

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

- 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 the 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 ΔH_{vap} is the same as the magnitude of ΔH_{cond} . The only difference is in the sign: $\Delta H_{\text{vap}} = -\Delta H_{\text{cond}}$.
- 12.5 Intermolecular forces are the forces that exist between molecules that attract the molecules to each other; intramolecular forces exist within a molecule and are the forces holding the atoms together in the molecule.
a) **Intermolecular** — Oil evaporates when individual oil molecules can escape the attraction of other oil molecules in the liquid phase.
b) **Intermolecular** — The process of butter (fat) melting involves a breakdown in the rigid, solid structure of fat molecules to an amorphous, less ordered system. The attractions between the fat molecules are weakened, but the bonds within the fat molecules are not broken.
c) **Intramolecular** — A process called oxidation tarnishes pure silver. Oxidation is a chemical change and involves the breaking of bonds and formation of new bonds.
d) **Intramolecular** — The decomposition of O_2 molecules into O atoms requires the breaking of chemical bonds, i.e., the force that holds the two O atoms together in an O_2 molecule.
Both a) and b) are physical changes, whereas c) and d) are chemical changes. In other words, intermolecular forces are involved in physical changes while intramolecular forces are involved in chemical changes.
- 12.6 a) **intermolecular** b) **intramolecular** c) **intermolecular** d) **intermolecular**

- 12.7 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.
- 12.8 a) **deposition** b) **sublimation** c) **crystallization** (freezing)
- 12.9 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.
- 12.10 **Sublimation and deposition**
- 12.11 The gaseous 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.
- 12.12 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.
- 12.13 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 numbers 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.
- 12.14 a) At the critical temperature, the molecules are moving so fast that they can no longer be condensed. This temperature decreases with weaker intermolecular forces because the forces are not strong enough to overcome molecular motion. Alternatively, as intermolecular forces increase, the **critical temperature increases**.
 b) As intermolecular forces increase, the **boiling point increases** because it becomes more difficult and takes more energy to separate molecules from the liquid phase.
 c) As intermolecular forces increase, the **vapor pressure decreases** for the same reason given in b). At any given temperature, strong intermolecular forces prevent molecules from easily going into the vapor phase and thus vapor pressure is decreased.
 d) As intermolecular forces increase, the **heat of vaporization increases** because more energy is needed to separate molecules from the liquid phase.
- 12.15 **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.
- 12.16 a) The final pressure will be the same, since the vapor pressure is constant as long as some liquid is present.
 b) The final pressure will be lower, according to Boyle's Law.
- 12.17 If the solid is denser than the liquid, the solid-liquid line slopes to the right; if less dense, to the left.
- 12.18 When water at 100°C touches skin, the heat released is from the lowering of the temperature of the water. The specific heat of water is approximately $75 \text{ J/mol}\cdot\text{K}$. When steam at 100°C touches skin, the heat released is from the condensation of the gas with a heat of condensation of approximately 41 kJ/mol . Thus, the amount of heat released from gaseous water condensing will be greater than the heat from hot liquid water cooling and the burn from the steam will be worse than that from hot water.

12.19 The total heat required is the sum of three processes:

1) Warming the ice from -6.00°C to 0.00°C

$$q_1 = Cm\Delta T = (2.09 \text{ J/g}^{\circ}\text{C}) (22.00 \text{ g}) [0.0 - (-6.00)]^{\circ}\text{C} = 275.88 \text{ J}$$

2) Phase change of ice at 0.00°C to water at 0.00°C

$$q_2 = n\Delta H_{\text{fus}} = (22.0 \text{ g}) \left(\frac{1 \text{ mol}}{18.02 \text{ g}} \right) \left(\frac{6.02 \text{ kJ}}{\text{mol}} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 7349.6115 \text{ J}$$

3) Warming the liquid from 0.00°C to 0.500°C

$$q_3 = Cm\Delta T = (4.21 \text{ J/g}^{\circ}\text{C}) (22.00 \text{ g}) [0.500 - (0.0)]^{\circ}\text{C} = 46.31 \text{ J}$$

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 $q_1 + q_2 + q_3 = (275.88 \text{ J} + 7349.6115 \text{ J} + 46.31 \text{ J}) = 7671.8015 = \mathbf{7.67 \times 10^3 \text{ J}}$.

12.20 $0.333 \text{ mol} \times 46.07 \text{ g/mol} = 15.34131 \text{ g}$ ethanol (unrounded)

Cooling vapor to boiling point:

$$q_1 = Cm\Delta T = (1.43 \text{ J/g}^{\circ}\text{C}) (15.34131 \text{ g}) (78.5 - 300)^{\circ}\text{C} = -4859.28 \text{ J (unrounded)}$$

Condensing vapor: (note $\Delta H_{\text{cond}} = -\Delta H_{\text{vap}}$)

$$q_2 = n\Delta H_{\text{cond}} = (0.333 \text{ mol}) (-40.5 \text{ kJ/mol}) (10^3 \text{ J/kJ}) = -13486.5 \text{ J (unrounded)}$$

Cooling liquid to 25.0°C :

$$q_3 = Cm\Delta T = (2.45 \text{ J/g}^{\circ}\text{C}) (15.34131 \text{ g}) (25.0 - 78.5)^{\circ}\text{C} = -2010.86 \text{ J (unrounded)}$$

$$q_{\text{total}} = q_1 + q_2 + q_3 = (-4859.28 \text{ J}) + (-13486.5 \text{ J}) + (-2010.86 \text{ J}) = -20356.64 = \mathbf{-2.04 \times 10^4 \text{ J}}$$

12.21 The Clausius-Clapeyron equation gives the relationship between vapor pressure and temperature. Boiling point is defined as the temperature when vapor pressure of liquid equals atmospheric pressure, usually assumed to be exactly 1 atm. So, the number of significant figures in the pressure of 1 atm given is not one, but is unlimited since it is an exact number. In the calculation below, 1.00 atm is used to emphasize the additional significant figures.

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad P_1 = 1.00 \text{ atm}; \quad T_1 = 122^{\circ}\text{C} + 273 = 395 \text{ K};$$

$$T_2 = 113^{\circ}\text{C} + 273 = 386 \text{ K}; \quad P_2 = ?$$

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

$$\frac{P_2}{1.00 \text{ atm}} = 0.7772105 \text{ (unrounded)}$$

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

12.22 The Clausius-Clapeyron equation gives the relationship between vapor pressure and temperature.

$$\ln \frac{P_2}{0.703 \text{ atm}} = \frac{-29.1 \frac{\text{kJ}}{\text{mol}}}{8.314 \text{ J/mol}\cdot\text{K}} \left(\frac{1}{368 \text{ K}} - \frac{1}{298 \text{ K}} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 2.23142 \text{ (unrounded)}$$

$$\frac{P_2}{0.703 \text{ atm}} = 9.33876 \text{ (unrounded)}$$

$$P_2 = (9.33876) (0.703 \text{ atm}) = 6.565149 = \mathbf{6.57 \text{ atm}}$$

- 12.23 At the boiling point, the vapor pressure equals the external pressure. Summarize the pressure and temperature variables and use the Clausius-Clapeyron equation to find the ΔH_{vap} .

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad P_1 = (621 \text{ torr}) \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 0.817105 \text{ atm}$$

$$P_2 = 1.00 \text{ atm} \quad T_1 = 85.2^\circ\text{C} + 273.2 = 358.4 \text{ K}; \quad T_2 = 95.6^\circ\text{C} + 273.2 = 368.8 \text{ K};$$

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

$$0.2019877 = -\Delta H_{\text{vap}}(-9.46377 \times 10^{-6})\text{J/mol}$$

$$\Delta H_{\text{vap}} = 21343.246 = \mathbf{2 \times 10^4 \text{ J/mol}}$$

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

- 12.24 The Clausius-Clapeyron equation gives the relationship between vapor pressure and temperature.

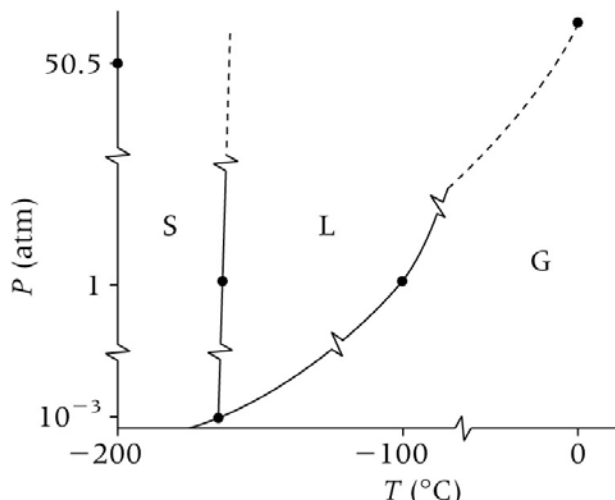
$$\ln \frac{42.8 \text{ atm}}{1 \text{ atm}} = \frac{-\Delta H_{\text{vap}}}{8.314 \text{ J/mol}\cdot\text{K}} \left(\frac{1}{(273 + (-100))\text{K}} - \frac{1}{(273 + (-164))\text{K}} \right)$$

