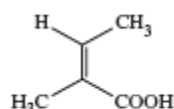


# Ch11

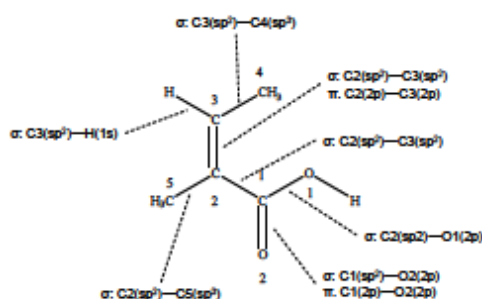
2. Explain why it is necessary to hybridize atomic orbitals when applying the valence-bond method—that is, why are there so few molecules that can be described by the overlap of pure atomic orbitals only?
2. (E) The overlap of pure atomic orbitals gives bond angles of  $90^\circ$  or  $180^\circ$ . These bond angles are suitable only for 3- and 4-atom compounds in which the central atom is an atom of the third (or higher) period of the periodic table. For central atoms from the second period of the periodic table, 3- and 4-atom compounds have bond angles closer to  $180^\circ$ ,  $120^\circ$ , and  $109.5^\circ$  than to  $90^\circ$ . These other bond angles can only be explained well through hybridization. *Second*, hybridization clearly distinguishes between the (hybrid) orbitals that form  $\sigma$  bonds and the  $p$  orbitals that form  $\pi$  bonds. It places those  $p$  orbitals in their proper orientation so that they can overlap side-to-side to form  $\pi$  bonds. *Third*, the bond angles of  $90^\circ$  and  $120^\circ$  that result when the octet of the central atom is expanded cannot be produced with pure atomic orbitals. Hybrid orbitals are necessary. *Finally*, the overlap of pure atomic orbitals does not usually result in all  $\sigma$  bonds being equivalent. Overlaps with hybrid orbitals produce equivalent bonds.

25. Angelic acid, shown below, occurs in sumbol root, a herb used as a stimulant.



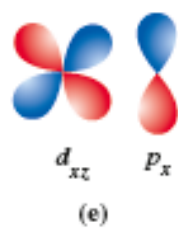
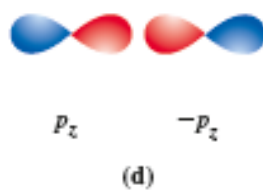
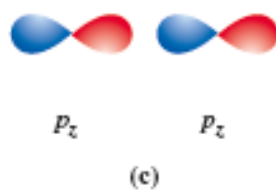
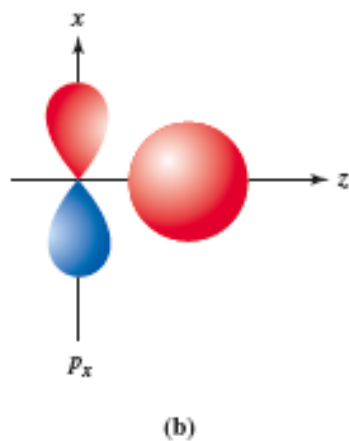
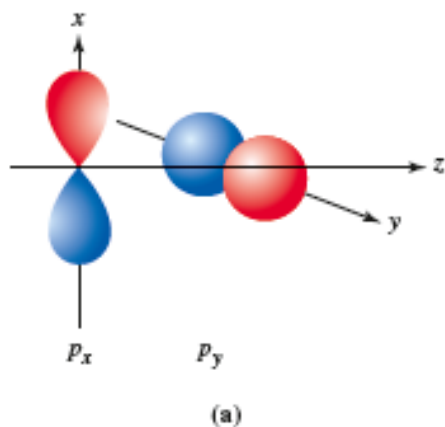
Represent the bonding in the angelic acid molecule by using the method in Figure 11-18 to indicate hybridization schemes and orbital overlaps. What is the maximum number of atoms that can lie in the same plane?

25. (M) The structure is shown below:



There are 8 atoms that are on the same plane (O1, O2, C1-5, H att. To C3). Furthermore, depending on the angle of rotation of the  $-\text{CH}_3$  groups (C4 and C5), two H atoms can also be added to this total.

86. Which of the following combinations of orbitals give rise to bonding molecular orbitals? For those combinations that do, label the resulting bonding molecular orbital as  $s$  or  $p$ .



86. (E)  
 (a) non-bonding, (b) non-bonding, (c) non-bonding (d) bonding,  $\sigma$  (e) bonding,  $\pi$ .

88. In your own words, define the following terms or symbols: (a)  $sp^2$ ; (b)  $\sigma_{2p}^*$ ; (c) bond order; (d)  $\pi$  bond.

88. (E)

- (a)  $sp^2$ : The result of hybridization of one  $s$  and  $2p$  orbitals, giving a trigonal planar geometry  
(b)  $\sigma_{2p}^*$ : The anti-bonding  $\sigma$  orbital created by the combination of two  $p$  orbitals  
(c) Bond order: One-half the difference between the number of bonding and antibonding orbitals  
(d)  $\pi$ -bond: A side-to-side overlap of the unhybridized orbitals (such as the  $p_x$  and  $p_y$  orbitals interacting on their sides.) In this bond, there is a region of high electron charge density above and below the plane of the bond.

