CHAPTER 8

PHYSICAL EQUILIBRIA

8.1   In a 1.0 L vessel at 20°C, there will be 17.5 Torr of water vapor. The ideal gas law can be used to calculate the mass of water present:

$PV = nRT$

let m = mass of water

$$\left(\frac{17.5 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}}\right)(1.0 \text{ L}) = \left(\frac{m}{18.02 \text{ g} \cdot \text{mol}^{-1}}\right)(0.082\ 06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(293 \text{ K})$$

$$m = \frac{(17.5 \text{ Torr})(1.0 \text{ L})(18.02 \text{ g} \cdot \text{mol}^{-1})}{(760 \text{ Torr} \cdot \text{atm}^{-1})(0.082\ 06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(293 \text{ K})}$$

$$m = 0.017 \text{ g}$$

8.3   (a) 99.2°C;   (b) 99.7°C

8.5   (a) The quantities $\Delta H°_{\text{vap}}$ and $\Delta S°_{\text{vap}}$ can be calculated using the

relationship $\ln P = -\dfrac{\Delta H°_{\text{vap}}}{R} \cdot \dfrac{1}{T} + \dfrac{\Delta S°_{\text{vap}}}{R}$

Because we have two temperatures with corresponding vapor pressures, we can set up two equations with two unknowns and solve for $\Delta H°_{\text{vap}}$ and $\Delta S°_{\text{vap}}$. If the equation is used as is, P must be expressed in atm, which is the standard reference state. Remember that the value used for P is really activity, which for pressure is P divided by the reference state of 1 atm, so that the quantity inside the ln term is dimensionless.

$$8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times \ln \frac{58 \text{ Torr}}{760 \text{ Torr}} = -\frac{\Delta H°_{\text{vap}}}{250.4 \text{ K}} + \Delta S°_{\text{vap}}$$

$$8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times \ln \frac{512 \text{ Torr}}{760 \text{ Torr}} = -\frac{\Delta H°_{\text{vap}}}{298.2 \text{ K}} + \Delta S°_{\text{vap}}$$

which give, upon combining terms,

$$-21.39\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -0.003\ 994\ \text{K}^{-1}\times\Delta H^\circ{}_{\text{vap}} + \Delta S^\circ{}_{\text{vap}}$$

$$-3.284\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -0.003\ 353\ \text{K}^{-1}\times\Delta H^\circ{}_{\text{vap}} + \Delta S^\circ{}_{\text{vap}}$$

Subtracting one equation from the other will eliminate the $\Delta S^\circ{}_{\text{vap}}$ term and allow us to solve for $\Delta H^\circ{}_{\text{vap}}$:

$$-18.11\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -0.000\ 641\times\Delta H^\circ{}_{\text{vap}}$$

$$\Delta H^\circ{}_{\text{vap}} = +28.3\ \text{kJ}\cdot\text{mol}^{-1}$$

(b) We can then use $\Delta H^\circ{}_{\text{vap}}$ to calculate $\Delta S^\circ{}_{\text{vap}}$ using either of the two equations:

$$-21.39\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -0.003\ 994\ \text{K}^{-1}\times(+28\ 200\ \text{J}\cdot\text{mol}^{-1}) + \Delta S^\circ{}_{\text{vap}}$$

$$\Delta S^\circ{}_{\text{vap}} = 91.2\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$-3.284\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -0.003\ 353\ \text{K}^{-1}\times(+28\ 200\ \text{J}\cdot\text{mol}^{-1}) + \Delta S^\circ{}_{\text{vap}}$$

$$\Delta S^\circ{}_{\text{vap}} = 91.3\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

(c) The $\Delta G^\circ{}_{\text{vap}}$ is calculated using $\Delta G^\circ{}_{\text{r}} = \Delta H^\circ{}_{\text{r}} - T\Delta S^\circ{}_{\text{r}}$

$$\Delta G^\circ{}_{\text{r}} = +28.3\ \text{kJ}\cdot\text{mol}^{-1} - (298\ \text{K})(91.2\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})/(1000\ \text{J}\cdot\text{kJ}^{-1})$$

$$\Delta G^\circ{}_{\text{r}} = +1.1\ \text{kJ}\cdot\text{mol}^{-1}$$

(d) The boiling point can be calculated using one of several methods. The easiest to use is the one developed in the last chapter:

$$\Delta G^\circ{}_{\text{vap}} = \Delta H^\circ{}_{\text{vap}} - T_{\text{B}}\ \Delta S^\circ{}_{\text{vap}} = 0$$

$$\Delta H^\circ{}_{\text{vap}} = T_{\text{B}}\ \Delta S^\circ{}_{\text{vap}}\ \text{or}\ T_{\text{B}} = \frac{\Delta H^\circ{}_{\text{vap}}}{\Delta S^\circ{}_{\text{vap}}}$$

$$T_{\text{B}} = \frac{28.2\ \text{kJ}\cdot\text{mol}^{-1}\ \times 1000\ \text{J}\cdot\text{kJ}^{-1}}{91.2\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}} = 309\ \text{K or }36°\text{C}$$

Alternatively, we could use the relationship $\ln\dfrac{P_2}{P_1} = -\dfrac{\Delta H^\circ{}_{\text{vap}}}{R}\left[\dfrac{1}{T_2} - \dfrac{1}{T_1}\right]$.

Here we would substitute, in one of the known vapor pressure points, the value of the enthalpy of vaporization and the condition that $P = 1$ atm at the normal boiling point.

8.7   (a) The quantities $\Delta H°_{vap}$ and $\Delta S°_{vap}$ can be calculated using the relationship

$$\ln P = -\frac{\Delta H°_{vap}}{R} \cdot \frac{1}{T} + \frac{\Delta S°_{vap}}{R}$$

Because we have two temperatures with corresponding vapor pressures (we know that the vapor pressure = 1 atm at the boiling point), we can set up two equations with two unknowns and solve for $\Delta H°_{vap}$ and $\Delta S°_{vap}$. If the equation is used as is, P must be expressed in atm, which is the standard reference state. Remember that the value used for P is really activity, which for pressure is P divided by the reference state of 1 atm, so that the quantity inside the ln term is dimensionless.

$$8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times \ln 1 = -\frac{\Delta H°_{vap}}{292.7 \text{ K}} + \Delta S°_{vap}$$

$$8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times \ln \frac{359 \text{ Torr}}{760 \text{ Torr}} = -\frac{\Delta H°_{vap}}{273.2 \text{ K}} + \Delta S°_{vap}$$

which give, upon combining terms,

$$0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.003\,416 \text{ K}^{-1} \times \Delta H°_{vap} + \Delta S°_{vap}$$

$$-6.235 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.003\,660 \text{ K}^{-1} \times \Delta H°_{vap} + \Delta S°_{vap}$$

Subtracting one equation from the other will eliminate the $\Delta S°_{vap}$ term and allow us to solve for $\Delta H°_{vap}$:

$$+6.235 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = +0.000\,244 \text{ K}^{-1} \times \Delta H°_{vap}$$

$$\Delta H°_{vap} = +25.6 \text{ kJ} \cdot \text{mol}^{-1}$$

(b) We can then use $\Delta H°_{vap}$ to calculate $\Delta S°_{vap}$ using either of the two equations:

$$0 = -0.003\,416 \text{ K}^{-1} \times (+25\,600 \text{ J} \cdot \text{mol}^{-1}) + \Delta S°_{vap}$$

$$\Delta S°_{vap} = 87.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$-6.235 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.003\,660 \text{ K}^{-1} \times (+25\,600 \text{ J} \cdot \text{mol}^{-1}) + \Delta S°_{vap}$$

$$\Delta S°_{vap} = 87.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

(c) The vapor pressure at another temperature is calculated using

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H°_{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