$$3.756538 = 0.00040822 \Delta H_{\text{vap}} \text{ (unrounded)}$$

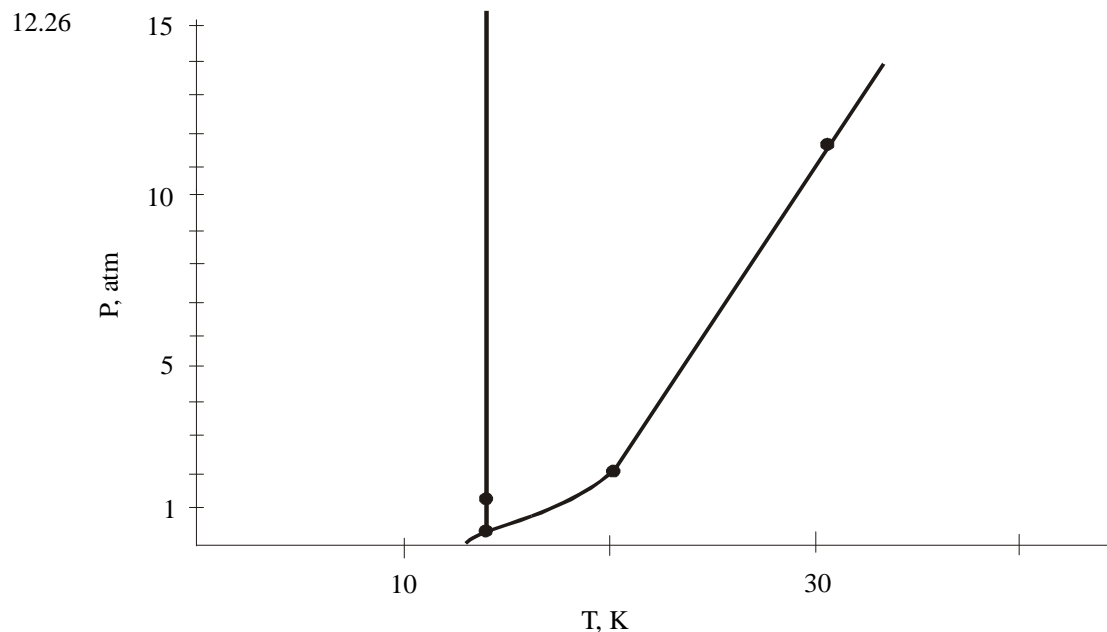
$$\Delta H_{\text{vap}} = (3.756538) / (0.00040822) = 9202.2 = \mathbf{9 \times 10^3 \text{ J/mol}}$$

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

- 12.25



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 Figure 12.9. 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 denser 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.

12.27 This is a step-wise problem to calculate the total heat required.

Melting SO_2 :

$$q_1 = n\Delta H_{\text{cond}} = (2.500 \text{ kg}) (10^3 \text{ g/1 kg}) (1 \text{ mol SO}_2 / 64.07 \text{ g SO}_2) (8.619 \text{ kJ/mol}) (10^3 \text{ J/kJ}) \\ = 336311.8 \text{ J (unrounded)}$$

Warming liquid SO_2 :

$$q_2 = Cm\Delta T = (0.995 \text{ J/g}\cdot^\circ\text{C}) (2.500 \text{ kg}) (10^3 \text{ g/1 kg}) (-10. - (-73))^\circ\text{C} = 156712.5 \text{ J (unrounded)}$$

Vaporizing SO_2 :

$$q_3 = n\Delta H_{\text{cond}} = (2.500 \text{ kg}) (10^3 \text{ g/1 kg}) (1 \text{ mol SO}_2 / 64.07 \text{ g SO}_2) (25.73 \text{ kJ/mol}) (10^3 \text{ J/kJ}) \\ = 1003980.0 \text{ J (unrounded)}$$

Warming gaseous SO_2 :

$$q_4 = Cm\Delta T = (0.622 \text{ J/g}\cdot^\circ\text{C}) (2.500 \text{ kg}) (10^3 \text{ g/1 kg}) (60. - (-10.))^\circ\text{C} = 108850.0 \text{ J (unrounded)}$$

$$q_{\text{total}} = q_1 + q_2 + q_3 + q_4 = (336311.8 \text{ J}) + (156712.5 \text{ J}) + (1003980.0 \text{ J}) + (108850.0 \text{ J}) \\ = 1605854.3 = \mathbf{1.605 \times 10^6 \text{ J}}$$

12.28 This problem is an application of the Clausius-Clapeyron equation. Convert the temperatures from $^\circ\text{C}$ to K and ΔH_{vap} from kJ/mol to J/mol to allow cancellation with the units in R.

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad P_1 = 2.3 \text{ atm}; \quad T_1 = 25.0^\circ\text{C} + 273 = 298 \text{ K};$$

$$T_2 = 135^\circ\text{C} + 273 = 408 \text{ K}; \quad P_2 = ?$$

$$\ln \frac{P_2}{2.3 \text{ atm}} = \frac{-24.3 \frac{\text{kJ}}{\text{mol}}}{8.314 \text{ J/mol}\cdot\text{K}} \left(\frac{1}{408 \text{ K}} - \frac{1}{298 \text{ K}} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 2.89834$$

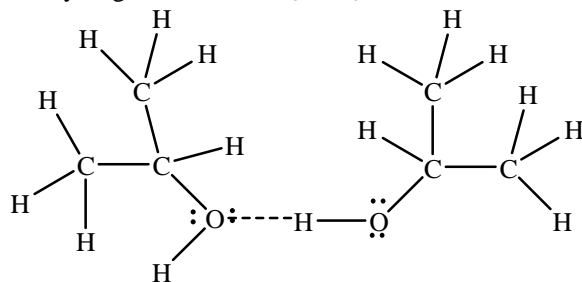
$$\ln \frac{P_2}{2.3 \text{ atm}} = 2.644311$$

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

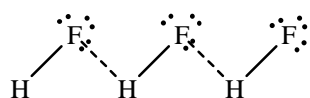
$$P_2 = (14.07374) (2.3 \text{ atm}) = 32.3696 = \mathbf{32 \text{ atm}}$$

- 12.29 a) At 20°C and 40°C, no liquid exists, only gas. At -40°C, liquid exists. At -120°C, **no liquid** exists, only solid.
 b) **No**, at any pressure below the triple-point pressure, the CO₂(s) will sublime.
 c) **No**
 d) **No**
- 12.30 Intermolecular forces involve interactions of lower (partial) charges at relatively larger distances than in covalent bonds.
- 12.31 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.
- 12.32 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 H₂Se that is too small to form hydrogen bonds.
- 12.33 The I-I distance within an I₂ molecule is shorter than the I-I distance between adjacent molecules. This is because the I-I interaction within an I₂ molecule is a true covalent bond and the I-I interaction between molecules is a dispersion force (intermolecular) which is considerably weaker.
- 12.34 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.
- 12.35 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.
- 12.36 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.
- 12.37 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.
 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.
- 12.38 a) **Hydrogen bonding** b) **Dipole-dipole** c) **Ionic bonds**
- 12.39 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.
 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 CH₃CH₃ (ethane) is a symmetrical nonpolar molecule.
 c) **Hydrogen bonding** dominates because hydrogen is bonded to nitrogen, which is one of the 3 atoms (N, O, or F) that participate in hydrogen bonding.
- 12.40 a) **Dispersion** b) **Dipole-dipole** c) **Hydrogen bonding**

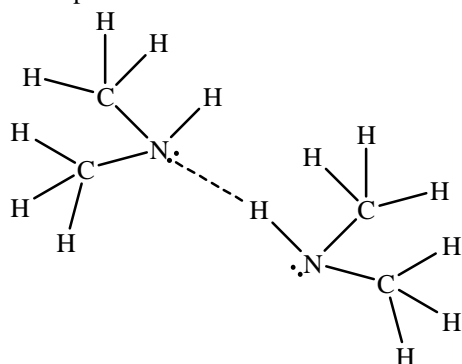
- 12.41 Hydrogen bonds are formed when a hydrogen atom is bonded to N, O, or F.
 a) The presence of an OH group leads to the formation of hydrogen bonds in $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$. There are no hydrogen bonds in CH_3SCH_3 .



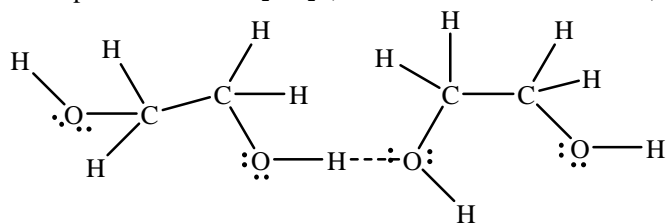
- b) The presence of H attached to F in HF leads to the formation of hydrogen bonds. There are no hydrogen bonds in HBr .



- 12.42 a) The presence of H directly attached to the N in $(\text{CH}_3)_2\text{NH}$ leads to hydrogen bonding. More than one arrangement is possible.



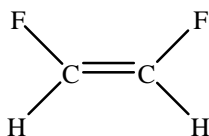
- b) Each of the H's directly attached to O's in $\text{HOCH}_2\text{CH}_2\text{OH}$ leads to hydrogen bonding. More than one arrangement is possible. In $\text{FCH}_2\text{CH}_2\text{F}$, the H atoms are bonded to C, thus there is no hydrogen bonding.



- 12.43 In the vaporization process, intermolecular forces between particles in the liquid phase must be broken as the particles enter the vapor phase. In other words, the question is asking for the strongest interparticle force that must be broken to vaporize the liquid.
- Dispersion**, because hexane, C_6H_{14} , is a nonpolar molecule.
 - Hydrogen bonding**; hydrogen is bonded to oxygen in water. A single water molecule can engage in as many as four hydrogen bonds.
 - Dispersion**, although the individual Si-Cl bonds are polar, the molecule has a symmetrical, tetrahedral shape and is therefore nonpolar.