96. Delocalized molecular orbitals are found in (a)  $H_2$ ; (b)  $HS^-$ ; (c)  $CH_4$ ; (d)  $CO_3^{2-}$ .

96. (E) The answer is (d). The Lewis structure of  $CO_3^{2-}$  and the result of its resonance structures is shown below:

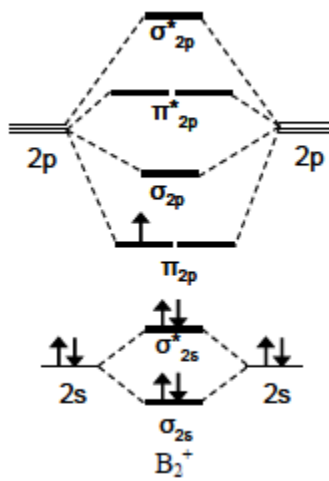
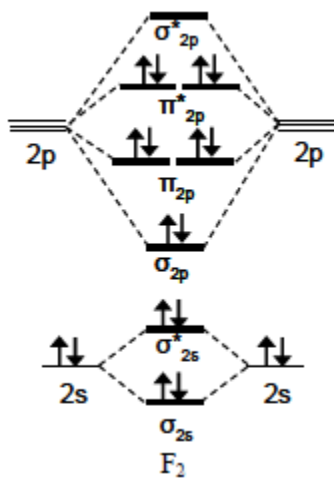
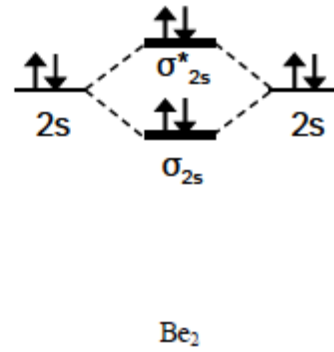
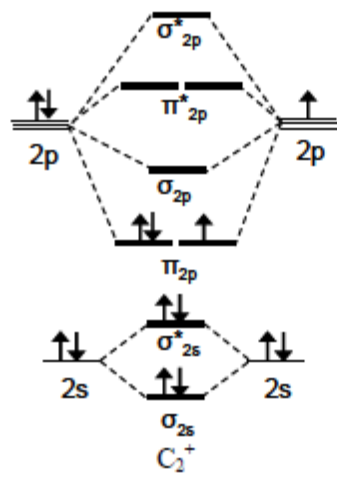


99. Explain why the molecular structure of  $BF_3$  cannot be adequately described through overlaps involving pure  $s$  and  $p$  orbitals.

99. (M) From VSEPR theory we conclude that  $BF_3$  is a trigonal planar molecule (as seen in Table 11.1). The valence-bond method using pure  $s$  and  $p$  orbitals incorrectly predicts a trigonal pyramidal shape with  $90^\circ$  F—B—F bond angles.

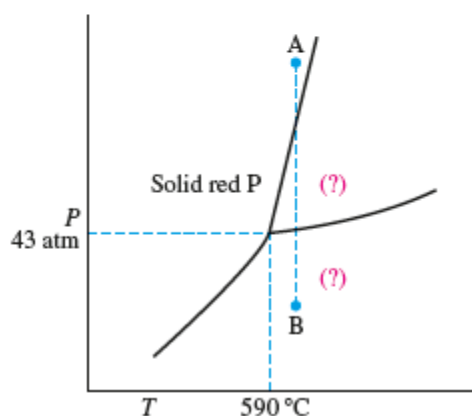
104. Use the valence molecular orbital configuration to determine which of the following species is expected to have the greatest electron affinity: (a)  $C_2^+$ ; (b)  $Be_2$ ; (c)  $F_2$ ; (d)  $B_2^+$ .

104. (M)



## Ch12

17. Butanol and pentane have approximately the same mass, however, the viscosity (at 20 °C) of butanol is  $\eta = 2.948$  cP, and the viscosity of pentane is  $\eta = 0.240$  cP. Explain this difference.
17. (E) The intermolecular interactions in butanol are dominated by H-bonding, which is much stronger than the London dispersion forces dominant in pentane.
20. Explain why vaporization occurs only at the surface of a liquid until the boiling point temperature is reached. That is, why does vapor not form throughout the liquid at all temperatures?
20. (E) Vapor cannot form throughout the liquid at temperatures below the boiling point because, for vapor to form, it must overcome the atmospheric pressure ( $\approx 1$  atm) or slightly more due to the pressure of the liquid. Formation of a bubble of vapor in the liquid, requires that it must push the liquid out of the way. This is not true at the surface. The vapor molecules simply move into the gas phase at the surface, which is mostly empty space.
51. Shown here is a portion of the phase diagram for phosphorus.
- (a) Indicate the phases present in the regions labeled with a question mark.
- (b) A sample of solid red phosphorus cannot be melted by heating in a container open to the atmosphere. Explain why this is so.
- (c) Trace the phase changes that occur when the pressure on a sample is reduced from point A to B, at constant temperature.