We need to insert the calculated value of the enthalpy of vaporization and one of the known vapor pressure points:

$$\ln \frac{P_{at\,8.5°C}}{1\,atm} = -\frac{25\,600\,J\cdot mol^{-1}}{8.314\,J\cdot K^{-1}\cdot mol^{-1}}\left[\frac{1}{291.7\,K} - \frac{1}{292.7\,K}\right]$$

$P_{at\,8.5°C} = 1.0\,atm$ or 7.6×10^2 Torr

8.9 (a) The quantities $\Delta H°_{vap}$ and $\Delta S°_{vap}$ can be calculated using the relationship

$$\ln P = \frac{\Delta H°_{vap}}{R}\cdot\frac{1}{T} + \frac{\Delta S°_{vap}}{R}$$

Because we have two temperatures with corresponding vapor pressures, we can set up two equations with two unknowns and solve for $\Delta H°_{vap}$ and $\Delta S°_{vap}$. If the equation is used as is, P must be expressed in atm, which is the standard reference state. Remember that the value used for P is really activity which, for pressure, is P divided by the reference state of 1 atm, so that the quantity inside the ln term is dimensionless.

$$8.314\,J\cdot K^{-1}\cdot mol^{-1} \times \ln \frac{35\,Torr}{760\,Torr} = -\frac{\Delta H°_{vap}}{161.2\,K} + \Delta S°_{vap}$$

$$8.314\,J\cdot K^{-1}\cdot mol^{-1} \times \ln \frac{253\,Torr}{760\,Torr} = -\frac{\Delta H°_{vap}}{189.6\,K} + \Delta S°_{vap}$$

which give, upon combining terms,

$$-25.59\,J\cdot K^{-1}\cdot mol^{-1} = -0.006\,203\,K^{-1} \times \Delta H°_{vap} + \Delta S°_{vap}$$

$$-9.145\,J\cdot K^{-1}\cdot mol^{-1} = -0.005\,274\,K^{-1} \times \Delta H°_{vap} + \Delta S°_{vap}$$

Subtracting one equation from the other will eliminate the $\Delta S°_{vap}$ term and allow us to solve for $\Delta H°_{vap}$:

$$-16.45\,J\cdot K^{-1}\cdot mol^{-1} = -0.000\,929 \times \Delta H°_{vap}$$

$$\Delta H°_{vap} = +17.7\,kJ\cdot mol^{-1}$$

(b) We can then use $\Delta H°_{vap}$ to calculate $\Delta S°_{vap}$ using either of the two equations:

$$-25.59 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.006\ 203 \text{ K}^{-1} \times (+17\ 700 \text{ J} \cdot \text{mol}^{-1}) + \Delta S°_{vap}$$

$$\Delta S°_{vap} = 84 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$-9.145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.005\ 274 \text{ K}^{-1} \times (+17\ 700 \text{ J} \cdot \text{mol}^{-1}) + \Delta S°_{vap}$$

$$\Delta S°_{vap} = 84 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

(c) The $\Delta G°_{vap}$ is calculated using $\Delta G°_r = \Delta H°_r - T\Delta S°_r$

$$\Delta G°_r = +17.7 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(84 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1})$$

$$\Delta G°_r = -7.3 \text{ kJ} \cdot \text{mol}^{-1}$$

Notice that the standard $\Delta G°_r$ is negative, so that the vaporization of arsine is spontaneous, which is as expected; under those conditions arsine is a gas at room temperature.

(d) The boiling point can be calculated from one of several methods. The easiest to use is that developed in the last chapter:

$$\Delta G°_{vap} = \Delta H°_{vap} - T_B \Delta S°_{vap} = 0$$

$$\Delta H°_{vap} = T_B \Delta S°_{vap} \text{ or } T_B = \frac{\Delta H°_{vap}}{\Delta S°_{vap}}$$

$$T_B = \frac{17.7 \text{ kJ} \cdot \text{mol}^{-1} \times 1000 \text{ J} \cdot \text{kJ}^{-1}}{84 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} = 211 \text{ K}$$

Alternatively, we could use the relationship $\ln \dfrac{P_2}{P_1} = -\dfrac{\Delta H°_{vap}}{R}\left[\dfrac{1}{T_2} - \dfrac{1}{T_1}\right]$.

Here, we would substitute, in one of the known vapor pressure points, the value of the enthalpy of vaporization and the condition that $P = 1$ atm at the normal boiling point.

8.11 (a) The quantities $\Delta H°_{vap}$ and $\Delta S°_{vap}$ can be calculated, using the relationship

$$\ln P = -\frac{\Delta H°_{vap}}{R} \cdot \frac{1}{T} + \frac{\Delta S°_{vap}}{R}$$

Because we have two temperatures with corresponding vapor pressures (we know that the vapor pressure = 1 atm at the boiling point), we can set

up two equations with two unknowns and solve for $\Delta H°_{vap}$ and $\Delta S°_{vap}$. If the equation is used as is, P must be expressed in atm which is the standard reference state. Remember that the value used for P is really activity which, for pressure, is P divided by the reference state of 1 atm, so that the quantity inside the ln term is dimensionless.

$$8.314\ \text{J·K}^{-1}\cdot\text{mol}^{-1}\times\ln 1 = -\frac{\Delta H°_{vap}}{315.58\ \text{K}} + \Delta S°_{vap}$$

$$8.314\ \text{J·K}^{-1}\cdot\text{mol}^{-1}\times\ln\frac{140\ \text{Torr}}{760\ \text{Torr}} = -\frac{\Delta H°_{vap}}{273.2\ \text{K}} + \Delta S°_{vap}$$

which give, upon combining terms,

$$0\ \text{J·K}^{-1}\cdot\text{mol}^{-1} = -0.003\,169\ \text{K}^{-1}\times\Delta H°_{vap} + \Delta S°_{vap}$$
$$-14.06\ \text{J·K}^{-1}\cdot\text{mol}^{-1} = -0.003\,660\ \text{K}^{-1}\times\Delta H°_{vap} + \Delta S°_{vap}$$

Subtracting one equation from the other will eliminate the $\Delta S°_{vap}$ term and allow us to solve for $\Delta H°_{vap}$.

$$-14.06\ \text{J·K}^{-1}\cdot\text{mol}^{-1} = -0.000\,491\ \text{K}^{-1}\times\Delta H°_{vap}$$
$$\Delta H°_{vap} = +28.6\ \text{kJ·mol}^{-1}$$

(b) We can then use $\Delta H°_{vap}$ to calculate $\Delta S°_{vap}$ using either of the two equations:

$$0 = -0.003\,169\ \text{K}^{-1}\times(+28\,600\ \text{J·mol}^{-1}) + \Delta S°_{vap}$$
$$\Delta S°_{vap} = 90.6\ \text{J·K}^{-1}\cdot\text{mol}^{-1}$$
$$-14.06\ \text{J·K}^{-1}\cdot\text{mol}^{-1} = -0.003\,660\ \text{K}^{-1}\times(+28\,600\ \text{J·mol}^{-1}) + \Delta S°_{vap}$$
$$\Delta S°_{vap} = 90.6\ \text{J·K}^{-1}\cdot\text{mol}^{-1}$$

(c) The vapor pressure at another temperature is calculated using

$$\ln\frac{P_2}{P_1} = -\frac{\Delta H°_{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

We need to insert the calculated value of the enthalpy of vaporization and one of the known vapor pressure points:

$$\ln\frac{P_{\text{at }25.0°\text{C}}}{1\ \text{atm}} = -\frac{28\,600\ \text{J·mol}^{-1}}{8.314\ \text{J·K}^{-1}\cdot\text{mol}^{-1}}\left[\frac{1}{298.2\ \text{K}} - \frac{1}{315.58\ \text{K}}\right]$$

$$P_{\text{at }25.0°\text{C}} = 0.53\ \text{atm or } 4.0\times10^2\ \text{Torr}$$