- 12.44 a) **Dispersion** b) **Dipole-dipole** c) **Hydrogen bonding**

- 12.45 Polarizability increases down a group and decreases from left to right because as atomic size increases, polarizability increases.
- 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.
 - Ethene** ($\text{CH}_2=\text{CH}_2$) has greater polarizability than ethane (CH_3CH_3) because π orbitals are more easily polarized than σ orbitals.
 - H_2Se** has greater polarizability than water because the selenium atom is larger than the oxygen atom.
- 12.46 a) **Ca** b) **$\text{CH}_3\text{CH}_2\text{CH}_3$** c) **$\text{CCl}_4$**
In all cases, the larger molecule (i.e., the one with more electrons) has the higher polarizability.
- 12.47 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.
- C_2H_6** C_2H_6 is a smaller molecule exhibiting weaker dispersion forces than C_4H_{10} .
 - $\text{CH}_3\text{CH}_2\text{F}$** $\text{CH}_3\text{CH}_2\text{F}$ 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 $\text{CH}_3\text{CH}_2\text{OH}$.
 - PH_3** PH_3 has weaker intermolecular forces (dipole-dipole) than NH_3 (hydrogen bonding).
- 12.48 a) **$\text{HOCH}_2\text{CH}_2\text{OH}$** has a larger intermolecular force, because there are more –OH groups to hydrogen bond.
- b) **CH_3COOH** has a larger intermolecular force, because hydrogen bonding is stronger than dipole-dipole forces.
- c) **HF** has a larger intermolecular force, because hydrogen bonding is stronger than dipole-dipole forces.
- 12.49 The weaker the intermolecular forces, the lower the boiling point.
- HCl** would have a lower boiling point than 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.
 - PH_3** , would have a lower boiling point than NH_3 because the intermolecular forces in PH_3 are weaker than those in NH_3 . Hydrogen bonding exists between NH_3 molecules but weaker dipole-dipole forces hold PH_3 molecules together.
 - 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 are since the iodine molecules are more polarizable because of their larger size.
- 12.50 a) **$\text{CH}_3\text{CH}_2\text{OH}$** , hydrogen bonding ($\text{CH}_3\text{CH}_2\text{OH}$) versus dispersion ($\text{CH}_3\text{CH}_2\text{CH}_3$)
- b) **NO**, dipole-dipole (NO) versus dispersion (N_2)
- c) **H_2Te** , the larger molecule has larger dispersion forces
- 12.51 The molecule in the pair with the weaker intermolecular attractive forces will have the lower boiling point.
- C_4H_8** , the cyclic molecule, cyclobutane, has less surface area exposed, so its dispersion forces are less than the straight chain molecule, C_4H_{10} .
 - PBr_3** , the dipole–dipole forces of phosphorous tribromide are weaker than the ionic forces of sodium bromide.
 - HBr**, the dipole-dipole forces of hydrogen bromide are weaker than the hydrogen bonding forces of water.
- 12.52 a) **CH_3OH** , hydrogen bonding (CH_3OH) versus dispersion forces (CH_3CH_3).
- b) **FNO**, greater polarity in FNO versus 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.

- 12.53 The trend in both atomic size and electronegativity predicts that the trend in increasing strength of hydrogen bonds is $N-H < O-H < F-H$. As the atomic size decreases and electronegativity increases, the electron density of the atom increases. High electron density strengthens the attraction to a hydrogen atom on another molecule. Fluorine is the smallest of the three and the most electronegative, so its hydrogen bonds would be the strongest. Oxygen is smaller and more electronegative than nitrogen, so hydrogen bonds for water would be stronger than hydrogen bonds for ammonia.
- 12.54 The molecules of motor oil are long chains of 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.
- 12.55 The ethylene glycol molecules have two sites (two $-OH$ groups) which can hydrogen bond; the propanol only one.
- 12.56 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."
- 12.57 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. Figure 12.20 explains the difference between these forces when *glass*, not *wax*, is used. 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.
- 12.58 The presence of the ethanol molecules breaks up some of the hydrogen bonding interactions present between the water molecules, lowering the surface tension.
- 12.59 Surface tension is defined as the energy needed to increase the surface area by a given amount, so units of energy per surface area describe this property.
- 12.60 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.
- 12.61 The stronger the intermolecular force, the greater the surface tension. All three molecules exhibit hydrogen bonding, but the extent of hydrogen bonding increases with the number of $O-H$ bonds present in each molecule. Molecule b) with 3 $O-H$ groups can form more hydrogen bonds than molecule c) with 2 $O-H$ groups, which in turn can form more hydrogen bonds than molecule a) with only 1 $O-H$ group.
 $CH_3CH_2CH_2OH < HOCH_2CH_2OH < HOCH_2CH(OH)CH_2OH$
 The greater the number of hydrogen bonds, the greater the energy requirements.
- 12.62 **$CH_3OH > H_2CO > CH_3CH_3$**
 The intermolecular forces would decrease as shown (hydrogen bonding $>$ dipole-dipole $>$ dispersion), as would the surface tension.
- 12.63 Viscosity is a measure of the resistance of a liquid to flow, and is greater for molecules with stronger intermolecular forces. The stronger the force attracting the molecules to each other, the harder it is for one molecule to move past another. Thus, the substance will not flow easily if the intermolecular force is strong. The ranking of decreasing viscosity is the opposite of that for increasing surface tension (Problem 12.61).
 $HOCH_2CH(OH)CH_2OH > HOCH_2CH_2OH > CH_3CH_2CH_2OH$

12.64 Viscosity and surface tension both increase with increasing strength of intermolecular forces.
CH₃CH₃ < H₂CO < CH₃OH

12.65 a) The more volatile substances (volatile organic pollutants) are preferentially pulled away from the less volatile substances.
b) The vapor pressure of the volatile organic pollutants increases as the temperature increases. The higher vapor pressure makes it easier to remove the vapor.

12.66 a) Calculate the energies involved using the heats of fusion.

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

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

Mercury takes more energy.

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

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

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

Methane takes more energy.

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

12.67 The pentanol has stronger intermolecular forces (hydrogen bonds) than the hexane (dispersion forces).

12.68 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.

12.69 A single water molecule can form 4 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.

12.70 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.

12.71 Water has a high surface tension. The debris on the surface provides shelter and nutrients for fish, insects, etc.

12.72 Water exhibits strong capillary action, which allows it to be easily absorbed by the plant's roots and transported to the leaves.

12.73 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.

12.74 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.

- 12.75 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.
- 12.76 When the unit cell is repeated infinitely in all directions, the crystal lattice is formed.
- 12.77 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 8 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 2 atoms. The face-centered cell has 6 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).
- 12.78 The unit cell is a simple cubic cell. According to the bottom row in Figure 12.27, two atomic radii (or one atomic diameter) equal the width of the cell.
- 12.79 The layers of a body-centered arrangement are not packed in the most efficient manner. The atoms are only in contact with four other atoms; in a face-centered cubic arrangement, they contact six other atoms. This leads to closer packing and more complete filling of the space in the face-centered arrangement.
- 12.80 Krypton is an atomic solid. In atomic solids, the only interparticle forces are (weak) dispersion forces. Copper is a metallic solid. In metallic solids, additional forces (metallic bonds) lead to different properties.
- 12.81 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.
- 12.82 a) **Conductivity decreases** with increasing temperature.
b) **Conductivity increases** with increasing temperature.
c) **Conductivity does not change** with temperature.
- 12.83 The density of a solid depends on the atomic mass of the element (greater mass = greater density), the atomic radius (how many atoms can fit in a given volume) and the type of unit cell, which determines the packing efficiency (how much of the volume is occupied by empty space).
- 12.84 The simple cubic structure unit cell contains 1 atom since the atoms at the 8 corners are shared by eight cells for a total of $8 \text{ atoms} \times \frac{1}{8} \text{ atom per cell} = 1 \text{ atom}$; the body-centered cell also has an atom in the center, for a total of 2 atoms; the face-centered cell has 6 atoms in the faces which are shared by two cells: $6 \text{ atoms} \times \frac{1}{2} \text{ atom per cell} = 3 \text{ atoms}$ plus another atom from the 8 corners for a total of 4 atoms.
a) Ni is **face-centered cubic** since there are 4 atoms/unit cell.
b) Cr is **body-centered cubic** since there are 2 atoms/unit cell.
c) Ca is **face-centered cubic** since there are 4 atoms/unit cell.
- 12.85 a) **one** b) **two** c) **four**
- 12.86 a) **Yes**, 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 6 in the CdO unit cell to 4 in the CdSe unit cell.
- 12.87 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.

- 12.88 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 are held together by dispersion forces.
 c) Methanol forms a **molecular solid** since the CH_3OH molecules are held together 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.
- 12.89 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)
- 12.90 Figure P12.90 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**.
- 12.91 Figure P12.91 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**.
- 12.92 a) 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 unit cell. 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^{2-} ions**. There are also **4 Zn^{2+} 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)
 $= (4 \times 65.41 \text{ amu}) + (4 \times 78.96 \text{ amu}) = \mathbf{577.48 \text{ amu}}$
 c) 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.

$$\text{Volume} = \left(\frac{\text{cm}^3}{5.42 \text{ g}} \right) \left(\frac{1.66054 \times 10^{-24} \text{ g}}{1 \text{ amu}} \right) (577.48 \text{ amu}) = 1.76924 \times 10^{-22} = \mathbf{1.77 \times 10^{-22} \text{ cm}^3}$$

 d) The volume of a cube equals (length of side)³.

$$\text{Side} = \sqrt[3]{1.76924 \times 10^{-22} \text{ cm}^3} = 5.6139 \times 10^{-8} = \mathbf{5.61 \times 10^{-8} \text{ cm}}$$
- 12.93 a) A face-centered cubic unit cell contains **4 atoms**.
 b) Volume = $(4.52 \times 10^{-8} \text{ cm})^3 = 9.23454 \times 10^{-23} = \mathbf{9.23 \times 10^{-23} \text{ cm}^3}$
 c) Mass of unit cell = $(1.45 \text{ g/cm}^3) (9.23454 \times 10^{-23} \text{ cm}^3) = 1.3390 \times 10^{-22} = \mathbf{1.34 \times 10^{-22} \text{ g}}$
 d) Mass of atom = $\left(\frac{1.3390 \times 10^{-22} \text{ g}}{1 \text{ Unit Cell}} \right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) \left(\frac{1 \text{ amu}}{1.66054 \times 10^{-27} \text{ kg}} \right) \left(\frac{1 \text{ Unit Cell}}{4 \text{ atoms}} \right)$
 $= 20.1592 = \mathbf{20.2 \text{ amu/atom}}$
- 12.94 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.
 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.
- 12.95 a) **conductor** b) **insulator** c) **conductor**

- 12.96 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.
- 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.