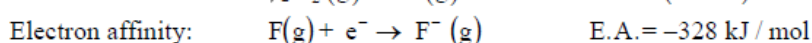
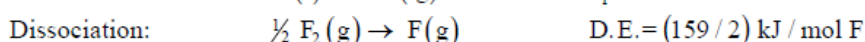
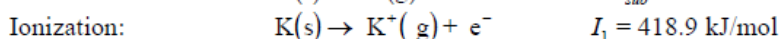
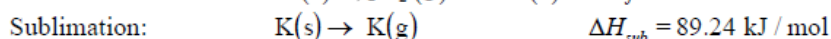
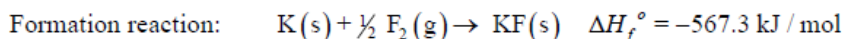
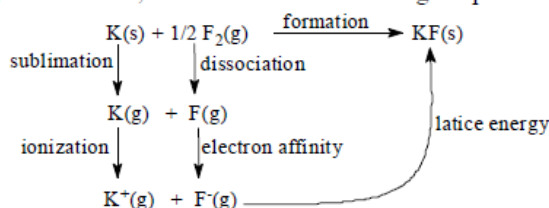


51. (M)

- (a) The upper-right region of the phase diagram is the liquid region, while the lower-right region is the region of gas.
- (b) Melting involves converting the solid into a liquid. As the phase diagram shows, the lowest pressure at which liquid exists is at the triple point pressure, namely, 43 atm. 1.00 atm is far below 43 atm. Thus, liquid cannot exist at this pressure, and solid sublimates to gas instead.
- (c) As we move from point *A* to point *B* by lowering the pressure, initially nothing happens. At a certain pressure, the solid liquefies. The pressure continues to drop, with the entire sample being liquid while it does, until another, lower pressure is reached. At this lower pressure the entire sample vaporizes. The pressure then continues to drop, with the gas becoming less dense as the pressure falls, until point *B* is reached.

86. Determine the lattice energy of KF(s) from the following data:  $\Delta H_f^\circ[\text{KF(s)}] = -567.3 \text{ kJ mol}^{-1}$ ; enthalpy of sublimation of K(s),  $89.24 \text{ kJ mol}^{-1}$ ; enthalpy of dissociation of  $\text{F}_2(\text{g})$ ,  $159 \text{ kJ mol}^{-1}$ ;  $I_1$  for K(g),  $418.9 \text{ kJ mol}^{-1}$ ; EA for F(g),  $-328 \text{ kJ mol}^{-1}$ .

86. (D) The cycle of reactions is shown. Recall that Hess's law (a state function), states that the enthalpy change is the same, whether a chemical change is produced by one reaction or several.

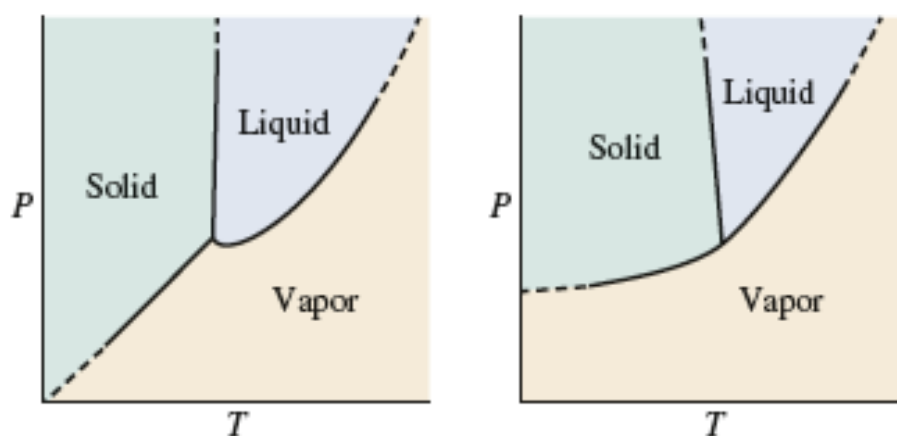


$$\Delta H_f^\circ = \Delta H_{sub} + I_1 + \text{D.E.} + \text{E.A.} + \text{lattice energy (L.E.)}$$

$$-567.3 \text{ kJ/mol} = 89.24 \text{ kJ/mol} + 418.9 \text{ kJ/mol} + (159/2) \text{ kJ/mol} - 328 \text{ kJ/mol} + \text{L.E.}$$

$$\text{L.E.} = -827 \text{ kJ/mol}$$

105. Sketched here are two hypothetical phase diagrams for a substance, but neither of these diagrams is possible. Indicate what is wrong with each of them.



105. (M) In the phase diagram on the left, the liquid-vapor curve dips down and then rises. This means that there can be a situation where raising the temperature will cause the vapor to condense to liquid – this is counterintuitive and does not correspond to the laws of thermodynamics as they operate in our universe. Also, a negative slope for the vapor pressure curve would correspond to a negative value of  $\Delta H_{\text{vap}}$ , but this quantity must always have a positive sign (vaporization is an endothermic process). In the diagram on the right, the liquid-vapor line has the same curvature as the solid-vapor line. This means that the heat of vaporization is the same as the heat of sublimation. This would mean that the heat of fusion is zero. Therefore no energy is needed to melt the solid, which is again counterintuitive and a physical impossibility.

107. The triple point temperature of bismuth is 544.5 K and the normal boiling point is 1832 K. Imagine that a 1.00 mol sample of bismuth is heated at a constant rate of  $1.00 \text{ kJ min}^{-1}$  in an apparatus in which the sample is maintained under a constant pressure of 1 atm. In the manner shown in Figure 12-24 and as much to scale as possible, that is in terms of times and temperatures, sketch the heating curve that would be obtained in heating the sample from 300 K to 2000 K. Use the following data.  $\Delta H_{\text{fus}} = 10.9 \text{ kJ mol}^{-1} \text{ Bi(s)}$ ;  $\Delta H_{\text{vap}} = 151.5 \text{ kJ mol}^{-1} \text{ Bi(l)}$ ; average molar heat capacities, in  $\text{J mol}^{-1} \text{ K}^{-1}$ , 28 for Bi(s), 31 for Bi(l), and 21 for Bi(g). [Hint: Under the conditions described, no vapor appears until the normal boiling point is reached.]