8.13   Table 6.2 contains the enthalpy of vaporization and the boiling point of methanol (at which the vapor pressure = 1 atm). Using this data and the equation

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H°_{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\ln \frac{P_{25.0°C}}{1} = -\frac{35\ 300\ \text{J} \cdot \text{mol}^{-1}}{8.314\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}\left[\frac{1}{298.2\ \text{K}} - \frac{1}{337.2\ \text{K}}\right]$$

$$P_{25.0°C} = 0.19\ \text{atm or } 1.5 \times 10^2\ \text{Torr}$$

8.15   (a) vapor;   (b) liquid;   (c) vapor;   (d) vapor

8.17   (a) 2.4 K;   (b) about 10 atm;   (c) 5.5 K;   (d) no

8.19   (a) At the lower pressure triple point, liquid helium-I and -II are in equilibrium with helium gas; at the higher pressure triple point, liquid helium-I and -II are in equilibrium with solid helium.   (b) helium-I

8.21   The pressure increase would bring CO_2 into the solid region.

8.23 $$\frac{dP}{dT} = \frac{\Delta H_{fus}}{T \cdot \Delta V_{fus}} \qquad \therefore \quad \Delta H_{fus} = \frac{dP}{dT} \cdot T \cdot \Delta V_{fus}$$

$$dP \approx P_2 - P_1 = 2000\ \text{bar} - 1\ \text{bar} = 1999\ \text{bar}$$

$$dT \approx T_2 - T_1 = 11.60°\text{C} - 5.52°\text{C} = 6.08°\text{C} = 6.08\ \text{K}$$

$$\Delta V_{fus} = V_2 - V_1 = \frac{78\ \text{g} \cdot \text{mol}^{-1}}{0.879\ \text{g} \cdot \text{cm}^{-3}} - \frac{78\ \text{g} \cdot \text{mol}^{-1}}{0.891\ \text{g} \cdot \text{cm}^{-3}} = 1.20\ \text{cm}^3 \cdot \text{mol}^{-1}$$

$$\left(1.20\ \text{cm}^3 \cdot \text{mol}^{-1}\right)\left(\frac{1\ \text{L}}{1000\ \text{cm}^3}\right) = 0.00120\ \text{L} \cdot \text{mol}^{-1}$$

$$\Delta H_{fus} = \frac{dP}{dT} \cdot T \cdot \Delta V_{fus} = \left(\frac{1999 \text{ bar}}{6.08 \text{ K}}\right)(278.67 \text{ K})(0.00120 \text{ L} \cdot \text{mol}^{-1})$$

$$= 110 \text{ L} \cdot \text{bar} \cdot \text{mol}^{-1}$$

$$\left(110 \text{ L} \cdot \text{bar} \cdot \text{mol}^{-1}\right)\left(101.325 \text{ J} \cdot \text{L}^{-1} \cdot \text{atm}^{-1}\right) = 11.0 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T} = \frac{11.0 \text{ kJ} \cdot \text{mol}^{-1}}{278.67 \text{ K}} = 39.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

8.25 (a) KCl is an ionic solid, so water would be the best choice; (b) CCl_4 is non-polar, so the best choice is benzene; (c) CH_3COOH is polar, so water is the better choice.

8.27 (a) hydrophilic, because NH_2 is polar, and has a lone pair and H atoms that can participate in hydrogen bonding to water molecules; hydrophobic, because the CH_3 group is not very polar; (c) hydrophobic, because the Br group is not very polar; (d) hydrophilic, because the carboxylic acid group has lone pairs on oxygen and an acidic proton that can participate in hydrogen bonding to water molecules.

8.29 (a) The solubility of $O_2(g)$ in water is $1.3 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1} \cdot \text{atm}^{-1}$.

$$\text{solubility at 50 kPa} = \frac{50 \text{ kPa}}{101.325 \text{ kPa} \cdot \text{atm}^{-1}} \times 1.3 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1} \cdot \text{atm}^{-1}$$

$$= 6.4 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$$

(b) The solubility of $CO_2(g)$ in water is $2.3 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} \cdot \text{atm}^{-1}$.

$$\text{solubility at 500 Torr} = \frac{500 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}} \times 2.3 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} \cdot \text{atm}^{-1}$$

$$= 1.5 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

(c) solubility $= 0.10 \text{ atm} \times 2.3 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} \cdot \text{atm}^{-1} = 2.3 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

8.31 (a) $4 \text{ mg} \cdot \text{L}^{-1} \times 1000 \text{ mL} \cdot \text{L}^{-1} \times 1.00 \text{ g} \cdot \text{mL}^{-1} \times 1 \text{ kg}/1000 \text{ g}$

$= 4 \text{ mg} \cdot \text{L}^{-1}$ or 4 ppm

(b) The solubility of O_2 (g) in water is 1.3×10^{-3} $mol \cdot L^{-1} \cdot atm^{-1}$ which can be converted to parts per million as follows:

In 1.00 L (corresponding to 1 kg) of solution there will be

1.3×10^{-3} mol O_2

1.3×10^{-3} $mol \cdot kg^{-1} \cdot atm^{-1}$ $O_2 \times 32.00$ $g \cdot mol^{-1}$ $O_2 \times 10^3$ $mg \cdot g^{-1}$

$= 42$ $mg \cdot kg^{-1} \cdot atm^{-1}$ or 42 $ppm \cdot atm^{-1}$

4 $mg \div 41$ $mg \cdot kg^{-1} \cdot atm^{-1} = 0.1$ atm

(c) $P = \dfrac{0.1\ atm}{0.21} = 0.5$ atm

8.33 (a) By Henry's law, the concentration of CO_2 in solution will double.

(b) No change in the equilibrium will occur; the partial pressure of CO_2 is unchanged and the concentration is unchanged.

8.35 (a) Because it is exothermic, the enthalpy change must be negative;

(b) $Li_2SO_4(s) \rightarrow 2\ Li^+(aq) + SO_4^{2-}(aq) + heat$;   (c) Given that

$\Delta H_L + \Delta H_{hydration} = \Delta H$ of solution, the enthalpy of hydration should be larger. If the lattice energy were greater, the overall process would be endothermic.

8.37 To answer this question we must first determine the molar enthalpies of solution and multiply this by the number of moles of solid dissolved to get the actual amount of heat released.

(a) $\Delta H°_{hydration} = +3.9$

$\Delta H = \dfrac{10.0\ g\ NaCl}{58.44\ g \cdot mol^{-1}} \times (+3.9\ kJ \cdot mol^{-1}) = 0.67$ kJ or 6.7×10^2 J

(b) $\Delta H°_{hydration} = -0.6$

$\Delta H = \dfrac{10.0\ g\ NaBr}{102.90\ g \cdot mol^{-1}} \times (-0.6\ kJ \cdot mol^{-1}) = 0.06$ kJ or -6×10 J

(c) $\Delta H°_{hydration} = -329$ $kJ \cdot mol^{-1}$

$$\Delta H = \frac{10.0 \text{ g AlCl}_3}{133.33 \text{ g} \cdot \text{mol}^{-1}} \times (-329 \text{ kJ} \cdot \text{mol}^{-1}) = -24.7 \text{ kJ}$$

(d) $\Delta H°_{\text{hydration}} = 25.7 \text{ k} \cdot \text{mol}^{-1}$

$$\Delta H = \frac{10.0 \text{ g NH}_4\text{NO}_3}{80.04 \text{ g} \cdot \text{mol}^{-1}} \times (+25.7 \text{ kJ} \cdot \text{mol}^{-1}) = +3.21 \text{ kJ}$$

8.39   All the enthalpies of solution are positive. Those of the alkali metal chlorides increase as the cation becomes larger and less strongly hydrated by water. All the alkali metal chlorides are soluble in water, but AgCl is not. AgCl has a relatively large positive enthalpy of solution. When dissolving is highly endothermic, the small increase in disorder due to solution formation may not be enough to compensate for the decrease in disorder for the surroundings, and a solution does not form. This is the case for AgCl.