12.97 a) **decrease** (metalloid) b) **increase** (metal) c) **decrease** (metalloid)

- 12.98 To calculate an approximate radius for polonium, first multiply the molar mass of Po by the inverse of the density of Po to find the volume per mole Po *metal*.

$$\text{Volume} = \left(\frac{\text{cm}^3}{9.142 \text{ g}} \right) \left(\frac{209 \text{ g}}{1 \text{ mol Po}} \right) = 22.861518 \text{ cm}^3/\text{mol Po (unrounded)}$$

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

The packing efficiency in the simple cubic unit cell is 52%.

Volume/mol of Po atoms = 22.861518 cm³/mol Po x 0.52 = 11.887999 cm³/mol Po atoms

$$\text{Volume of one Po atom} = \left(\frac{11.88799 \text{ cm}^3}{1 \text{ mol Po atoms}} \right) \left(\frac{1 \text{ mol Po atoms}}{6.022 \times 10^{23} \text{ Po atoms}} \right) = 1.97409 \times 10^{-23} \text{ cm}^3/\text{atom}$$

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

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

$$r = \sqrt[3]{\frac{3V}{4\pi}} = \sqrt[3]{\frac{3(1.97409 \times 10^{-23} \text{ cm}^3)}{4\pi}} = 1.676588 \times 10^{-8} = \mathbf{1.68 \times 10^{-8} \text{ cm}}$$

- 12.99 To calculate an approximate radius for copper, first multiply the molar mass of Cu by the inverse of the density of Cu to find the volume per mole Cu *metal*.

$$\text{Volume} = \left(\frac{\text{cm}^3}{8.95 \text{ g}} \right) \left(\frac{63.55 \text{ g}}{1 \text{ mol Cu}} \right) = 7.1005586 \text{ cm}^3/\text{mol Cu (unrounded)}$$

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

The packing efficiency in the face-centered cubic unit cell is 74%.

Volume/mol of Cu atoms = 7.1005586 cm³/mol Cu x 0.74 = 5.2544134 cm³/mol Cu atoms

$$\text{Volume of one Cu atom} = \left(\frac{5.2544134 \text{ cm}^3}{1 \text{ mol Cu atoms}} \right) \left(\frac{1 \text{ mol Cu atoms}}{6.022 \times 10^{23} \text{ Cu atoms}} \right) = 8.725363 \times 10^{-24} \text{ cm}^3/\text{atom}$$

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

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

$$r = \sqrt[3]{\frac{3V}{4\pi}} = \sqrt[3]{\frac{3(8.725363 \times 10^{-24} \text{ cm}^3)}{4\pi}} = 1.2771198 \times 10^{-8} = \mathbf{1.28 \times 10^{-8} \text{ cm}}$$

- 12.100 a) Edge of unit cell = $\sqrt[3]{\left(\frac{\text{cm}^3}{10.28 \text{ g}} \right) \left(\frac{95.94 \text{ g Mo}}{1 \text{ mol Mo}} \right) \left(\frac{1 \text{ mol Mo}}{6.022 \times 10^{23} \text{ Mo atoms}} \right) (2 \text{ Mo atom})}$
 $= 3.1412218 \times 10^{-8} = \mathbf{3.141 \times 10^{-8} \text{ cm}}$

$$\text{b) Volume} = \left(\frac{\text{cm}^3}{10.28 \text{ g}} \right) \left(\frac{95.94 \text{ g}}{1 \text{ mol Mo}} \right) = 9.3326848 \text{ cm}^3/\text{mol Mo (unrounded)}$$

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

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

Volume/mol of Mo atoms = $9.3326848 \text{ cm}^3/\text{mol Mo} \times 0.68 = 6.346226 \text{ cm}^3/\text{mol Mo atoms}$

$$\text{Volume of one Mo atom} = \left(\frac{6.346226 \text{ cm}^3}{1 \text{ mol Mo atoms}} \right) \left(\frac{1 \text{ mol Mo atoms}}{6.022 \times 10^{23} \text{ Mo atoms}} \right) = 1.05384 \times 10^{-23} \text{ cm}^3/\text{atom}$$

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

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

$$r = \sqrt[3]{\frac{3V}{4\pi}} = \sqrt[3]{\frac{3(1.05384 \times 10^{-23} \text{ cm}^3)}{4\pi}} = 1.36007 \times 10^{-8} = \mathbf{1.360 \times 10^{-8} \text{ cm}}$$

$$\begin{aligned} 12.101 \quad \text{Avogadro's Number} &= \left(\frac{180.9479 \text{ g}}{\text{mol}} \right) \left(\frac{\text{cm}^3}{16.634 \text{ g}} \right) \left(\frac{10^{-2} \text{ m}}{1 \text{ cm}} \right)^3 \left(\frac{0.01 \text{ \AA}}{10^{-12} \text{ m}} \right)^3 \left(\frac{2 \text{ atoms}}{(3.3058 \text{ \AA})^3} \right) \\ &= 6.0222269 \times 10^{23} = \mathbf{6.022 \times 10^{23} \text{ atoms/mol}} \end{aligned}$$

12.102 A metal's strength (as well as its other properties) depends on the number of valence electrons in the metal. An alloy of tin in copper is harder than pure copper because tin contributes additional valence electrons for the metallic bonding.

12.103 In an n-type semiconductor, an atom with more valence electrons than the host is doped in. The "extra" electrons are free to move in the conduction band. In a p-type semiconductor, an atom with fewer valence electrons than the host is doped in. This creates "holes" in the valence band, which allows valence electrons to move more readily. Either of these increases the conductivity of the host.

12.104 These liquid crystal molecules generally have a long, cylindrical shape and a structure that allows intermolecular attractions through dispersion, dipole-dipole, and/or hydrogen bonding forces, but inhibits perfect crystalline molecular packing. This allows an electric field to orient the polar molecules in approximately the same direction, so, like crystalline solids; liquid crystals may pack at the molecular level with a high degree of order.

12.105 A substance whose physical properties are the same in all directions is called isotropic; otherwise, the substance is anisotropic. Liquid crystals flow like liquids but have a degree of order that gives them the anisotropic properties of a crystal.

12.106 Modern ceramics, like traditional clay ceramics, are hard and resist heat and chemical attack. Additionally, modern ceramics show superior electrical and magnetic properties. Silicon nitride is virtually inert chemically, retains its strength at high temperatures, and is an electrical insulator. Boron nitride is an electrical insulator in its graphite-like form, and is converted to an extremely hard and durable diamond-like structure at high temperature and pressure.

12.107 The average molar mass of a polymer sample is different from the molar mass of an individual chain because the degree of polymerization differs from chain to chain. As a result, the chain length within a sample varies, so molar masses vary.

12.108 The radius of gyration is the average distance from the center of mass of the polymer to the outside edge of the chain. A tighter random-coil shape and shorter length for the polymer will give a smaller radius of gyration.

12.109 The size (molar mass), concentration of the polymer, and the strength of the intermolecular forces influence the viscosity of a polymer solution.

Chain entanglement and intermolecular forces influence the viscosity of a molten polymer.

Non-crystallized polymer chains form polymer glass.

- 12.110 Increased branching in a polymer results in less tightly packed molecules and a less rigid polymer. High-density polyethylene (HDPE) is more rigid than low-density polyethylene (LDPE). HDPE is used to make rigid food containers, such as 2-Liter soft drink bottles. LDPE is used to make less rigid food containers, such as sandwich bags. Crosslinking results in very strong polymers. Kevlar, used in bulletproof vests, is highly crosslinked.
- 12.111 Germanium and silicon are elements in group 4A with 4 valence electrons. If germanium or silicon is doped with an atom with more than 4 valence electrons, an n-type semiconductor is produced. If it is doped with an atom with fewer than 4 valence electrons, a p-type semiconductor is produced.
- a) Phosphorus has 5 valence electrons so an **n-type semiconductor** will form by doping Ge with P.
 b) Indium has 3 valence electrons so a **p-type semiconductor** will form by doping Si with In.

12.112 a) **n-type** b) **p-type**

12.113 The degree of polymerization is the number of monomer, or repeat units that are bonded together in the polymer chain. Since the molar mass of one monomer unit, $C_6H_5CHCH_2$, is 104.14 g/mol, there are $(3.5 \times 10^5 \text{ g/mol} / 104.14 \text{ g/mol}) = 3361$ monomer units. Reporting in correct significant figures, $n = 3.4 \times 10^3$.

12.114 Molar mass (g/mol) = 1565 units \times 62.49 g/mol = $9.779685 \times 10^4 = 9.780 \times 10^4 \text{ g/mol}$

12.115 The length of the repeat unit, l_0 , is given (0.252 pm). Calculate the degree of polymerization, n , by dividing the molar mass of the polymer chain ($M = 2.8 \times 10^5 \text{ g/mol}$) by the molar mass of one monomer unit (CH_3CHCH_2 , $M = 42.08 \text{ g/mol}$). Substitute these values into the equation below:
 The degree of polymerization = $(2.8 \times 10^5 \text{ g/mol}) / (42.08 \text{ g/mol}) = 6653.99$ (unrounded)

$$\text{Radius of gyration} = R_g = \sqrt{\frac{n l_0^2}{6}}$$

$$R_g = \sqrt{\frac{(6653.99)(0.252 \text{ pm})^2}{6}} = 8.39201 = \mathbf{8.4 \text{ pm}}$$

Note that the length of the repeat unit may actually be 0.252 nm, which leads to a radius of gyration = 7.9 nm.