**107. (D)** We need to calculate five different times. They are shown below.

1. Heat the solid to its melting point  $T_1 =$

$$1 \text{ mol Bi} \times \frac{0.028 \text{ kJ}}{\text{K mol}} \times (554.5 \text{ K} - 300 \text{ K}) \times \frac{1 \text{ min}}{1.00 \text{ kJ}} = 7.1 \text{ min}$$

2. Melt the solid  $T_2 = 1 \text{ mol Bi} \times \frac{10.9 \text{ kJ}}{\text{K mol}} \times \frac{1 \text{ min}}{1.00 \text{ kJ}} = 10.9 \text{ min}$

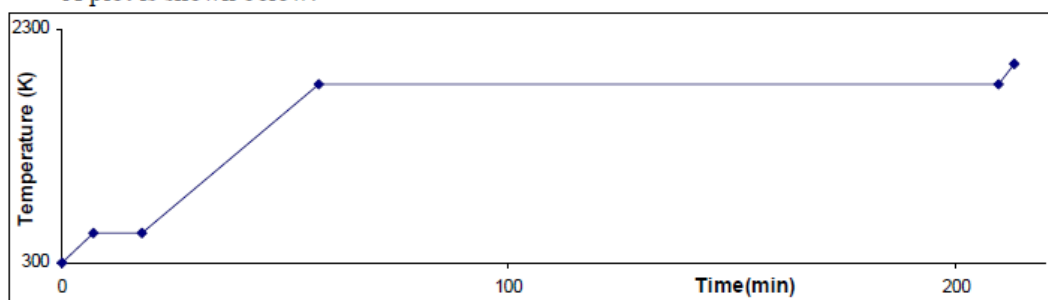
3. Heat the liquid to its boiling point  $T_3 =$

$$1 \text{ mol Bi} \times \frac{0.031 \text{ kJ}}{\text{K mol}} \times (1832 \text{ K} - 554.5 \text{ K}) \times \frac{1 \text{ min}}{1.00 \text{ kJ}} = 39.6 \text{ min}$$

4. Vaporize the liquid  $T_4 = 1 \text{ mol Bi} \times \frac{151.5 \text{ kJ}}{\text{K mol}} \times \frac{1 \text{ min}}{1.00 \text{ kJ}} = 151.5 \text{ min}$

5. Heat the gas to 2000 K  $T_5 = 1 \text{ mol Bi} \times \frac{0.021 \text{ kJ}}{\text{K mol}} \times (2000 \text{ K} - 1832 \text{ K}) \times \frac{1 \text{ min}}{1.00 \text{ kJ}} = 3.5 \text{ min}$

A plot is shown below:

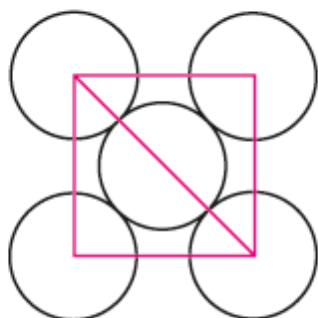


**134.** One of the substances is out of order in the following list based on increasing boiling point. Identify it, and put it in its proper place:  $\text{N}_2$ ,  $\text{O}_3$ ,  $\text{F}_2$ ,  $\text{Ar}$ ,  $\text{Cl}_2$ . Explain your reasoning.

**134. (E)**  $\text{O}_3$  is the one that is out of place. The correct order of boiling points based on molar masses is:  $\text{N}_2 < \text{F}_2 < \text{Ar} < \text{O}_3 < \text{Cl}_2$ .  $\text{O}_3$  is the only polar molecule in the group, but this is not important enough to put it after the more massive  $\text{Cl}_2$  (bp: 162 K for  $\text{O}_3$  and 239 K for  $\text{Cl}_2$ ).



- 139.** The fcc unit cell is a cube with atoms at each of the corners and in the center of each face, as shown here. Copper has the fcc crystal structure. Assume an atomic radius of 128 pm for a Cu atom.



- (a) What is the length of the unit cell of Cu?  
 (b) What is the volume of the unit cell?  
 (c) How many atoms belong to the unit cell?  
 (d) What percentage of the volume of the unit cell is occupied?  
 (e) What is the mass of a unit cell of copper?  
 (f) Calculate the density of copper.

**139. (M)**

- (a) Unit cell length: we note from the picture that the hypotenuse of the right triangle equals  $4 \times r$ .

$$L^2 + L^2 = (4r)^2 = 16 \cdot (128 \text{ pm})^2 = 2.621 \times 10^5$$

$$L = \sqrt{2.621 \times 10^5 / 2} = 362 \text{ pm}$$

- (b) volume =  $(362 \text{ pm})^3 = 4.74 \times 10^7 \text{ pm}^3$

- (c)  $8 \text{ corners} \times 1/8 + 6 \text{ faces} \times 1/2 = 4 \text{ atoms/unit cell}$ .