8.41   (a) $m_{\text{NaCl}} = \dfrac{\left(\dfrac{10.0 \text{ g NaCl}}{58.44 \text{ g} \cdot \text{mol}^{-1}} \right)}{0.250 \text{ kg}} = 0.684 \, m$

(b) $m_{\text{NaOH}} = \dfrac{\left(\dfrac{\text{mass NaOH}}{40.00 \text{ g} \cdot \text{mol}^{-1}} \right)}{0.345 \text{ kg}} = 0.22 \, m$

mass NaOH $= 3.0$ g

(c) $m_{\text{urea}} = \dfrac{\left(\dfrac{1.54 \text{ g urea}}{60.06 \text{ g} \cdot \text{mol}^{-1} \text{ urea}} \right)}{(515 \text{ cm}^3)(1.00 \text{ g} \cdot \text{cm}^{-3}) \left(\dfrac{1 \text{ kg}}{1000 \text{ g}} \right)} = 0.0498 \, m$

8.43   (a)   1 kg of 5.00% K_3PO_4 will contain 50.0 g K_3PO_4 and 950.0 g H_2O.

$\dfrac{\left(\dfrac{50.0 \text{ g K}_3\text{PO}_4}{212.27 \text{ g} \cdot \text{mol}^{-1} \text{ K}_3\text{PO}_4} \right)}{0.950 \text{ kg}} = 0.248 \, m$

(b)   The mass of 1.00 L of solution will be 1043 g, which will contain

$1043 \text{ g} \times 0.0500 = 52.2 \text{ g K}_3\text{PO}_4.$

$$\frac{\left(\dfrac{52.2 \text{ g K}_3\text{PO}_4}{212.27 \text{ g} \cdot \text{mol}^{-1} \text{ K}_3\text{PO}_4}\right)}{1.00 \text{ L}} = 0.246 \text{ M}$$

8.45 (a) If x_{MgCl_2} is 0.0175, then there are 0.0175 mol MgCl_2 for every 0.9825 mol H_2O. The mass of water will be

$18.02 \text{ g} \cdot \text{mol}^{-1} \times 0.9825 \text{ mol} = 17.70 \text{ g}$ or 0.017 70 kg.

$$m_{\text{Cl}^-} = \frac{\left(\dfrac{2 \text{ Cl}^-}{\text{MgCl}_2}\right)(0.0175 \text{ mol MgCl}_2)}{0.017 \ 70 \text{ kg solvent}} = 1.98 \ m$$

(b) $m_{\text{Cl}^-} = \dfrac{\left(\dfrac{7.12 \text{ g NaOH}}{40.00 \text{ g} \cdot \text{mol}^{-1} \text{ NaOH}}\right)}{0.325 \text{ kg solvent}} = 0.548 \ m$

(c) 1.000 L of 15.00 M HCl(aq) will contain 15.00 mol with a mass of

$15.00 \times 36.46 \text{ g} \cdot \text{mol}^{-1} = 546.9 \text{ g}$. The density of the 1.000 L of solution

is $1.0745 \text{ g} \cdot \text{cm}^{-3}$ so the total mass in the solution is 1074.5 g. This leaves

$1074.5 \text{ g} - 546.9 \text{ g} = 527.6 \text{ g}$ as water.

$\dfrac{15.00 \text{ mol HCl}}{0.5276 \text{ kg solvent}} = 28.43 \ m$

8.47 (a) Molar mass of $\text{CaCl}_2 \cdot 6 \text{ H}_2\text{O} = 219.08 \text{ g} \cdot \text{mol}^{-1}$, which consists of

110.98 g CaCl_2 and 108.10 g of water.

$$m_{\text{CaCl}_2} = \frac{x \text{ mol CaCl}_2 \cdot 6 \text{ H}_2\text{O}}{0.500 \text{ kg} + x \, (6 \times 0.018 \ 02 \text{ kg H}_2\text{O})}$$

Note: $18.02 \text{ g H}_2\text{O} = 0.018 \ 02 \text{ kg H}_2\text{O} = 1.000 \text{ mol H}_2\text{O}$

$x =$ number of moles of $\text{CaCl}_2 \cdot 6 \text{ H}_2\text{O}$ needed to prepare a solution of

molality m_{CaCl_2}, in which each mole of $\text{CaCl}_2 \cdot 6 \text{ H}_2\text{O}$ produces 6(0.018

02 kg) of water as solvent (assuming we begin with 0.250 kg H_2O).

For a 0.175 m solution of $\text{CaCl}_2 \cdot 6 \text{ H}_2\text{O}$,

$$0.175\ m = \frac{x}{0.500\ \text{kg} + x(6)(0.018\ 02\ \text{kg H}_2\text{O})}$$

$x = 0.0875\ \text{mol} + x(0.0189\ \text{mol})$

$x - 0.0189\ x = 0.0875\ \text{mol}$

$0.981\ x = 0.0875\ \text{mol}$

$x = 0.0892\ \text{mol CaCl}_2 \cdot 6\ \text{H}_2\text{O}$

$\therefore (0.0892\ \text{mol CaCl}_2 \cdot 6\ \text{H}_2\text{O}) \times \left(\dfrac{219.08\ \text{g CaCl}_2 \cdot 6\ \text{H}_2\text{O}}{1\ \text{mol CaCl}_2 \cdot 6\ \text{H}_2\text{O}} \right) = 19.5\ \text{g CaCl}_2 \cdot 6\ \text{H}_2\text{O}$

(b) Molar mass of $\text{NiSO}_4 \cdot 6\ \text{H}_2\text{O} = 262.86\ \text{g} \cdot \text{mol}^{-1}$, which consists of

154.77 g NiSO_4 and 108.09 g H_2O.

$$m_{\text{NiSO}_4} = \frac{x\ \text{mol NiSO}_4 \cdot 6\ \text{H}_2\text{O}}{0.500\ \text{kg} + x\,(6 \times 0.018\,02\ \text{kg H}_2\text{O})}$$

where x = number of moles of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ needed to prepare a solution

of molality m_{NiSO_4}, in which each mole of $\text{NiSO}_4 \cdot 6\ \text{H}_2\text{O}$ produces

6(0.018 02 kg) of water as solvent. Assuming we begin with

0.500 kg H_2O, for a 0.33 m solution of $\text{NiSO}_4 \cdot 6\ \text{H}_2\text{O}$,

$$0.33\ m = \frac{x}{0.500\ \text{kg} + x(6)(0.018\ 02\ \text{kg H}_2\text{O})}$$

$x = 0.16\ \text{mol} + x(0.0357\ \text{mol})$

$x - 0.0357\ x = 0.16\ \text{mol}$

$0.964\ x = 0.16\ \text{mol}$

$x = 0.17\ \text{mol NiSO}_4 \cdot 6\ \text{H}_2\text{O}$

$\therefore (0.17\ \text{mol NiSO}_4 \cdot 6\ \text{H}_2\text{O}) \times \left(\dfrac{262.86\ \text{g NiSO}_4 \cdot 6\ \text{H}_2\text{O}}{1\ \text{mol NiSO}_4 \cdot 6\ \text{H}_2\text{O}} \right) = 45\ \text{g NiSO}_4 \cdot 6\ \text{H}_2\text{O}$