12.116 The degree of polymerization = $(2.30 \times 10^4 \text{ g/mol}) / (192.2 \text{ g/mol}) = 119.667$ (unrounded)

$$\text{Radius of gyration} = R_g = \sqrt{\frac{n l_0^2}{6}}$$

$$\text{Radius of gyration} = \sqrt{\frac{(119.667)(1.075 \text{ nm})^2}{6}} = 4.80087 = \mathbf{4.80 \text{ nm}}$$

12.117 The vapor pressure of H_2O is 4.6 torr at 0°C , 9.2 torr at 10°C , and 19.8 torr at 22°C .

$$\begin{aligned} \text{Mass } H_2O \text{ at } 22^\circ\text{C} = PV / RT &= \frac{\left[\left(\frac{44\%}{100\%} \right) (19.8 \text{ torr}) \right] (0.75 \text{ L})}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \right) ((273 + 22) \text{ K})} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) \left(\frac{18.02 \text{ g } H_2O}{1 \text{ mol } H_2O} \right) \\ &= 0.006396687 \text{ g } H_2O \text{ (unrounded)} \end{aligned}$$

$$\begin{aligned} \text{Mass } H_2O \text{ at } 0^\circ\text{C} = PV / RT &= \frac{(4.6 \text{ torr})(0.75 \text{ L})}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \right) ((273.2 + 0.0) \text{ K})} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) \left(\frac{18.02 \text{ g } H_2O}{1 \text{ mol } H_2O} \right) \\ &= 0.003647005 \text{ g } H_2O \text{ (unrounded)} \end{aligned}$$

$$\text{Mass } H_2O \text{ condensed} = (0.006396687 \text{ g } H_2O) - (0.003647005 \text{ g } H_2O) = 0.00274968 = \mathbf{0.0027 \text{ g } H_2O}$$

b) Repeat the calculation at 10°C

$$\text{Mass H}_2\text{O at 10}^\circ\text{C} = PV / RT = \frac{(9.2 \text{ torr})(0.75 \text{ L})}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)\left((273 + 10) \text{ K}\right)} \left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) \left(\frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}}\right)$$

$$= 0.007041427 \text{ g H}_2\text{O (unrounded)}$$

At equilibrium, 0.0070 g of H₂O could be in the vapor state. Since only 0.0063 g of H₂O are actually present, no liquid would condense at 10°C.

12.118 At 22°C the vapor pressure of water is 19.8 torr (from Table 5.3).

a) Once compressed, the N₂ gas would still be saturated with water. The vapor pressure depends on the temperature, which has not changed. Therefore, the partial pressure of water in the compressed gas remains the same at **19.8 torr**.

b) In order to maintain the vapor pressure of water at 19.8 torr, some of the water must condense to liquid. The volume is now one-half the original volume (5.00 L / 2 = 2.50 L). The mass of water contained in the “lost” volume may be calculated.

$$\text{Moles H}_2\text{O at 22}^\circ\text{C} = n = PV / RT = \frac{(19.8 \text{ torr})(2.50 \text{ L})}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)\left((273 + 22) \text{ K}\right)} \left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) = 0.002689 \text{ mol H}_2\text{O}$$

$$\text{Mass H}_2\text{O at 22}^\circ\text{C} = (0.002689 \text{ mol H}_2\text{O}) \left(\frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}}\right) = 0.0484558 = \mathbf{0.0485 \text{ g H}_2\text{O}}$$

$$12.119 \text{ Volume} = \left(\frac{\text{cm}^3}{3.62 \text{ g}}\right) \left(\frac{137.3 \text{ g}}{1 \text{ mol Ba}}\right) = 37.928176 \text{ cm}^3/\text{mol Ba (unrounded)}$$

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

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

Volume/mol of Ba atoms = 37.928176 cm³/mol Ba x 0.68 = 25.791116 cm³/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:

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

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

12.120 First use the Clausius-Clapeyron equation to determine the heat of vaporization of hexane.

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad P_1 = 121 \text{ mm Hg} \quad P_2 = 760 \text{ mm Hg}$$

$$T_1 = 20.0^\circ\text{C} + 273.2 = 293.2 \text{ K}; \quad T_2 = 68.7^\circ\text{C} + 273.2 = 341.9 \text{ K};$$

$$\ln \frac{760 \text{ mm Hg}}{121 \text{ mm Hg}} = \frac{-\Delta H_{\text{vap}}}{8.314 \text{ J/mol}\cdot\text{K}} \left(\frac{1}{341.9 \text{ K}} - \frac{1}{293.2 \text{ K}}\right)$$

$$1.8375279 = -\Delta H_{\text{vap}}(-5.84327 \times 10^{-5}) \text{ J/mol}$$

$$\Delta H_{\text{vap}} = 3.1447 \times 10^4 = \mathbf{3.14 \times 10^4 \text{ J/mol}}$$

The LFL of hexane is 1.1%. Or, the mole fraction of hexane is 0.011. According to Dalton’s Law, the partial pressure of hexane at the flash point can be found:

$$P_{\text{hexane}} = (X_{\text{hexane}})(P_{\text{total}})$$

$$P_{\text{hexane}} = (0.011)(760 \text{ mm Hg}) = 8.36 = \mathbf{8.4 \text{ mm Hg}}$$

Use the Clausius-Clapeyron to find the temperature of this particular vapor pressure:

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad P_1 = 760 \text{ mm Hg} \quad P_2 = 8.4 \text{ mm Hg}$$

$$T_1 = 68.7^\circ\text{C} + 273.2 = 341.9 \text{ K}; \quad T_2 = ? \quad \Delta H_{\text{vap}} = 3.1447 \times 10^4 \text{ J/mol}$$

$$\ln \frac{8.4 \text{ mm Hg}}{760 \text{ mm Hg}} = \frac{-3.1447 \times 10^4 \text{ J/mol}}{8.314 \text{ J/mol}\cdot\text{K}} \left(\frac{1}{T_2} - \frac{1}{341.9 \text{ K}} \right)$$

$$-4.5050867 = -3782.415 \left(\frac{1}{T_2} \right) + 11.06293$$

$$T_2 = 242.961 = 243.0 \text{ K} - 273.2 = -30.2^\circ\text{C}$$

12.121 a) I, II, III, V

b) IV

c) V \rightarrow IV \rightarrow liquid \rightarrow 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

12.122 The lowest energy will be for a photon striking an **edge** (4.48 eV).

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{(4.48 \text{ eV})} \left(\frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}} \right) \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}} \right) = 276.9696 = \mathbf{277 \text{ nm}}$$

12.123 a) The silicon ingot is a cylinder with $r = \frac{1}{2}$ (diameter) = $\frac{1}{2}(5.20 \text{ in}) = 2.60 \text{ in} = 6.604 \text{ cm}$. Use the density of Si ($d = 2.34 \text{ g/cm}^3$) and mass of the ingot to determine its volume. Solve for the height of the cylinder using $V = \pi r^2 h$. Divide cylinder height by wafer thickness to determine the number of wafers possible.

$$\text{Volume Si} = (\text{cm}^3 / 2.34 \text{ g}) (10^3 \text{ g/kg}) (4.00 \text{ kg}) = 1709.402 \text{ cm}^3$$

$$\text{Height} = h = V / \pi r^2 = (1709.402 \text{ cm}^3) / [\pi(5.20 \text{ in}/2)^2(2.54 \text{ cm/in})^2] = 12.476 \text{ cm (unrounded)}$$

$$\text{Number of wafers} = [(12.476 \text{ cm}) (10^{-2} \text{ m/cm})] / (1.12 \times 10^{-4} \text{ m/wafer})$$

$$= 1113.928 = \mathbf{1.11 \times 10^3 \text{ wafers}}$$

b) A single wafer is also a cylinder with dimensions $h = 1.12 \times 10^{-4} \text{ m}$ and $r = 5.20 \text{ in} / 2$. The volume of the cylinder can be converted to mass using the density ($d = 2.34 \text{ g/cm}^3$).

$$\text{Mass} = \pi r^2 h d = \pi[(5.20 \text{ in} / 2) (2.54 \text{ cm/in})]^2 [(1.12 \times 10^{-4} \text{ m}) (1 \text{ cm} / 10^{-2} \text{ m})] (2.34 \text{ g/cm}^3)$$

$$= 3.5909 = \mathbf{3.59 \text{ g}}$$

c) Silicon reacts with oxygen to form silicon dioxide, $\text{SiO}_2(s)$. This oxide coating interferes with the operation of the wafer and is removed by gaseous hydrogen fluoride, $\text{HF}(g)$. In a double displacement reaction, silicon's 4 valence electrons combine with 4 fluorine atoms: $\text{SiO}_2(s) + 4 \text{HF}(g) \rightarrow \text{SiF}_4(g) + 2 \text{H}_2\text{O}(g)$

$$\text{d) Moles HF} = (3.5909 \text{ g Si}) \left(\frac{1 \text{ mol Si}}{28.09 \text{ g Si}} \right) \left(\frac{0.750\%}{100\%} \right) \left(\frac{4 \text{ mol HF}}{1 \text{ mol Si}} \right) = 3.83506 \times 10^{-3} = \mathbf{3.84 \times 10^{-3} \text{ mol HF}}$$

12.124 a) The enthalpy of vaporization must be determined first.