- (d) Volume % is the ratio between the volume taken up by the atoms and the volume of the unit cell.

$$\frac{\text{vol of atoms}}{\text{vol of cells}} = \frac{4 \times (4/3) \pi (128 \text{ pm})^3}{4.74 \times 10^7 \text{ pm}^3} \times 100 = 74\%$$

- (e)

$$\frac{\text{mass of Cu}}{\text{unit cell}} = \frac{4 \text{ atoms}}{\text{unit cell}} \times \frac{1 \text{ mol Cu}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{63.546 \text{ g Cu}}{1 \text{ mol Cu}} = 4.221 \times 10^{-22} \text{ g}$$

- (f)  $D = m/V$

$$D = \frac{4.221 \times 10^{-22} \text{ g Cu}}{4.74 \times 10^7 \text{ pm}^3} \times \frac{(1 \times 10^{-10} \text{ pm})^3}{(1 \text{ cm})^3} = 8.91 \text{ g/cm}^3$$

## Ch13

- 47.** The aqueous solubility at 20 °C of Ar at 1.00 atm is equivalent to 33.7 mL Ar(g), measured at STP, per liter of water. What is the molarity of Ar in water that is saturated with air at 1.00 atm and 20 °C? Air contains 0.934% Ar by volume. Assume that the volume of water does not change when it becomes saturated with air.

- 47. (M)** We use the STP molar volume (22.414 L = 22,414 mL) to determine the molarity of Ar under 1 atmosphere of pressure and then use Henry's law.

$$k_{\text{Ar}} = \frac{C}{P_{\text{Ar}}} = \frac{\frac{33.7 \text{ mL Ar}}{1 \text{ L soln}} \times \frac{1 \text{ mol Ar}}{22,414 \text{ mL at STP}}}{1 \text{ atm pressure}} = \frac{0.00150 \text{ M}}{\text{atm}}$$

In the atmosphere, the partial pressure of argon is  $P_{\text{Ar}} = 0.00934 \text{ atm}$ . (Recall that pressure fractions equal volume fractions for ideal gases.) We now compute the concentration of argon in aqueous solution.

$$C = k_{\text{Ar}} P_{\text{Ar}} = \frac{0.00150 \text{ M}}{\text{atm}} \times 0.00934 \text{ atm} = 1.40 \times 10^{-5} \text{ M Ar}$$

- 53.** Calculate the vapor pressure at 25 °C of a solution containing 165 g of the *nonvolatile* solute, glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , in 685 g  $\text{H}_2\text{O}$ . The vapor pressure of water at 25 °C is 23.8 mmHg.

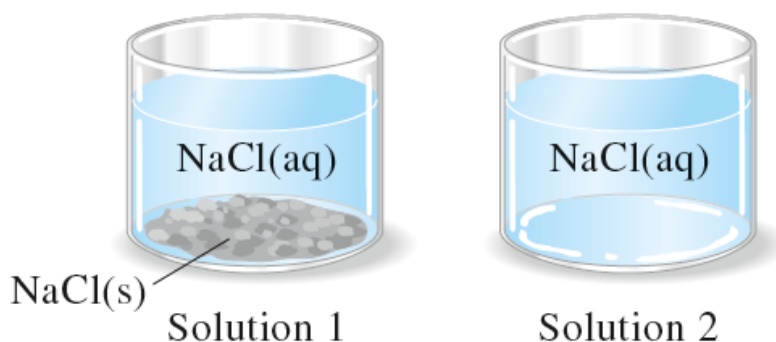
- 53. (M)** We need to determine the mole fraction of water in this solution.

$$n_{\text{glucose}} = 165 \text{ g C}_6\text{H}_{12}\text{O}_6 \times \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180.2 \text{ g C}_6\text{H}_{12}\text{O}_6} = 0.916 \text{ mol C}_6\text{H}_{12}\text{O}_6$$

$$n_{\text{water}} = 685 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 38.0 \text{ mol H}_2\text{O} \quad \chi_{\text{water}} = \frac{38.0 \text{ mol H}_2\text{O}}{(38.0 + 0.916) \text{ total moles}} = 0.976$$

$$P_{\text{soln}} = \chi_{\text{water}} P_{\text{water}}^* = 0.976 \times 23.8 \text{ mmHg} = 23.2 \text{ mmHg}$$

58. The two NaCl(aq) solutions pictured are at the same temperature.



- (a) Above which solution is the vapor pressure of water,  $P_{\text{H}_2\text{O}}$ , greater? Explain.  
 (b) Above one of these solutions, the vapor pressure of water,  $P_{\text{H}_2\text{O}}$ , remains *constant*, even as water evaporates from solution. Which solution is this? Explain.  
 (c) Which of these solutions has the higher boiling point? Explain.

58. (E)

- (a) The vapor pressure of water is greater above the solution that has the higher mole fraction of water, according to Raoult's law. This also is the solution that has the smaller mole fraction of NaCl, namely, the unsaturated Solution 2.  
 (b) As water evaporates from the unsaturated solution, its concentration changes and so does its vapor pressure, according to Raoult's law. This does not happen with the saturated solution (Solution 1). Its concentration and thus its vapor pressure remains constant as the solvent evaporates.  
 (c) The solution with the higher boiling point is the more concentrated solution (the saturated solution, Solution 1) because the boiling point increases as the amount of dissolved solute increases.