8.49 (a) $P = x_{\text{solvent}} \times P_{\text{pure solvent}}$

At 100°C, the normal boiling point of water, the vapor pressure of water

is 1.00 atm. If the mole fraction of sucrose is 0.100, then the mole fraction

of water is 0.900:

$P = 0.900 \times 1.000\ \text{atm} = 0.900\ \text{atm}$ or 684 Torr

(b) First, the molality must be converted to mole fraction. If the molality is $0.100 \text{ mol} \cdot \text{kg}^{-1}$, then there will be 0.100 mol sucrose per 1000 g of water.

$$x_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{sucrose}} = \frac{\dfrac{1000\text{ g}}{18.02\text{ g} \cdot \text{mol}^{-1}}}{\dfrac{1000\text{ g}}{18.02\text{ g} \cdot \text{mol}^{-1}} + 0.100\text{ mol}} = 0.998$$

$P = 0.998 \times 1.000 \text{ atm} = 0.998 \text{ atm or } 758 \text{ Torr}$

8.51 (a) The vapor pressure of water at $0°C$ is 4.58 Torr. The concentration of the solution must be converted to mole fraction in order to perform the calculation. A solution that is 2.50% ethylene glycol by mass will contain 2.50 g of ethylene glycol per 97.50 g of water.

$$x_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{ethylene\ glycol}} = \frac{\dfrac{97.50\text{ g}}{18.02\text{ g} \cdot \text{mol}^{-1}}}{\dfrac{97.50\text{ g}}{18.02\text{ g} \cdot \text{mol}^{-1}} + \dfrac{2.50\text{ g}}{62.07\text{ g} \cdot \text{mol}^{-1}}} = 0.993$$

$P = x_{solvent} \times P_{pure\ solvent}$

$P = 0.993 \times 4.58 \text{ Torr} = 4.55 \text{ Torr}$

(b) The vapor pressure of water is 355.26 Torr at $80°C$. The concentration given in $\text{mol} \cdot \text{kg}^{-1}$ must be converted to mole fraction.

$$x_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{Na^+} + n_{OH^-}} = \frac{\dfrac{1000\text{ g}}{18.02\text{ g} \cdot \text{mol}^{-1}}}{\dfrac{1000\text{ g}}{18.02\text{ g} \cdot \text{mol}^{-1}} + 2 \times 0.155\text{ mol}} = 0.9944$$

$P = 0.9972 \times 355.26 \text{ Torr} = 354.3 \text{ Torr}$

(c) At $10°C$, the vapor pressure of water is 9.21 Torr. The concentratioin must be expressed in terms of mole fraction:

$$x_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{urea}} = \frac{\dfrac{100\text{ g}}{18.02\text{ g} \cdot \text{mol}^{-1}}}{\dfrac{100\text{ g}}{18.02\text{ g} \cdot \text{mol}^{-1}} + \dfrac{5.95\text{ g}}{60.06\text{ g} \cdot \text{mol}^{-1}}} = 0.982$$

$P = 0.982 \times 9.21 \text{ Torr} = 9.04 \text{ Torr}$

The change in the vapor pressure will therefore be $9.21 - 9.04 = 0.17$ Torr

8.53 (a) From the relationship $P = x_{\text{solvent}} \times P_{\text{pure solvent}}$ we can calculate the mole fraction of the solvent:

$$94.8 \text{ Torr} = x_{\text{solvent}} \times 100.0 \text{ Torr}$$

$$x_{\text{solvent}} = 0.948$$

The mole fraction of the unknown compound will be $1.000 - 0.948 = 0.052$.

(b) The molar mass can be calculated by using the definition of mole fraction for either the solvent or solute. In this case, the math is slightly easier if the definition of mole fraction of the solvent is used:

$$x_{\text{solvent}} = \frac{n_{\text{solvent}}}{n_{\text{unknown}} + n_{\text{solvent}}}$$

$$0.948 = \frac{\dfrac{100 \text{ g}}{78.11 \text{ g} \cdot \text{mol}^{-1}}}{\dfrac{100 \text{ g}}{78.11 \text{ g} \cdot \text{mol}^{-1}} + \dfrac{8.05 \text{ g}}{M_{\text{unknown}}}}$$

$$M_{\text{unknown}} = \frac{8.05 \text{ g}}{\left[\left(\dfrac{100 \text{ g}}{78.11 \text{ g} \cdot \text{mol}^{-1}}\right) \Big/ 0.948\right] - \left(\dfrac{100 \text{ g}}{78.11 \text{ g} \cdot \text{mol}^{-1}}\right)} = 115 \text{ g} \cdot \text{mol}^{-1}$$

8.55 (a) $\Delta T_{b} = ik_{b}m$

Because sucrose is a nonelectrolyte, $i = 1$.

$$\Delta T_{b} = 0.51 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times 0.10 \text{ mol} \cdot \text{kg}^{-1} = 0.051 \text{ K or } 0.051°C$$

The boiling point will be $100.000°C + 0.051°C = 100.051°C$.

(b) $\Delta T_{b} = ik_{b}m$

For NaCl, $i = 2$.

$$\Delta T_{b} = 2 \times 0.51 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times 0.22 \text{ mol} \cdot \text{kg}^{-1} = 0.22 \text{ K or } 0.22°C$$

The boiling point will be $100.00°C + 0.22°C = 100.22°C$.

(c) $\Delta T_{b} = ik_{b}m$

$$\Delta T_{b} = 2 \times 0.51 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \frac{\left(\dfrac{0.230 \text{ g}}{25.94 \text{ g} \cdot \text{mol}^{-1}}\right)}{0.100 \text{ kg}} = 0.090 \text{ K or } 0.090°C$$

The boiling point will be $100.000°C + 0.090°C$ or $100.090°C$.

8.57 (a) Pure water has a vapor pressure of 760.00 Torr at 100°C. The mole

fraction of the solution can be determined from $P = x_{solvent} \times P_{pure\ solvent}$.

$751\ \text{Torr} = x_{solvent} \times 760.00\ \text{Torr}$

$x_{solvent} = 0.988$

The mole fraction needs to be converted to molality:

$$x_{solvent} = 0.988 = \frac{n_{H_2O}}{n_{H_2O} + n_{solute}}$$

Because the absolute amount of solution is not important, we can assume

that the total number of moles = 1.00.

$$0.988 = \frac{n_{H_2O}}{1.00\ \text{mol}}$$

$n_{H_2O} = 0.988\ \text{mol};\ n_{solute} = 0.012\ \text{mol}$

$$\text{molality} = \frac{0.012\ \text{mol}}{\left(\dfrac{0.988\ \text{mol} \times 18.02\ \text{g}\cdot\text{mol}^{-1}}{1000\ \text{g}\cdot\text{kg}^{-1}}\right)} = 0.67\ \text{mol}\cdot\text{kg}^{-1}$$

Knowing the mole fraction, one can calculate ΔT_b:

$\Delta T_b = k_b m$

$\Delta T_b = 0.51\ \text{K}\cdot\text{mol}\cdot\text{kg}^{-1} \times 0.67\ \text{mol}\cdot\text{kg}^{-1} = 0.34\ \text{K or } 0.34°\text{C}$

Boiling point $= 100.00°\text{C} + 0.34°\text{C} = 100.34°\text{C}$

(b) The procedure is the same as in (a). Pure benzene has a vapor pressure

of 760.00 Torr at 80.1°C. The mole fraction of the solution can be

determined from

$P = x_{solvent} \times P_{pure\ solvent}$

$740\ \text{Torr} = x_{solvent} \times 760.00\ \text{Torr}$

$x_{solvent} = 0.974$

The mole fraction needs to be converted to molality:

$$x_{solvent} = 0.974 = \frac{n_{benzene}}{n_{benzene} + n_{solute}}$$

Because the absolute amount of solution is not important, we can assume

that the total number of moles = 1.00:

$$0.974 = \frac{n_{benzene}}{1.00 \text{ mol}}$$

$n_{benzene} = 0.974$ mol; $n_{solute} = 0.026$ mol

$$\text{molality} = \frac{0.026 \text{ mol}}{\left(\dfrac{0.974 \text{ mol} \times 78.11 \text{ g} \cdot \text{mol}^{-1}}{1000 \text{ g} \cdot \text{kg}^{-1}} \right)} = 0.34 \text{ mol} \cdot \text{kg}^{-1}$$