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

$$\ln \frac{1.00 \text{ torr}}{10.0 \text{ torr}} = \frac{-\Delta H_{\text{vap}}}{8.314 \text{ J/mol}\cdot\text{K}} \left(\frac{1}{(273.2 + 54.3)\text{K}} - \frac{1}{(273.2 + 95.3)\text{K}} \right)$$

$$-2.302585 = -0.0000408625 \Delta H_{\text{vap}}$$

$$\Delta H_{\text{vap}} = (-2.302585) / (-0.000040862) = 56350.28 = \mathbf{5.6 \times 10^4 \text{ J/mol}}$$

The subtraction of the 1/T terms limits the significant figures.

$$\ln \frac{P_2}{10.0 \text{ torr}} = \frac{-56350.28 \frac{\text{J}}{\text{mol}}}{8.314 \text{ J/mol}\cdot\text{K}} \left(\frac{1}{(273 + 25)\text{K}} - \frac{1}{(273.2 + 95.3)\text{K}} \right) = -4.351269 \text{ (unrounded)}$$

$$\frac{P_2}{10.0 \text{ torr}} = 0.0128897$$

$$P_2 = (0.0128897) (10.0 \text{ torr}) = 0.128897 = \mathbf{0.13 \text{ torr}}$$

$$\begin{aligned} \text{b) } V = nRT / P &= \frac{(1.0 \text{ mg}) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) \left((273 + 25)\text{K} \right)}{(0.128897 \text{ torr})} \left(\frac{760 \text{ torr}}{1 \text{ atm}} \right) \left(\frac{10^{-3} \text{ g}}{1 \text{ mg}} \right) \left(\frac{1 \text{ mol}}{152.16 \text{ g}} \right) \\ &= 0.94805 = \mathbf{0.95 \text{ L}} \end{aligned}$$

12.125 The Clausius-Clapeyron equation can be solved for the temperature that will give a vapor pressure of 5.0×10^{-5} torr.

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

$$P_2 = 5.0 \times 10^{-5} \text{ torr}; \quad T_2 = ?$$

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

$$-3.17805 = -7108.49 \left(\frac{1}{(T)\text{K}} - \frac{1}{(293)\text{K}} \right) \text{ (unrounded)}$$

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

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

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

- 12.126 a) Molar mass of fraction 1 (g/mol) = 273 units x 100.02 g/mol = $2.7305 \times 10^4 = \mathbf{2.73 \times 10^4 \text{ g/mol}}$
 Molar mass of fraction 2 (g/mol) = 330 units x 100.02 g/mol = $3.30066 \times 10^4 = \mathbf{3.30 \times 10^4 \text{ g/mol}}$
 Molar mass of fraction 3 (g/mol) = 368 units x 100.02 g/mol = $3.6807 \times 10^4 = \mathbf{3.68 \times 10^4 \text{ g/mol}}$
 Molar mass of fraction 4 (g/mol) = 483 units x 100.02 g/mol = $4.83097 \times 10^4 = \mathbf{4.83 \times 10^4 \text{ g/mol}}$
 Molar mass of fraction 5 (g/mol) = 525 units x 100.02 g/mol = $5.25105 \times 10^4 = \mathbf{5.25 \times 10^4 \text{ g/mol}}$
 Molar mass of fraction 6 (g/mol) = 575 units x 100.02 g/mol = $5.75115 \times 10^4 = \mathbf{5.75 \times 10^4 \text{ g/mol}}$

b) Average molar mass (g/mol) =

$$\frac{(100.02 \text{ g/mol}) [273(0.10) + 330(0.40) + 368(1.00) + 483(0.70) + 525(0.30) + 575(0.10)]}{(0.10 + 0.40 + 1.00 + 0.70 + 0.30 + 0.10) \text{ mol}}$$

$$= 4.1562 \times 10^4 = \mathbf{4.2 \times 10^4 \text{ g/mol}}$$

$$\begin{aligned} \text{c) } \mathcal{M} &= \{ [(2.73 \times 10^4 \text{ g/mol})^2 (0.10 \text{ mol}) + (3.30 \times 10^4 \text{ g/mol})^2 (0.40 \text{ mol}) + (3.68 \times 10^4 \text{ g/mol})^2 (1.00 \text{ mol}) \\ &+ (4.83 \times 10^4 \text{ g/mol})^2 (0.70 \text{ mol}) + (5.25 \times 10^4 \text{ g/mol})^2 (0.30 \text{ mol}) + (5.75 \times 10^4 \text{ g/mol})^2 (0.10 \text{ mol})] \} / 108,040 \text{ g} \\ &= 4.3085 \times 10^4 = \mathbf{4.3 \times 10^4 \text{ g/mol}} \end{aligned}$$

- 12.127 a) Use the volume of the liquid water and the density of water to find the moles of water present in the volume of the greenhouse. Find the pressure of this number of moles of water vapor using the Ideal Gas Equation.

$$P = \frac{nRT}{V} = \frac{\left[4.20\text{L} \left(\frac{1\text{ mL}}{10^{-3}\text{ L}}\right) \left(\frac{1.00\text{ g}}{\text{mL}}\right) \left(\frac{1\text{ mol H}_2\text{O}}{18.02\text{ g H}_2\text{O}}\right)\right] \left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right) \left((273 + 26)\text{K}\right)}{(256\text{ m}^3)} \left(\frac{10^{-3}\text{ m}^3}{1\text{ L}}\right)$$

$$= 2.223496 \times 10^{-2} = \mathbf{2.23 \times 10^{-2}\text{ atm}}$$

- b) 25.2 torr is needed to saturate the air, so the volume of liquid water needed is:

$$V = (4.20\text{ L}) \left(\frac{25.2\text{ torr}}{2.223496 \times 10^{-2}\text{ atm}}\right) \left(\frac{1\text{ atm}}{760\text{ torr}}\right) = 6.26325 = \mathbf{6.26\text{ L H}_2\text{O}}$$

- 12.128 The formulas are **TaC** and **TaN**.

- 12.129 The density of Fe is 7.874 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.

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

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

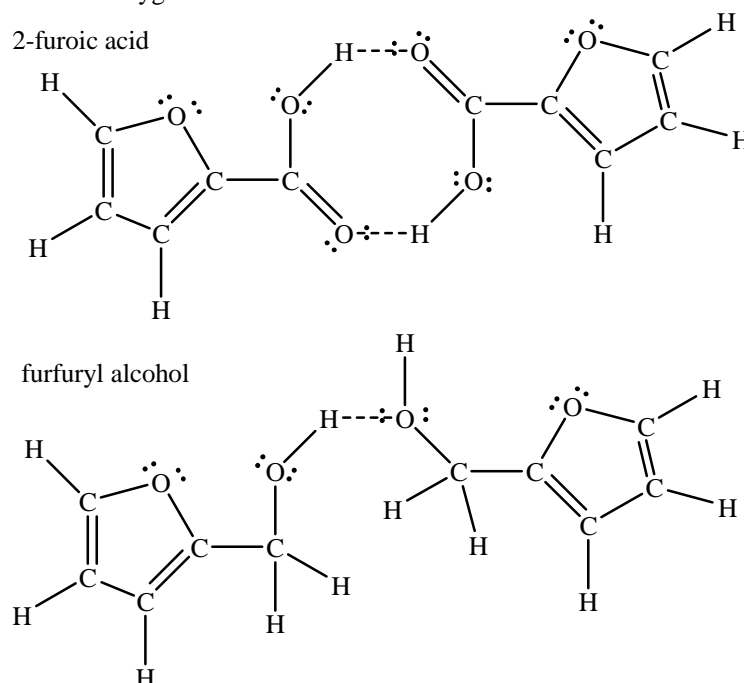
Volume / mole Fe atoms = $(7.09296\text{ cm}^3/\text{mol Fe}) (68\% / 100\%) = 4.82321\text{ cm}^3/\text{mol Fe atoms}$ (unrounded)

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

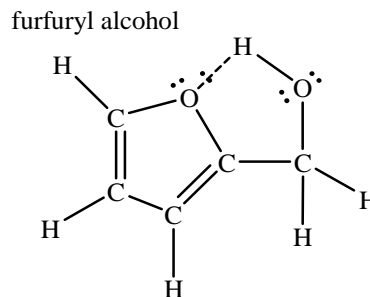
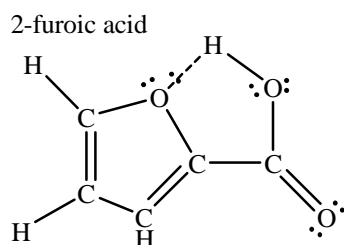
Atoms / mol = $(4.82321\text{ cm}^3/\text{mol Fe atoms}) (1\text{ Fe atom} / 8.38 \times 10^{-24}\text{ cm}^3)$

$$= 5.7556 \times 10^{23} = \mathbf{5.8 \times 10^{23}\text{ atoms/mol}}$$

- 12.130 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.