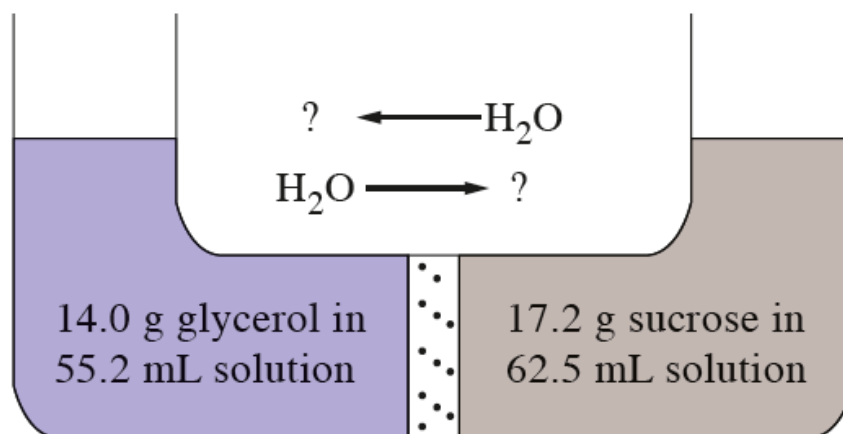
59. A 0.72 g sample of polyvinyl chloride (PVC) is dissolved in 250.0 mL of a suitable solvent at 25 °C. The solution has an osmotic pressure of 1.67 mmHg. What is the molar mass of the PVC?

59. (M) We first compute the concentration of the solution. Then, assuming that the solution volume is the same as that of the solvent (0.2500 L), we determine the amount of solute dissolved, and finally the molar mass.

$$\frac{n}{V} = \frac{\pi}{RT} = \frac{1.67 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298.2 \text{ K}} = 8.98 \times 10^{-5} \text{ M}$$

$$\text{solute amount} = 0.2500 \text{ L} \times \frac{8.98 \times 10^{-5} \text{ mol}}{1 \text{ L}} = 2.25 \times 10^{-5} \text{ mol} \quad M = \frac{0.72 \text{ g}}{2.25 \times 10^{-5} \text{ mol}} = 3.2 \times 10^4 \text{ g/mol}$$

68. The two solutions pictured here are separated by a semipermeable membrane that permits only the passage of water molecules. In what direction will a net flow of water occur, that is, from left to right or right to left? Glycerol is  $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$ ; sucrose is  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ .



68. (M) We need to determine the molarity of each solution. The solution with the higher molarity has the higher osmotic pressure, and water will flow from the more dilute into the more concentrated solution, in an attempt to create two solutions of equal concentrations.

$$[\text{C}_3\text{H}_8\text{O}_3] = \frac{14.0 \text{ g C}_3\text{H}_8\text{O}_3 \times \frac{1 \text{ mol C}_3\text{H}_8\text{O}_3}{92.09 \text{ g C}_3\text{H}_8\text{O}_3}}{55.2 \text{ mL soln} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 2.75 \text{ M}$$

$$[\text{C}_{12}\text{H}_{22}\text{O}_{11}] = \frac{17.2 \text{ g C}_{12}\text{H}_{22}\text{O}_{11} \times \frac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{342.3 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}}}{62.5 \text{ mL soln} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 0.804 \text{ M}$$

Thus, water will move from the  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  solution into the  $\text{C}_3\text{H}_8\text{O}_3$  solution, that is, from right to left.

90. Four aqueous solutions of acetone,  $\text{CH}_3\text{COCH}_3$ , are prepared at different concentrations: (a) 0.100%  $\text{CH}_3\text{COCH}_3$ , by mass; (b) 0.100 M  $\text{CH}_3\text{COCH}_3$ ; (c) 0.100 *m*  $\text{CH}_3\text{COCH}_3$ ; and (d)  $\chi_{\text{acetone}} = 0.100$ . Estimate the highest partial pressure of water at 25 °C to be found in the equilibrium vapor above these solutions. Also, estimate the lowest freezing point to be found among these solutions.

90. (D) At the outset, we observe that the solution having the highest mole fraction of water (the most dilute solution) will have the highest partial pressure of water in its equilibrium vapor. Also, the solution with the lowest mole fraction of water (the most concentrated solution) will have the lowest freezing point. We need to identify these two solutions, and to achieve this we need a simple way to compare concentrations, which are given here in disparate units. Let's look at the solutions one at a time. Keep in mind that 1 L of water contains about  $1000 \text{ g H}_2\text{O} \div 18.02 \text{ g/mol} \approx 55.49 \text{ mol H}_2\text{O}$  (55.49 M).

*Solution (a):* The concentration 0.100%  $\text{CH}_3\text{COCH}_3$  by mass is equivalent to 1.00 g  $\text{CH}_3\text{COCH}_3/1000 \text{ g}$  solution, which in turn is about 1.00 g  $\text{CH}_3\text{COCH}_3/\text{L}$  solution. (The density of the solution will be very nearly the same as that of water.) A 1.00-g sample of  $\text{CH}_3\text{COCH}_3$  is the same as  $1.00 \text{ g}/58.1 \text{ g/mol} \ll 0.10 \text{ mol CH}_3\text{COCH}_3$ .

*Solution (b):* The 0.100 M  $\text{CH}_3\text{COCH}_3$  has 0.100 mol  $\text{CH}_3\text{COCH}_3$  per liter. Solution (b) is more concentrated than (a), so (b) cannot be the solution with the highest water vapor pressure.