Knowing the mole fraction, one can calculate ΔT_b :

$\Delta T_b = k_b m$

$\Delta T_b = 2.53 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times 0.34 \text{ mol} \cdot \text{kg}^{-1} = 0.86$ K or 0.86°C

Boiling point $= 80.1°C + 0.86°C = 81.0°C$

8.59 $\Delta T_b = 61.51°C - 61.20°C = 0.31°C$ or 0.31 K

$\Delta T_b = k_b \times \text{molality}$

$0.31 \text{ K} = 4.95 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \text{molality}$

$$0.31 \text{ K} = 4.95 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \frac{\left(\dfrac{1.05 \text{ g}}{M_{unknown}} \right)}{0.100 \text{ kg}}$$

$$\frac{0.100 \text{ kg} \times 0.31 \text{ K}}{4.95 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}} = \frac{1.05 \text{ g}}{M_{unknown}}$$

$$M_{unknown} = \frac{1.05 \text{ g} \times 4.95 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}}{0.100 \text{ kg} \times 0.31 \text{ K}} = 1.7 \times 10^2 \text{ g} \cdot \text{mol}^{-1}$$

8.61 (a) $\Delta T_f = i k_f m$

Because sucrose is a nonelectrolyte, $i = 1$.

$\Delta T_f = 1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times 0.10 \text{ mol} \cdot \text{kg}^{-1} = 0.19$ K or 0.19°C

The freezing point will be $0.000°C - 0.19°C = -0.19°C$.

(b) $\Delta T_f = i k_f m$

For NaCl, $i = 2$

$\Delta T_f = 2 \times 1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times 0.22 \text{ mol} \cdot \text{kg}^{-1} = 0.82$ K or 0.82°C

The freezing point will be $0.00°C - 0.82°C = -0.82°C$.

(c) $\Delta T_f = i k_f m$

$i = 2$ for LiF

$$\Delta T_f = 2 \times 1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \frac{\left(\dfrac{0.120 \text{ g}}{25.94 \text{ g} \cdot \text{mol}^{-1}}\right)}{0.100 \text{ kg}} = 0.172 \text{ K or } 0.172°C$$

The freezing point will be $0.000°C - 0.172°C = -0.172°C$.

8.63 $\Delta T_f = 179.8°C - 176.9°C = 2.9°C$ or 2.9 K

$\Delta T_f = k_f m$

$2.9 \text{ K} = (39.7 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1})m$

$2.9 \text{ K} = (39.7 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1})\dfrac{\left(\dfrac{1.14 \text{ g}}{M_{unknown}}\right)}{0.100 \text{ kg}}$

$\dfrac{0.100 \text{ kg} \times 2.9 \text{ K}}{39.7 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}} = \dfrac{1.14 \text{ g}}{M_{unknown}}$

$M_{unknown} = \dfrac{1.14 \text{ g} \times 39.7 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}}{0.100 \text{ kg} \times 2.9 \text{ K}} = 1.6 \times 10^2 \text{ g} \cdot \text{mol}^{-1}$

8.65   (a) First, calculate the molality using the change in boiling point, and then use that value to calculate the change in freezing point.

$\Delta T_b = k_b m$

$\Delta T_b = 82.0°C - 80.1°C = 1.9°C$ or 1.9 K

$1.9 \text{ K} = 2.53 \text{ K} \cdot \text{Kg} \cdot \text{mol}^{-1} \times \text{molality}$

$\text{molality} = 0.75 \text{ mol} \cdot \text{kg}^{-1}$

$\Delta T_f = k_f m$

$\Delta T_f = 5.12 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times 0.75 \text{ mol} \cdot \text{kg}^{-1}$

$\Delta T_f = 3.84 \text{ K or } 3.84°C$

The freezing point will be $5.5°C - 3.84°C = 1.7°C$

(b) $\Delta T_f = k_f m$

Because the freezing point of water $= 0.00°C$, the freezing point of the solution equals the freezing point depression.

$3.04 \text{ K} = 1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \text{molality}$

$\text{molality} = 1.63 \text{ mol} \cdot \text{kg}^{-1}$

(c) $\Delta T_\mathrm{f} = k_\mathrm{f} m$

$1.94\ \mathrm{K} = (1.86\ \mathrm{K\cdot kg\cdot mol^{-1}})m$

$1.94\ \mathrm{K} = 1.86\ \mathrm{K\cdot kg\cdot mol^{-1}} \times \dfrac{n_\mathrm{solute}}{\mathrm{kg\,(solvent)}}$

$1.94\mathrm{K} = 1.86\ \mathrm{K\cdot kg\cdot mol^{-1}} \times \dfrac{n_\mathrm{solute}}{0.200\ \mathrm{kg}}$

$n_\mathrm{solute} = 0.209\ \mathrm{mol}$

8.67 (a) A 1.00% aqueous solution of NaCl will contain 1.00 g of NaCl for 99.0 g of water. To use the freezing point depression equation, we need the molality of the solution:

$$\text{molality} = \dfrac{\left(\dfrac{1.00\ \mathrm{g}}{58.44\ \mathrm{g\cdot mol^{-1}}}\right)}{0.0990\ \mathrm{kg}} = 0.173\ \mathrm{mol\cdot kg^{-1}}$$

$\Delta T_\mathrm{f} = i k_\mathrm{f} m$

$\Delta T_\mathrm{f} = i\,(1.86\ \mathrm{K\cdot kg\cdot mol^{-1}})(0.173\ \mathrm{mol\cdot kg^{-1}}) = 0.593\ \mathrm{K}$

$i = 1.84$

(b) molality of all solute species (undissociated NaCl(aq) plus Na^+ (aq) + Cl^- (aq)) $= 1.84 \times 0.173\ \mathrm{mol\cdot kg^{-1}} = 0.318\ \mathrm{mol\cdot kg^{-1}}$

(c) If all the NaCl had dissociated, the total molality in solution would have been $0.346\ \mathrm{mol\cdot kg^{-1}}$, giving an i value equal to 2. If no dissociation had taken place, the molality in solution would have equaled 0.173 $\mathrm{mol\cdot kg^{-1}}$.

$\mathrm{NaCl(aq)} \qquad \rightarrow\ Na^+(aq) + Cl^-(aq)$
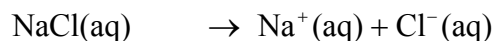
$0.173\ \mathrm{mol\cdot kg^{-1}} - x \qquad x \qquad x$

$0.173\ \mathrm{mol\cdot kg^{-1}} - x + x + x = 0.318\ \mathrm{mol\cdot kg^{-1}}$

$0.173\ \mathrm{mol\cdot kg^{-1}} + x = 0.318\ \mathrm{mol\cdot kg^{-1}}$

$x = 0.145\ \mathrm{mol\cdot kg^{-1}}$

$\text{\% dissociation} = \dfrac{0.145\ \mathrm{mol\cdot kg^{-1}}}{0.173\ \mathrm{mol\cdot kg^{-1}}} \times 100 = 83.8\%$

8.69 For an electrolyte that dissociates into two ions, the van't Hoff i factor will be 1 plus the degree of dissociation, in this case 0.075. This can be readily seen for the general case MX. Let A = initial concentration of MX (if none is dissociated) and let Y = the concentration of MX that subsequently dissociates:

$$MX(aq) \longrightarrow M^{n+}(aq) + X^{n-}(aq)$$
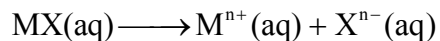
$$A - Y \qquad\qquad Y \qquad\quad Y$$

The total concentration of solute species is $(A - Y) + Y + Y = A + Y$

The value of i will then be equal to A + Y or 1.075.