12.131 Determine the total mass of water, with a partial pressure of 31.0 torr, contained in the air. Then calculate the total mass of water, with a partial pressure of 10.0 torr, contained in the air. The difference between these two values is the amount of water removed. The mass of water and the heat of condensation are necessary to find the amount of energy removed from the water.

a) $n = PV / RT$

Mass H₂O (31.0 torr) = mol H₂O x (18.02 g/mol)

$$= \frac{(31.0 \text{ torr})(2.4 \times 10^6 \text{ m}^3)}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)\left((273.2 + 22.0) \text{ K}\right)} \left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) \left(\frac{1 \text{ L}}{10^{-3} \text{ m}^3}\right) \left(\frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}}\right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}}\right) \left(\frac{1 \text{ ton}}{10^3 \text{ kg}}\right)$$

$$= 72.7871 \text{ tons H}_2\text{O (unrounded)}$$

Mass H₂O (10.0 torr) = mol H₂O x (18.02 g/mol)

$$= \frac{(10.0 \text{ torr})(2.4 \times 10^6 \text{ m}^3)}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)\left((273.2 + 22.0) \text{ K}\right)} \left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) \left(\frac{1 \text{ L}}{10^{-3} \text{ m}^3}\right) \left(\frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}}\right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}}\right) \left(\frac{1 \text{ ton}}{10^3 \text{ kg}}\right)$$

$$= 23.4797 \text{ tons H}_2\text{O (unrounded)}$$

Mass of water removed = (72.7871 tonnes H₂O) – (23.4797 tonnes H₂O) = 49.3074 = **49.3 tons H₂O**

b) The heat of condensation for water is –40.7 kJ/mol.

$$\text{Heat} = (49.3074 \text{ tons H}_2\text{O}) \left(\frac{10^3 \text{ kg}}{1 \text{ ton}}\right) \left(\frac{10^3 \text{ g}}{1 \text{ kg}}\right) \left(\frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}}\right) \left(\frac{-40.7 \text{ kJ}}{1 \text{ mol H}_2\text{O}}\right)$$

$$= -1.113658 \times 10^8 = \mathbf{-1.11 \times 10^8 \text{ kJ}}$$

12.132 At the boiling point, the vapor pressure equals the atmospheric pressure, so the two boiling points can be used to find the heat of vaporization for amphetamine using the Clausius-Clapeyron equation.

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

$P_1 = 760 \text{ torr}$

$T_1 = 201^\circ\text{C} = (273 + 201) = 474 \text{ K}$

$P_2 = 13 \text{ torr}$

$T_2 = 83^\circ\text{C} = (273 + 83) = 356 \text{ K}$

$\Delta H_{\text{vap}} = ?$

$$\ln \frac{13 \text{ torr}}{760 \text{ torr}} = \frac{-\Delta H_{\text{vap}}}{8.314 \text{ J/mol}\cdot\text{K}} \left(\frac{1}{356 \text{ K}} - \frac{1}{474 \text{ K}} \right)$$

$-4.068369076 = -0.000084109 \Delta H_{\text{vap}}$ (unrounded)

$\Delta H_{\text{vap}} = (-4.068369076) / (-0.000084109) = 48370.199 \text{ J/mol (unrounded)}$

Use the Clausius-Clapeyron equation to find the vapor pressure of amphetamine at 20.°C

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

$$P_1 = 13 \text{ torr} \quad T_1 = 83^\circ\text{C} = (273 + 83) = 356 \text{ K}$$

$$P_2 = ? \quad T_2 = 20.^\circ\text{C} = (273 + 20.) = 293 \text{ K}$$

$$\Delta H_{\text{vap}} = 48370.199 \text{ J/mol}$$

$$\ln \frac{P_2}{13 \text{ torr}} = \frac{-48370.199 \frac{\text{J}}{\text{mol}}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{293 \text{ K}} - \frac{1}{356 \text{ K}} \right) = -3.5139112 \text{ (unrounded)}$$

$$\frac{P_2}{13 \text{ torr}} = 0.0297802 \text{ (unrounded)}$$

$$P_2 = (0.0297802) (13 \text{ torr}) (1 \text{ atm} / 760 \text{ torr}) = 5.09398 \times 10^{-4} \text{ atm (unrounded)}$$

At this pressure and a temperature of 20.°C, use the ideal gas equation to calculate the concentration of amphetamine in the air. Use a volume of 1 m³. Moles from the ideal gas equation times the molar mass gives the mass in a cubic meter.

$$\text{Moles} = n = \frac{PV}{RT} = \frac{(5.09398 \times 10^{-4} \text{ atm})(1 \text{ m}^3)}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(293 \text{ K})} \left(\frac{1 \text{ L}}{10^{-3} \text{ m}^3} \right) = 0.02117612 \text{ mol amphetamine}$$

$$(0.02117612 \text{ mol}) \left(\frac{135.20 \text{ g amphetamine}}{1 \text{ mol}} \right) = 2.8630114 = \mathbf{2.9 \text{ g/m}^3}$$

$$12.133 \text{ a) Unit cell edge} = \sqrt[3]{\frac{\text{cm}^3}{3.52 \text{ g}} \left(\frac{12.01 \text{ g C}}{1 \text{ mol C}} \right) \left(\frac{1 \text{ mol C}}{6.022 \times 10^{23} \text{ C atoms}} \right) (8 \text{ C atoms})}$$

$$= 3.5654678 \times 10^{-8} = \mathbf{3.57 \times 10^{-8} \text{ cm}}$$

$$12.133 \text{ b) C atoms/unit cell} = \left(\frac{(3.5654678 \times 10^{-8} \text{ cm})^3}{1 \text{ Unit Cell}} \right) \left(\frac{3.01 \text{ g C}}{\text{cm}^3} \right) \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) \left(\frac{6.022 \times 10^{23} \text{ C atoms}}{1 \text{ mol C}} \right)$$

$$= 6.8409 = \mathbf{6.84 \text{ C atoms/unit cell}}$$

12.134 **No**, filling all the available holes (8) in the face-centered cubic lattice leads to a stoichiometry of 2:1 (8 holes/4 atoms).

12.135 Gallium is not a “normal” liquid (the density of the solid is lower than that of the liquid, like water), so its liquid-solid line would slope left (negative) and the triple-point temperature would be higher than the normal melting point.

12.136 a) Determine the vapor pressure of ethanol in the bottle by applying the Clausius-Clapeyron equation (see Figure 12.6 – use $P_2 = 760 \text{ torr}$ and $T_2 = 78.5^\circ\text{C}$). The ΔH_{vap} (40.5 kJ/mol) is given in Figure 12.1.

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

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

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

$$\Delta H_{\text{vap}} = 40.5 \text{ kJ/mol}$$

$$\ln \frac{760. \text{ torr}}{P_1} = \frac{-40.5 \frac{\text{kJ}}{\text{mol}}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{(351.6) \text{ K}} - \frac{1}{(262) \text{ K}} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 4.738085 \text{ (unrounded)}$$

$$\frac{760. \text{ torr}}{P_1} = 114.215 \text{ (unrounded)}$$

$$P_1 = 6.65410 = 6.65 \text{ torr}$$

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.

$$\text{Mole} = \frac{PV}{RT} = \frac{(6.65410 \text{ torr})(4.7 \text{ L}) \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right)}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (262 \text{ K})} = 0.00191306 \text{ mol C}_2\text{H}_6\text{O (unrounded)}$$

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

$$\text{Mass C}_2\text{H}_6\text{O} = (0.00191306 \text{ mol C}_2\text{H}_6\text{O}) (46.07 \text{ g/mol C}_2\text{H}_6\text{O}) = 0.088134785 = \mathbf{8.8 \times 10^{-2} \text{ g C}_2\text{H}_6\text{O}}$$

b) If the calculation above is carried out at $T_1 = 20.^\circ\text{C} = 293 \text{ K}$, the mass of ethanol present in the vapor, if excess liquid was present, is 0.56 g. Since this exceeds the 0.33 g available, **all of the ethanol will vaporize.**

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

$$\ln \frac{P_2}{760 \text{ torr}} = \frac{-40.5 \frac{\text{kJ}}{\text{mol}}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{(273.2) \text{ K}} - \frac{1}{(351.6) \text{ K}} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -3.97586 \text{ (unrounded)}$$

$$\frac{P_2}{760 \text{ torr}} = 0.018763 \text{ (unrounded)}$$

$$P_2 = (0.018763) (760 \text{ torr}) = 14.2599 \text{ torr (unrounded)}$$

$$\text{Mole} = \frac{PV}{RT} = \frac{(14.2599 \text{ torr})(4.7 \text{ L}) \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right)}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (273.2 \text{ K})} = 0.00393168 \text{ mol C}_2\text{H}_6\text{O (unrounded)}$$

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

$$\text{Mass C}_2\text{H}_6\text{O} = (0.00393168 \text{ mol C}_2\text{H}_6\text{O}) (46.07 \text{ g/mol C}_2\text{H}_6\text{O}) = 0.18113 \text{ g C}_2\text{H}_6\text{O (unrounded)}$$

$$\begin{aligned} \text{m(g) ethanol in liquid} &= \text{m(g) ethanol (total)} - \text{m(g) ethanol in vapor} \\ &= 0.33 \text{ g} - 0.18113 \text{ g} = 0.148867 = \mathbf{0.15 \text{ g C}_2\text{H}_6\text{O}} \end{aligned}$$

12.137 a) To heat the substance to the melting point:

Warming the substance from $-40.^\circ\text{C}$ to $-20.^\circ\text{C}$

$$q_1 = Cm\Delta T = (1.0 \text{ J/g}^\circ\text{C}) (25 \text{ g}) [-20. - (-40.)]^\circ\text{C} = 500 \text{ J}$$

$$\text{Time required: } (500 \text{ J}) \left(\frac{1 \text{ min}}{450 \text{ J}} \right) = \mathbf{1.1 \text{ min}}$$

b) To melt the sample:

Phase change of the substance from solid at $-20.^\circ\text{C}$ to liquid at $-20.^\circ\text{C}$

$$q_2 = n\Delta H_{\text{fus}} = (25 \text{ g}) \left(\frac{180. \text{ J}}{1 \text{ g}} \right) = 4500 \text{ J}$$

$$\text{Time required: } (4500 \text{ J}) \left(\frac{1 \text{ min}}{450 \text{ J}} \right) = \mathbf{10. \text{ min}}$$

c) Warming the liquid from $-20.^\circ\text{C}$ to 85°C

$$q_3 = Cm\Delta T = (2.5 \text{ J/g}^\circ\text{C}) (25 \text{ g}) [85 - (-20.)]^\circ\text{C} = 6562.5 \text{ J}$$

$$\text{Time required: } (6562.5 \text{ J}) \left(\frac{1 \text{ min}}{450 \text{ J}} \right) = 14.583 = \mathbf{15 \text{ min}}$$

