

36. a. ionic

b. LD mostly; C - F bonds are polar, but polymers like teflon are so large the LD forces are the predominant intermolecular forces.

c. LD

d. dipole, LD

e. H-bonding, LD

f. dipole, LD

g. LD

40.  $\text{CH}_3\text{CO}_2\text{H}$ : H-bonding + dipole forces + LD forces

$\text{CH}_2\text{ClCO}_2\text{H}$ : H-bonding + larger electronegative atom replacing H (greater dipole) + LD forces

$\text{CH}_3\text{CO}_2\text{CH}_3$ : dipole forces (no H-bonding) + LD forces

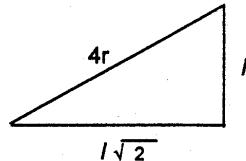
From the intermolecular forces listed above, we predict  $\text{CH}_3\text{CO}_2\text{CH}_3$  to have the weakest intermolecular forces and  $\text{CH}_2\text{ClCO}_2\text{H}$  to have the strongest. The boiling points are consistent with this view.

44.  $\text{H}_2\text{O}$  will rise higher in a glass tube because of a greater attraction for glass than for polyethylene.

$$48. n\lambda = 2d \sin \theta, d = \frac{n\lambda}{2 \sin \theta} = \frac{1 \times 2.63 \text{ \AA}}{2 \times \sin 15.55^\circ} = 4.91 \text{ \AA} = 4.91 \times 10^{-10} \text{ m} = 491 \text{ pm}$$

$$\sin \theta = \frac{n\lambda}{2d} = \frac{2 \times 2.63 \text{ \AA}}{2 \times 4.91 \text{ \AA}} = 0.536, \theta = 32.4^\circ$$

54. From Exercise 10.53:



$$16 r^2 = l^2 + 2l^2$$

$$l = 4r/\sqrt{3} = 2.309 r$$

$$l = 2.309 (222 \text{ pm}) = 513 \text{ pm} = 5.13 \times 10^{-8} \text{ cm}$$

In bcc, there are 2 atoms/unit cell. For a unit cell:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{2 \text{ atoms Ba} \times \frac{1 \text{ mol Ba}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{137.3 \text{ g Ba}}{\text{mol Ba}}}{(5.13 \times 10^{-8} \text{ cm})^3} = \frac{3.38 \text{ g}}{\text{cm}^3}$$

60. To make a p-type semiconductor we need to dope the material with atoms that have fewer valence electrons. The average number of valence electrons is four when 50-50 mixtures of group 3A and group 5A elements are considered. We could dope with more of the Group 3A element or with atoms of Zn or Cd. Cadmium is the most common impurity used to produce p-type GaAs semiconductors. To make a n-type GaAs semiconductor, dope with an excess group 5A element or dope with a Group 6A element such as sulfur.

72. a. diamond: atomic, covalent network      b.  $\text{PH}_3$ : molecular      c.  $\text{H}_2$ : molecular  
 d. Mg: atomic, metallic      e.  $\text{KCl}$ : ionic      f. quartz: covalent network  
 g.  $\text{NH}_4\text{NO}_3$ : ionic      h.  $\text{SF}_2$ : molecular      i. Ar: atomic, group 8A  
 j. Cu: atomic, metallic      k.  $\text{C}_6\text{H}_{12}\text{O}_6$ : molecular

78. a. Structure (a):

$$\text{Ba: } 2 \text{ Ba inside unit cell; Tl: } 8 \text{ corners} \times \frac{1/8 \text{ Tl}}{\text{corner}} = 1 \text{ Tl; Cu: } 4 \text{ edges} \times \frac{1/4 \text{ Cu}}{\text{edge}} = 1 \text{ Cu}$$

$$\text{O: } 6 \text{ faces} \times \frac{1/2 \text{ O}}{\text{face}} + 8 \text{ edges} \times \frac{1/4 \text{ O}}{\text{edge}} = 5 \text{ O; Formula} = \text{TlBa}_2\text{CuO}_3$$

Structure (b):

Tl and Ba are the same as in structure i.

$$\text{Ca: } 1 \text{ Ca inside unit cell; Cu: } 8 \text{ edges} \times \frac{1/4 \text{ Cu}}{\text{edge}} = 2 \text{ Cu}$$

$$\text{O: } 10 \text{ faces} \times \frac{1/2 \text{ O}}{\text{face}} + 8 \text{ edges} \times \frac{1/4 \text{ O}}{\text{edge}} = 7 \text{ O; Formula} = \text{TlBa}_2\text{CaCu}_2\text{O}_7$$