The freezing point change is then easy to calculate:

$$\Delta T_f = ik_f m$$
$$= 1.075 \times 1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times 0.10 \text{ mol} \cdot \text{kg}^{-1}$$
$$= 0.20$$

Freezing point of the solution will be $0.00°C - 0.20°C = -0.20°C$.

8.71 (a) $\Pi = iRT \times \text{molarity}$
$$= 1 \times 0.082\,06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 293 \text{ K} \times 0.010 \text{ mol} \cdot \text{L}^{-1}$$
$$= 0.24 \text{ atm or } 1.8 \times 10^2 \text{ Torr}$$

(b) Because HCl is a strong acid, it should dissociate into two ions, H^+ and Cl^-, so $i = 2$.

$$\Pi = 2 \times 0.082\,06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 293 \text{ K} \times 1.0 \text{ mol} \cdot \text{L}^{-1}$$
$$= 48 \text{ atm}$$

(c) $CaCl_2$ should dissociate into 3 ions in solution, therefore $i = 3$.

$$\Pi = 3 \times 0.082\,06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 293 \text{ K} \times 0.010 \text{ mol} \cdot \text{L}^{-1}$$
$$= 0.72 \text{ atm or } 5.5 \times 10^2 \text{ Torr}$$

8.73 The polypeptide is a nonelectrolye, so $i = 1$.

$$\Pi = iRT \times \text{molarity}$$

$$\Pi = \frac{3.74 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}} = 1 \times 0.082\,06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 300 \text{ K} \times \frac{\left(\dfrac{0.40 \text{ g}}{M_{\text{unknown}}}\right)}{1.0 \text{ L}}$$

$$M_{unknown} = \frac{0.082\ 06\ \text{L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \times 300\ \text{K} \times 0.40\ \text{g} \times 760\ \text{Torr}\cdot\text{atm}^{-1}}{3.74\ \text{Torr} \times 1.0\ \text{L}}$$

$$= 2.0 \times 10^3\ \text{g}\cdot\text{mol}^{-1}$$

8.75 We assume the polymer to be a nonelectrolyte, so $i = 1$.

$\Pi = iRT \times \text{molarity}$

$$\Pi = \frac{5.4\ \text{Torr}}{760\ \text{Torr}\cdot\text{atm}^{-1}} = 1 \times 0.082\ 06\ \text{L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \times 293\ \text{K} \times \frac{\left(\dfrac{0.10\ \text{g}}{M_{unknown}}\right)}{0.100\ \text{L}}$$

$$M_{unknown} = \frac{0.082\ 06\ \text{L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \times 293\ \text{K} \times 0.10\ \text{g} \times 760\ \text{Torr}\cdot\text{atm}^{-1}}{5.4\ \text{Torr} \times 0.100\ \text{L}}$$

$$= 3.4 \times 10^3\ \text{g}\cdot\text{mol}^{-1}$$

8.77 (a) $C_{12}H_{22}O_{11}$ should be a nonelectrolyte, so $i = 1$.

$\Pi = iRT \times \text{molarity}$

$\quad = 1 \times 0.082\ 06\ \text{L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \times 293\ \text{K} \times 0.050\ \text{mol}\cdot\text{L}^{-1}$

$\quad = 1.2\ \text{atm}$

(b) NaCl dissociates to give 2 ions in solution, so $i = 2$.

$\Pi = iRT \times \text{molarity}$

$\quad = 2 \times 0.082\ 06\ \text{L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \times 293\ \text{K} \times 0.0010\ \text{mol}\cdot\text{L}^{-1}$

$\quad = 0.048\ \text{atm}$ or 36 Torr

(c) AgCN dissociates in solution to give two ions $(Ag^+$ and $CN^-)$, so $i = 2$.

$\Pi = iRT \times \text{molarity}$

We must assume that the AgCN does not significantly affect either the volume or density of the solution, which is reasonable given the very small amount of it that dissolves.

$$\Pi = 2 \times 0.082\,06\ \text{L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \times 293\ \text{K} \times$$

$$\dfrac{\left(\dfrac{2.3 \times 10^{-5}\ \text{g}}{133.89\ \text{g}\cdot\text{mol}^{-1}}\right)}{\left(\dfrac{100\ \text{g H}_2\text{O}}{1\ \text{g}\cdot\text{cm}^{-3}\ \text{H}_2\text{O} \times 1000\ \text{cm}^3\cdot\text{L}^{-1}}\right)}$$

$$= 8.3 \times 10^{-5}\ \text{atm}$$

8.79 $$\Pi = n\dfrac{RT}{V} = \dfrac{m}{M}\dfrac{RT}{V}$$

where m is the mass of unknown compound.

$$M = \dfrac{mRT}{V\Pi}$$

$$M = \dfrac{(0.166\ \text{g})(0.082\,06\ \text{L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(293\ \text{K})}{(0.010\ \text{L})\left(\dfrac{1.2\ \text{Torr}}{760\ \text{Torr}\cdot\text{atm}^{-1}}\right)} = 2.5 \times 10^5\ \text{g}\cdot\text{mol}^{-1}$$

8.81 (a) To determine the vapor pressure of the solution, we need to know the mole fraction of each component.

$$x_{\text{benzene}} = \dfrac{1.50\ \text{mol}}{1.50\ \text{mol} + 0.50\ \text{mol}} = 0.75$$

$$x_{\text{toluene}} = 1 - x_{\text{benzene}} = 0.25$$

$$P_{\text{total}} = (0.75 \times 94.6\ \text{Torr}) + (0.25 \times 29.1\ \text{Torr}) = 78.2\ \text{Torr}$$

The vapor phase composition will be given by

$$x_{\text{benzene in vapor phase}} = \dfrac{P_{\text{benzene}}}{P_{\text{total}}} = \dfrac{0.75 \times 94.6\ \text{Torr}}{78.2\ \text{Torr}} = 0.91$$

$$x_{\text{toluene in vapor phase}} = 1 - 0.91 = 0.09$$

The vapor is richer in the more volatile benzene, as expected.

(b) The procedure is the same as in (a) but the number of moles of each component must be calculated first:

$$n_{\text{benzene}} = \dfrac{15.0\ \text{g}}{78.11\ \text{g}\cdot\text{mol}^{-1}} = 0.192$$

$$n_{\text{toluene}} = \dfrac{65.3\ \text{g}}{92.14\ \text{g}\cdot\text{mol}^{-1}} = 0.709$$

$$x_{\text{benzene}} = \frac{0.192\ \text{mol}}{0.192\ \text{mol} + 0.709\ \text{mol}} = 0.213$$

$$x_{\text{toluene}} = 1 - x_{\text{benzene}} = 0.787$$

$$P_{\text{total}} = (0.213 \times 94.6\ \text{Torr}) + (0.787 \times 29.1\ \text{Torr}) = 43.0\ \text{Torr}$$