Phase change of the substance from liquid at 85°C to gas at 85°C

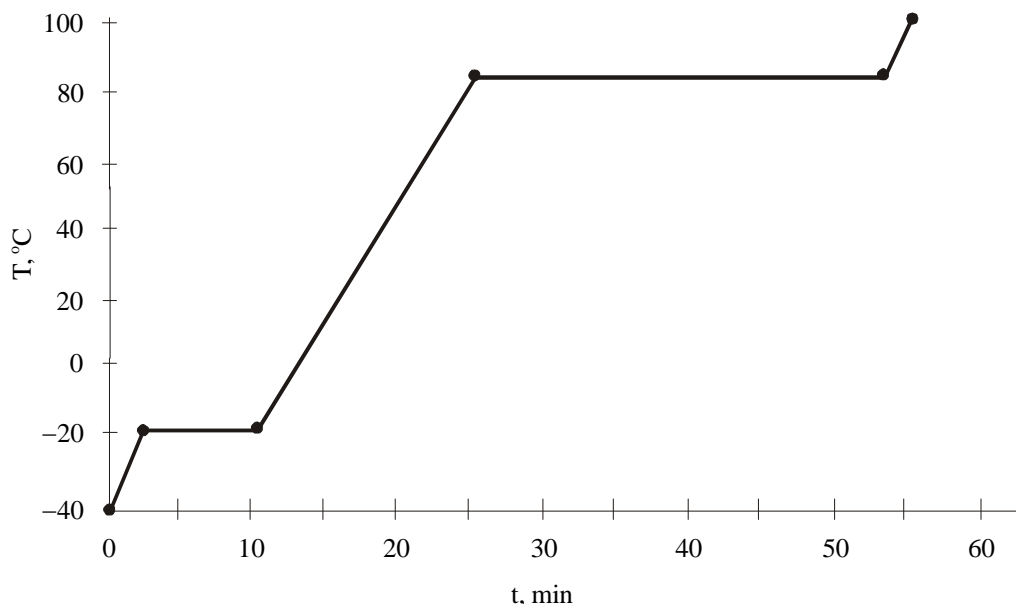
$$q_4 = n\Delta H_{\text{vap}} = (25 \text{ g}) \left(\frac{500. \text{ J}}{1 \text{ g}} \right) = 12500 \text{ J}$$

$$\text{Time required: } (12500 \text{ J}) \left(\frac{1 \text{ min}}{450 \text{ J}} \right) = 27.78 = \mathbf{28 \text{ min}}$$

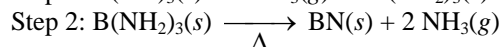
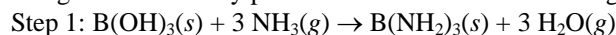
5) Warming the liquid from 85°C to 100.°C

$$q_5 = Cm\Delta T = (0.5 \text{ J/g}^\circ\text{C}) (25 \text{ g}) [100 - 85]^\circ\text{C} = 187.5 \text{ J}$$

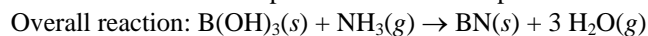
$$\text{Time required: } (187.5 \text{ J}) \left(\frac{1 \text{ min}}{450 \text{ J}} \right) = 0.417 = \mathbf{0.4 \text{ min}}$$



12.138 Balanced chemical equations are necessary. See the section on ceramic materials for the reactions. These equations may be combined to produce an overall equation with an overall yield. From this point on it becomes a straight stoichiometry problem with the aid of the ideal gas equation.



Yields are 85.5% for step 1 and 86.8% for step 2.



Overall fractional yield = (85.5% / 100%) (86.8% / 100%) = 0.74214 (unrounded)

Find the limiting reactant. Since the overall reaction has a 1:1 mole ratio, the reactant with the fewer moles will be limiting.

$$\begin{aligned} \text{Moles B(OH)}_3 &= (1.00 \text{ t B(OH)}_3) \left(\frac{10^3 \text{ kg}}{1 \text{ t}} \right) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol B(OH)}_3}{61.83 \text{ g B(OH)}_3} \right) \\ &= 1.6173378 \times 10^4 \text{ mol B(OH)}_3 \text{ (unrounded)} \end{aligned}$$

$$\begin{aligned} \text{Moles NH}_3 &= PV / RT = \frac{(3.07 \times 10^3 \text{ kPa})(12.5 \text{ m}^3)}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \right) (275 \text{ K})} \left(\frac{1 \text{ atm}}{101.325 \text{ kPa}} \right) \left(\frac{1 \text{ L}}{10^{-3} \text{ m}^3} \right) \\ &= 1.6774744 \times 10^4 \text{ mol NH}_3 \text{ (unrounded)} \end{aligned}$$

Thus, B(OH)₃ is limiting.

$$\begin{aligned} \text{Mass BN} &= (1.6173378 \times 10^4 \text{ mol B(OH)}_3) \left(\frac{1 \text{ mol BN}}{1 \text{ mol B(OH)}_3} \right) \left(\frac{24.82 \text{ g BN}}{1 \text{ mol BN}} \right) \left(\frac{74.214\%}{100\%} \right) = 2.97912 \times 10^5 \\ &= \mathbf{2.98 \times 10^5 \text{ g BN}} \end{aligned}$$

- 12.139 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.

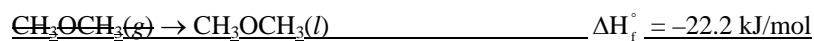
12.140 a) $\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

$$\ln \frac{0.526 \text{ atm}}{1.00 \text{ atm}} = \frac{-\Delta H_{\text{vap}}}{8.314 \text{ J/mol}\cdot\text{K}} \left(\frac{1}{(273.2 + (-37.8))\text{K}} - \frac{1}{(273.2 + (-23.7))\text{K}} \right)$$

$$-0.642454 = -0.00002888 \Delta H_{\text{vap}} \text{ (unrounded)}$$

$$\Delta H_{\text{vap}} = [(-0.642454) / (-0.00002888)] (1 \text{ kJ}/10^3 \text{ J}) = 22.248972 = \mathbf{22.2 \text{ kJ/mol}}$$

b) Use Hess's Law, using the reverse of the answer in part a.



- 12.141 A body-centered unit cell contains two atoms, which would weigh $2 (22.99 \text{ amu}) = \mathbf{45.98 \text{ amu}}$.

- 12.142 In the NaCl type lattice, there are four ions of each type.

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

- 12.143 $[\eta]_{\text{solvent}} = K\mathcal{M}^\alpha$

a) $[\eta]_{\text{benzene}} = (9.5 \times 10^{-3} \text{ mL/g}) (104,160 \text{ g/mol})^{0.74} = 49$

$$[\eta]_{\text{cyclohexane}} = (8.1 \times 10^{-2} \text{ mL/g}) (104,160 \text{ g/mol})^{0.50} = 26$$

Benzene has stronger interactions with the polymer.

b) $[\eta]_{\text{benzene}} = (9.5 \times 10^{-3} \text{ mL/g}) (52,000 \text{ g/mol})^{0.74} = 29$

If you have standards of known molar mass and you measure $[\eta]$, K and (a) can be determined for that polymer and solvent pair. Then a measured $[\eta]$ can be used, along with the values of K and (a), to determine the molar mass of a sample.

c) $[\eta]_{\text{benzene}} = (8.3 \times 10^{-2} \text{ mL/g}) (104,160 \text{ g/mol})^{0.50} = 27$

$$[\eta]_{\text{cyclohexane}} = (2.6 \times 10^{-1} \text{ mL/g}) (104,160 \text{ g/mol})^{0.70} = 850$$

Polyisobutylene has weaker interactions with benzene than polystyrene does, but much stronger interactions with the solvent cyclohexane than polystyrene does.

- 12.144 The heat lost by the coffee equals the heat required to raise the temperature of the ice to 0°C , melt the ice and warm the water from the molten ice.

$$-(\text{heat of coffee}) = (\text{heat to warm the ice}) + (\text{heat to melt ice}) + (\text{heat to warm water from ice})$$

$$-(248 \text{ mL}) (1.0 \text{ g/mL}) (4.184 \text{ J/g}\cdot^\circ\text{C}) (T_f - 98.4)^\circ\text{C}$$

$$= (23.0 \text{ g}) (2.09 \text{ J/g}\cdot^\circ\text{C}) (0.0 - (-2.2))^\circ\text{C} + (23.0 \text{ g ice}) (1 \text{ mol H}_2\text{O} / 18.02 \text{ g ice}) (6.02 \text{ kJ/mol}) (10^3 \text{ J/1 kJ}) \\ + (23.0 \text{ g}) (4.184 \text{ J/g}\cdot^\circ\text{C}) (T_f - 0.0)^\circ\text{C}$$

$$-(1037.632 \text{ J}) (T_f - 98.4) = 105.754 \text{ J} + (7683.68 \text{ J}) + (96.232 \text{ J}) (T_f - 0.0)$$

$$102102.9888 - 1037.632 T_f = 7789.434 + 96.232 T_f$$

$$(96.232 + 1037.632) T_f = 102102.9888 - 7789.434$$

$$T_f = (102102.9888 - 7789.434) / (96.232 + 1037.632) = 83.178895 = \mathbf{83.2^\circ\text{C}}$$

12.145 $\text{Volume} = \left(\frac{70.8 \text{ g}}{\text{L}} \right) \left(\frac{1 \text{ L}}{1 \text{ dm}^3} \right) (1 \text{ dm}^3) \left(\frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} \right) \left(\frac{22.4 \text{ L}}{1 \text{ mol}} \right) = 786.6667 = \mathbf{8 \times 10^2 \text{ L}}$