*Solution (c):* The 0.100 m  $\text{CH}_3\text{COCH}_3$  has 0.100 mol  $\text{CH}_3\text{COCH}_3$  per kg  $\text{H}_2\text{O}$ . Because water is the preponderant component in the solution, the density of the solution will be very nearly that of water, and the 0.100 m  $\text{CH}_3\text{COCH}_3 \approx 0.100 \text{ M CH}_3\text{COCH}_3$ . So, as with (b), solution (c) cannot be the solution with the highest water vapor pressure.

*Solution (d):* In the solution  $\chi_{\text{acetone}} = 0.100$ , acetone molecules comprise one-tenth of all the molecules, or there is one acetone molecule for every nine water molecules. In a liter of this solution there would be about  $55.5 \div 9 \approx 6 \text{ mol CH}_3\text{COCH}_3$ . This is clearly the most concentrated of the solutions.

To summarize, solution (a) has the highest water vapor pressure and solution (d) has the lowest freezing point. Our next task is to apply Raoult's law to solution (a), which requires the mole fraction of water in solution (a). One kilogram of this solution contains 1.00 g per  $58.1 \text{ g/mol} = 0.0172 \text{ mol CH}_3\text{COCH}_3$  and  $999 \text{ g per } 18.02 \text{ g/mol} = 55.44 \text{ mol H}_2\text{O}$ . The mole fraction of the water is  $\chi_{\text{water}} = 55.44/(55.44 + 0.0172) \approx 1.00$ . The mole fraction is only very slightly less than 1.00, so the water vapor pressure above this solution will be only very slightly less than the vapor pressure of pure water at 25 °C, namely, 23.8 mmHg.

To apply Equation 13.5 for freezing-point depression to solution (d), we must first express its concentration in molality. In a solution that has 1.00 mol  $\text{CH}_3\text{COCH}_3$  for every 9.00 mol  $\text{H}_2\text{O}$ , there is 1.00 mol of the solute for every  $(9.00 \text{ mol} \times 18.02 \text{ g/mol}) = 162 \text{ g H}_2\text{O}$ . The molality of the solution is  $1.00 \text{ mol CH}_3\text{COCH}_3/0.162 \text{ kg H}_2\text{O} = 6.17 \text{ m CH}_3\text{COCH}_3$ . The approximate freezing-point depression for this solution is

$$T_f = -K_f \times m = -1.86 \text{ }^\circ\text{C} \times 6.17 \text{ m} \approx -11.5 \text{ }^\circ\text{C}$$

and the approximate freezing point of the solution is  $-11.5 \text{ }^\circ\text{C}$ . This result is only approximate because we have used Equation 13.5 for a much more concentrated solution than that for which the equation is intended.



104. Demonstrate that

- (a) for a *dilute aqueous* solution, the numerical value of the molality is essentially equal to that of the molarity.  
 (b) in a *dilute* solution, the solute mole fraction is proportional to the molality.  
 (c) in a *dilute aqueous* solution, the solute mole fraction is proportional to the molarity.

104. (D)

- (a) Let's begin with the definition of molality for an aqueous solution. We assume that the mass of the solvent is essentially equal to the mass of the solution, since the solution is a dilute one.

Next we assume that the density of this dilute solution is that of pure water, 1.00 g/mL, and then apply some definitions (1 kg = 1000 g and 1 L = 1000 mL).

$$\text{molality} \approx \frac{\text{moles solute}}{1 \text{ kg solution}} \times \frac{1 \text{ kg solution}}{1000 \text{ g solution}} \times \frac{1.00 \text{ g solution}}{1 \times 10^{-3} \text{ L solution}} \approx \frac{\text{moles solute}}{1 \text{ L solution}} = \text{molarity}$$

- (b) We begin with the definition of mole fraction for the solute. Then we assume that the amount of solute is quite small compared to the amount of solvent, and use the molar mass ( $M$ ) of the solvent, along with the fact that 1 kg = 1000 g.

$$\begin{aligned} \chi_{\text{solute}} &= \frac{\text{moles solute}}{\text{moles solute} + \text{moles solvent}} \approx \frac{\text{moles solute}}{\text{moles solvent}} \times \frac{1 \text{ mol solvent}}{M \text{ g solvent}} \times \frac{1000 \text{ g solvent}}{1 \text{ kg solvent}} \\ &\approx \frac{1000 \text{ g/kg} \times \text{moles solute}}{M_{\text{solvent}} \times 1 \text{ kg solvent}} = \frac{\text{moles solute}}{1 \text{ kg solvent}} \times \frac{1000 \text{ g/kg}}{M_{\text{solvent}}} = \text{molality} \times \frac{1000 \text{ g/kg}}{M_{\text{solvent}}} \end{aligned}$$

Thus, mole fraction of a solute indeed is proportional to its molality in a dilute solution.

- (c) For a dilute aqueous solution, we begin with the result of part (b) and first use the definition of molality and then assume that the mass of the solvent is essentially equal to the mass of the solution.

$$\chi_{\text{solute}} \approx \text{molality} \times \frac{1000 \text{ g/kg}}{M_{\text{solvent}}} \approx \frac{\text{moles solute}}{1 \text{ kg solvent}} \times \frac{1000 \text{ g/kg}}{M_{\text{solvent}}} \times \frac{1 \text{ kg solvent}}{1 \text{ kg solution}}$$

Now we assume that the density of this dilute solution is that of pure water, 1.00 g/mL, and then apply some definitions (1 kg = 1000 g and 1 L = 1000 mL).

$$\begin{aligned} \chi_{\text{solute}} &\approx \frac{\text{moles solute}}{1 \text{ kg solvent}} \times \frac{1000 \text{ g/kg}}{M_{\text{solvent}}} \times \frac{1 \text{ kg solvent}}{1 \text{ kg soln}} \times \frac{1 \text{ kg soln}}{1000 \text{ g soln}} \times \frac{1.00 \text{ g soln}}{1 \text{ mL soln}} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \\ &\approx \frac{\text{moles solute}}{1 \text{ L solution}} \times \frac{1000 \text{ g/kg}}{M_{\text{solvent}}} = \text{molarity} \times \frac{1000 \text{ g/kg}}{M_{\text{solvent}}} \end{aligned}$$

Thus molarity of dilute aqueous solutions is proportional to mole fraction of the solute.