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

$$P_1 = 760. \text{ torr, } T_1 = 56.5^\circ\text{C} + 273.2 = 329.7 \text{ K; } P_2 = 630. \text{ torr, } T_2 = ?$$

$$\ln\left(\frac{760.}{630.}\right) = \frac{32.0 \times 10^3 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol}} \left( \frac{1}{T_2} - \frac{1}{329.7} \right), 0.188 = 3.85 \times 10^3 \left( \frac{1}{T_2} - 3.033 \times 10^{-3} \right)$$

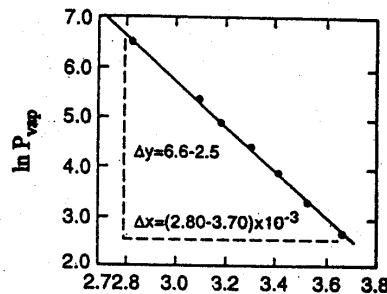
$$\frac{1}{T_2} - 3.033 \times 10^{-3} = 4.88 \times 10^{-3}, \frac{1}{T_2} = 3.082 \times 10^{-3}, T_2 = 324.5 \text{ K} = 51.3^\circ\text{C}$$

$$\ln\left(\frac{630. \text{ torr}}{P_2}\right) = \frac{32.0 \times 10^3 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol}} \left( \frac{1}{298.2} - \frac{1}{324.5} \right), \ln 630. - \ln P_2 = 1.05$$

$$\ln P_2 = 5.40, P_2 = e^{5.40} = 221 \text{ torr}$$

80. Again we graph  $\ln P_{\text{vap}}$  vs  $1/T$ . The slope of the line equals  $-\Delta H_{\text{vap}}/R$ .

T(K)	$10^3/T (\text{K}^{-1})$	$P_{\text{vap}}$ (torr)	$\ln P_{\text{vap}}$
273	3.66	14.4	2.67
283	3.53	26.6	3.28
293	3.41	47.9	3.87
303	3.30	81.3	4.40
313	3.19	133	4.89
323	3.10	208	5.34
353	2.83	670.	6.51



$$\text{slope} = \frac{6.6 - 2.5}{(2.80 \times 10^{-3} - 3.70 \times 10^{-3}) \text{ K}^{-1}} = -4600 \text{ K}$$

$$\frac{1000}{T}$$

$$-4600 \text{ K} = \frac{-\Delta H_{\text{vap}}}{R} = \frac{-\Delta H_{\text{vap}}}{8.3145 \text{ J/K} \cdot \text{mol}}$$

$$\Delta H_{\text{vap}} = 38 \text{ kJ/mol}$$

To determine the normal boiling point, we can use the following formula:

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

At the normal boiling point, the vapor pressure equals 1.00 atm or 760. torr. At 273 K, the vapor pressure is 14.4. torr (from data in the problem).

$$\ln\left(\frac{14.4}{760.}\right) = \frac{38,000 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol}} \left( \frac{1}{T_2} - \frac{1}{273 \text{ K}} \right), -3.97 = 4.6 \times 10^3 (1/T_2 - 3.66 \times 10^{-3})$$

$$-8.6 \times 10^{-4} + 3.66 \times 10^{-3} = 1/T_2 = 2.80 \times 10^{-3}, T_2 = 357 \text{ K} = \text{normal boiling point}$$

92. a. 3

- b. Triple point at  $95.31^\circ\text{C}$ : rhombic, monoclinic, gas  
Triple point at  $115.18^\circ\text{C}$ : monoclinic, liquid, gas  
Triple point at  $153^\circ\text{C}$ : rhombic, monoclinic, liquid
- c. From the phase diagram, the monoclinic solid phase is stable at  $T = 100^\circ\text{C}$  and  $P = 1 \text{ atm}$ .
- d. Normal melting point =  $115.21^\circ\text{C}$ ; normal boiling point =  $444.6^\circ\text{C}$ ; The normal melting and boiling points occur at  $P = 1.0 \text{ atm}$ .
- e. Rhombic is the densest phase since the rhombic-monoclinic equilibrium line has a positive slope and since the solid-liquid lines also have positive slope.
- f. No;  $P = 1.0 \times 10^{-3} \text{ atm}$  is at a pressure somewhere between the  $95.31^\circ\text{C}$  and  $115.18^\circ\text{C}$  triple points. At this pressure, the rhombic and gas phases are never in equilibrium with each other, so rhombic sulfur cannot sublime at  $P = 1.0 \times 10^{-3} \text{ atm}$ . However, monoclinic sulfur can sublime at this pressure.