C}_2\text{H}_6\text{O} = (0.0023892652 \text{ mol C}_2\text{H}_6\text{O})(46.07 \text{ g/mol C}_2\text{H}_6\text{O}) = 0.11007345 = \mathbf{0.11 \text{ g C}_2\text{H}_6\text{O}}$$

$$\text{b) } \ln \frac{P_2}{P_1} = -\frac{\Delta H_{\text{vap}}^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad P_1 = ? \quad T_1 = (273 + 20.^\circ\text{C}) = 293 \text{ K}$$

$$P_2 = 760. \text{ torr} \quad T_2 = (273.15 + 78.5^\circ\text{C}) = 351.6 \text{ K}$$

$$\Delta H_{\text{vap}}^\circ = 38.6 \text{ kJ/mol}$$

$$\ln \frac{760. \text{ torr}}{P_1} = \frac{-38.6 \text{ kJ/mol}}{8.314 \text{ J/mol}\cdot\text{K}} \left( \frac{1}{351.6 \text{ K}} - \frac{1}{293 \text{ K}} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 2.640939266$$

$$\frac{760. \text{ torr}}{P_1} = 14.02637191$$

$$P_1 = 54.18365 \text{ torr}$$

Determine the number of moles by substituting  $P$ ,  $V$ , and  $T$  into the ideal gas equation. Assume that the volume the liquid takes up in the 4.7 L space is negligible.

$$n = \frac{PV}{RT} = \frac{(54.18365 \text{ torr})(4.7 \text{ L})}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(293 \text{ K})} \left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) = 0.0139297 \text{ mol C}_2\text{H}_6\text{O}$$

Convert moles of ethanol to mass of ethanol using the molar mass ( $\mathcal{M} = 46.07 \text{ g/mol}$ ).

$$\text{Mass (g) of C}_2\text{H}_6\text{O} = (0.0139297 \text{ mol C}_2\text{H}_6\text{O})(46.07 \text{ g/mol C}_2\text{H}_6\text{O}) = 0.6417413 = 0.64 \text{ g C}_2\text{H}_6\text{O}$$

The mass of ethanol present in the vapor, if excess liquid was present, is 0.64 g. Since this exceeds the 0.33 g available, **all of the ethanol will vaporize.**

$$\text{c) } 0.0^\circ\text{C} = (273.2 + 0.0) = 273.2 \text{ K}$$

$$\ln \frac{P_2}{760 \text{ torr}} = \frac{-38.6 \text{ kJ/mol}}{8.314 \text{ J/mol}\cdot\text{K}} \left( \frac{1}{273.2 \text{ K}} - \frac{1}{351.6 \text{ K}} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -3.789341845$$

$$\frac{P_2}{760 \text{ torr}} = 0.0226104781$$

$$P_2 = (0.0226104781)(760 \text{ torr}) = 17.18396 \text{ torr}$$

$$n = \frac{PV}{RT} = \frac{(17.18396 \text{ torr})(4.7 \text{ L})}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(273.2 \text{ K})} \left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) = 0.0047378757 \text{ mol C}_2\text{H}_6\text{O}$$

Convert moles of ethanol to mass of ethanol using the molar mass ( $\mathcal{M} = 46.07 \text{ g/mol}$ ).

$$\text{Mass C}_2\text{H}_6\text{O} = (0.0047378757 \text{ mol C}_2\text{H}_6\text{O})(46.07 \text{ g/mol C}_2\text{H}_6\text{O}) = 0.2182739 \text{ g C}_2\text{H}_6\text{O}$$

Mass (g) of ethanol in liquid = mass (g) of ethanol (total) – mass (g) of ethanol in vapor

$$\text{Mass (g) of ethanol in liquid} = 0.33 \text{ g} - 0.2182739 \text{ g} = 0.1117261 = \mathbf{0.11 \text{ g C}_2\text{H}_6\text{O}}$$

12.93 Plan: This problem involves carefully examining the figures showing the different cells pictured in the chapter.

Solution:

a) The atoms touch along the body diagonal. The two corner atoms each contribute one radius (r), and the center atom contributes a diameter (2r). The total for the body diagonal = **4r**.

b) The face diagonal is the hypotenuse of a right triangle with the other two sides being the unit cell edge (a). Using the Pythagorean Theorem ( $a^2 + b^2 = c^2$ ) with  $a = b =$  the unit cell edge, and  $c =$  the face diagonal:

$$a^2 + b^2 = c^2$$

$$a^2 + a^2 = 2 a^2 = c^2$$

$$c = \text{face diagonal} = \sqrt{2} a$$

c) The body-diagonal is the hypotenuse (c) of a triangle with one of the other sides being a face-diagonal (b) and the remaining side being a unit cell edge (a). Again, the Pythagorean Theorem is applied.

$$a^2 + b^2 = c^2$$

From part a:

$$a^2 + b^2 = (4r)^2$$

From part b:

$$a^2 + (\sqrt{2} a)^2 = (4r)^2$$

$$a^2 + 2 a^2 = 16r^2$$

Rearranging:

$$3a^2 = 16r^2$$

$$a^2 = \frac{16r^2}{3}$$

$$a = \frac{4r}{\sqrt{3}}$$

d) A body-centered cubic unit cell contains **2 atoms**. There is one atom in the center of the cell; eight atoms in the corners are each 1/8 in the cell (i.e., shared by eight cells), so there is a net of one more atom – 1/8 x 8.

e) Fraction filled = (volume of atoms present)/(volume of unit cell)  
= [2 atoms x volume of one atom]/(answer from part c)

Find the volume of one atom using the equation for the volume of a sphere:  $\frac{4}{3}\pi r^3$

Find the volume of the unit cell by cubing the value of the edge length from part c:

Volume of a cube = length x width x height

$$\text{Fraction filled} = \frac{2 \left[ \frac{4}{3} \pi r^3 \right]}{\left[ \frac{4r}{\sqrt{3}} \right]^3} = \frac{8.37758r^3}{12.3168r^3} = \mathbf{0.68017}$$

12.94 a) **A and B** can form intermolecular H bonds since both have a hydrogen atom bonded to an oxygen atom.

b) Highest viscosity = strongest intermolecular forces. **B** has the highest viscosity.