- 110.** A solution contains 750 g of ethanol and 85.0 g of sucrose ( $180 \text{ g mol}^{-1}$ ). The volume of the solution is 810.0 mL. Determine
- (a) the density of the solution
  - (b) the percent of sucrose in the solution
  - (c) the mole fraction of sucrose
  - (d) the molality of the solution
  - (e) the molarity of the solution

**110. (M)**

(a) density =  $m/V$

$$D = \frac{750 \text{ g} + 85.0 \text{ g}}{810.0 \text{ mL}} = 1.03 \text{ g/mL}$$

(b)

$$\text{wt}\% = \frac{\text{mass}_{\text{sucrose}}}{\text{mass}_{\text{sucrose}} + \text{mass}_{\text{ethanol}}} \times 100\% = \frac{85.0 \text{ g}}{85.0 \text{ g} + 750 \text{ g}} \times 100\% = 10.2\%$$

(c)

$$\text{mol}_{\text{suc.}} = 85.0 \text{ g} \times \frac{1 \text{ mol}}{180.0 \text{ g}} = 0.4722 \text{ mol}$$

$$\text{mol}_{\text{EtOH}} = 750.0 \text{ g} \times \frac{1 \text{ mol}}{34.07 \text{ g}} = 22.01 \text{ mol}$$

$$\chi_{\text{suc.}} = \frac{0.4722 \text{ mol}}{0.4722 \text{ mol} + 22.01 \text{ mol}} = 0.0210$$

(d) molality = mol/kg solvent. We note that the density of ethanol is 0.789 g/mL or 0.789 kg/L.

$$\text{molality} = \frac{0.4722 \text{ mol}}{0.810 \text{ L} \times 0.789 \text{ kg} \cdot \text{L}^{-1}} = 0.740 \text{ M}$$

(e) molarity = mol/Vol solvent

$$\text{Molarity} = \frac{0.4722 \text{ mol}}{0.810 \text{ L}} = 0.583 \text{ M}$$

**119.** Explain the important distinctions between each pair of terms: **(a)** molality and molarity; **(b)** ideal and nonideal solution; **(c)** unsaturated and supersaturated solution; **(d)** fractional crystallization and fractional distillation; **(e)** osmosis and reverse osmosis.

**119. (E)**

- (a)** Molality and molarity: Molality is a measure of concentration expressed as the ratio of moles of solute and kilograms of solvent. Molarity is a measure of concentration expressed as the ratio between the moles of solute and the volume of the final solution.
- (b)** Ideal and non-ideal solutions: In an ideal solution, the properties of the solution can be determined from the properties of the bulk phases of solutes and solvent. Furthermore, there are no interactions between solute particles. In case of non-ideal solutions, forces of attraction between unlike molecules exceed those between like molecules, and the properties of such solutions generally cannot be predicted from bulk pure components.
- (c)** Unsaturated and supersaturated solution: An unsaturated solution is one that can still accommodate the dissolution of more solute in it. A supersaturated solution is one that for various reasons has more solute dissolved in it than otherwise would be possible at that given temperature.
- (d)** Fractional crystallization and fractional distillation: Fractional crystallization is a process of purifying a solid, whereby a solution saturated in the species that we need to purify is cooled just enough to fractionally crystallize the pure solid. Fractional distillation is a process of purifying a mixture of solvents by raising and/or lowering the temperature just enough to selectively distill away a lower boiling point component of a solution.
- (e)** Osmosis and reverse osmosis: Osmosis is the process by which water migrates across a water-permeable membrane from one side with lower molality to the side with higher ionic molality. Reverse osmosis is the process of forcing water to go from a region of high molality to a lower one by exerting a pressure greater than the osmotic pressure, thereby concentrating the solution with the higher molality.



**128.** Which aqueous solution from the column on the right has the property listed on the left? Explain your choices.

Property	Solution
1. lowest electrical conductivity	a. 0.10 <i>m</i> KCl(aq)
2. lowest boiling point	b. 0.15 <i>m</i> C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> (aq)
3. highest vapor pressure of water at 25 °C	c. 0.10 <i>m</i> CH <sub>3</sub> COOH(aq)
4. lowest freezing point	d. 0.05 <i>m</i> NaCl

**128. (E)**

- (1) Solution with lowest conductivity: (b) 0.15 *m* C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>, because it is a non-electrolyte.
- (2) Lowest boiling point: (d) 0.05 *m* NaCl, because the molality of the solute is the smallest, making boiling-point elevation the smallest value.
- (3) Highest vapor pressure of water: (d), for the same reason as above.
- (4) Lowest freezing point: (a), because the molality of the solute is the highest (2×0.10 *m*).