The vapor phase composition will be given by

$$x_{\text{benzene in vapor phase}} = \frac{P_{\text{benzene}}}{P_{\text{total}}} = \frac{0.213 \times 94.6\ \text{Torr}}{43.0\ \text{Torr}} = 0.469$$

$$x_{\text{toluene in vapor phase}} = 1 - 0.469 = 0.531$$

8.83 To calculate this quantity, we must first find the mole fraction of each that will be present in the mixture. This value is obtained from the relationship

$$P_{\text{total}} = [x_{1,1\text{-dichloroethane}} \times P_{\text{pure 1,1-dichloroethane}}]$$

$$+[x_{1,1\text{-dichlorotetrafluoroethane}} \times P_{\text{pure 1,1-dichlorotetrafluoroethane}}]$$

$$157\ \text{Torr} = [x_{1,1\text{-dichloroethane}} \times 228\ \text{Torr}] + [x_{1,1\text{-dichlorotetrafluoroethane}} \times 79\ \text{Torr}]$$

$$157\ \text{Torr} = [x_{1,1\text{-dichloroethane}} \times 228\ \text{Torr}] + [(1 - x_{1,1\text{-dichloroethane}}) \times 79\ \text{Torr}]$$

$$157\ \text{Torr} = 79\ \text{Torr} + [(x_{1,1\text{-dichloroethane}} \times 228\ \text{Torr}) - (x_{1,1\text{-dichloroethane}} \times 79\ \text{Torr})]$$

$$78\ \text{Torr} = x_{1,1\text{-dichloroethane}} \times 149\ \text{Torr}$$

$$x_{1,1\text{-dichloroethane}} = 0.52$$

$$x_{1,1\text{-dichlorotetrafluoroethane}} = 1 - 0.52 = 0.48$$

To calculate the number of grams of 1,1-dichloroethane, we use the definition of mole fraction. Mathematically, it is simpler to use the $x_{1,1\text{-dichlorotetrafluoroethane}}$ definition:

$$n_{1,1\text{-dichlorotetrafluoroethane}} = \frac{100.0\ \text{g}}{170.92\ \text{g} \cdot \text{mol}^{-1}} = 0.5851\ \text{mol}$$

$$x_{1,1\text{-dichlorotetrafluoroethane}} = \frac{0.5851\ \text{mol}}{0.5851\ \text{mol} + \dfrac{m}{98.95\ \text{g} \cdot \text{mol}^{-1}}} = 0.48$$

$$0.5851\ \text{mol} = 0.48 \times \left[0.5851\ \text{mol} + \frac{m}{98.95\ \text{g} \cdot \text{mol}^{-1}} \right]$$

$$0.5851\ \text{mol} - (0.48 \times 0.5851\ \text{mol}) = 0.48 \times \left[\frac{m}{98.95\ \text{g} \cdot \text{mol}^{-1}} \right]$$

$$0.3042\ \text{mol} = 0.004\,851\ \text{mol} \cdot \text{g}^{-1} \times m$$

$$m = 63\ \text{g}$$

8.85 Raoult's Law applies to the vapor pressure of the mixture, so positive deviation means that the vapor pressure is higher than expected for an ideal solution. Negative deviation means that the vapor pressure is lower than expected for an ideal solution. Negative deviation will occur when the interactions between the different molecules are somewhat stronger than the interactions between molecules of the same kind   (a) For methanol and ethanol, we expect the types of intermolecular attractions in the mixture to be similar to those in the component liquids, so that an ideal solution is predicted.   (b) For HF and H_2O, the possibility of intermolecular hydrogen bonding between water and HF would suggest that negative deviation would be observed, which is the case. HF and H_2O form an azeotrope that boils at $111°C$, a temperature higher than the boiling point of either HF $(19.4°C)$ or water.   (c) Because hexane is nonpolar and water is polar with hydrogen bonding, we would expect a mixture of these two to exhibit positive deviation (the interactions between the different molecules would be weaker than the intermolecular forces between like molecules). Hexane and water do form an azeotrope that boils at $61.6°C$, a temperature below the boiling point of either hexane or water.

8.87 $x_{methanol} = 0.65$ and $x_{ethanol} = 0.35$

$P_{methanol} = x_{methanol} \cdot P^*_{methanol} = (0.65)(122.7 \text{ Torr}) = 80 \text{ Torr}$

$P_{ethanol} = x_{ethanol} \cdot P^*_{ethanol} = (0.35)(58.9 \text{ Torr}) = 21 \text{ Torr}$

from the ideal gas law we know that $n \propto P$, therefore:

$$x_{methanol} = \frac{n_{methanol}}{n_{methanol} + n_{ethanol}} = \frac{P_{methanol}}{P_{methanol} + P_{ethanol}} = \frac{80 \text{ Torr}}{80 \text{ Torr} + 21 \text{ Torr}} = 0.79$$

and

$$x_{ethanol} = \frac{n_{ethanol}}{n_{methanol} + n_{ethanol}} = \frac{P_{ethanol}}{P_{methanol} + P_{ethanol}} = \frac{21 \text{ Torr}}{80 \text{ Torr} + 21 \text{ Torr}} = 0.21$$

8.89   (a) stronger;   (b) low;   (c) high;   (d) weaker;   (e) weak, low;   (f) low;   (g) strong, high

8.91 (a, b) Viscosity and surface tension decrease with increasing temperature; at high temperatures the molecules readily move away from their neighbors because of increased kinetic energy. (c) Evaporation rate and vapor pressure increase with increasing temperature because the kinetic energy of the molecules increase with temperature, and the molecules are more likely to escape into the gas phase.

8.93 If the external pressure is lowered, water boils at a lower temperature. The boiling temperature is the temperature at which the vapor pressure equals the external pressure. Vapor pressure increases with temperature. If the external pressure is reduced, the vapor pressure of the water will reach that value at a lower temperature; thus, lowering the external pressure lowers the boiling temperature.

8.95 (a) No. Solid helium will melt before converting to a gas at 5 K. (b) Yes. Raising the temperature of rhombic sulfur at 1 atm will result in a phase change to monoclinic sulfur at 96°C. (c) Rhombic sulfur is the form observed. (d) At 100°C and 1 atm, the monoclinic form is more stable. (e) No. The phase diagram shows no area where solid diamond and gaseous carbon are adjacent.

8.97 (a) $\dfrac{25.0 \text{ Torr}}{31.83 \text{ Torr}} \times 100 = 78.5\%$; (b) At $25°C$ the vapor pressure of water is only 23.76 Torr, so some of the water vapor in the air would condense as dew or fog.

8.99 (a) At 30°C, the vapor pressure of pure water = 31.83 Torr. According to Raoult's law, $P = x_{\text{solvent}} \cdot P_{\text{pure}}$. To calculate the x_{solvent}: 0.50 m NaCl gives 0.50 moles Na^+ and 0.50 moles Cl^- per kg solvent. The number of moles of solvent is 1000 kg $\div 18.02$ g·mol^{-1} = 55.49 mol. The total number of moles = 0.50 mol + 0.50 mol + 55.49 mol = 56.49 mol.

$$x_{\text{solvent}} = \frac{55.49 \text{ mol}}{56.49 \text{ mol}} = 0.9823$$

$$P = x_{\text{solvent}} \cdot P_{\text{pure}} = 0.9823 \times 31.83 \text{ Torr} = 31.26 \text{ Torr}$$

(b)

At 100°C, $P_{\text{pure}} = 760 \text{ Torr} : P = x_{\text{solvent}} \cdot P_{\text{pure}} = 0.9823 \times 760 \text{ Torr} = 747 \text{ Torr}$

At 0°C, $P_{\text{pure}} = 4.58 \text{ Torr}; P = x_{\text{solvent}} \cdot P_{\text{pure}} = 0.9823 \times 4.58 \text{ Torr} = 4.50 \text{ Torr}$

8.101 $\Delta T = 77.19°C - 76.54°C = 0.65° \ 0.65 \text{ K}$

$$\Delta T_{\text{b}} = ik_{\text{b}}m = ik_{\text{b}} \frac{\left(\dfrac{m_{\text{solute}}}{M_{\text{solute}}} \right)}{\text{kg solvent}}$$

$$M_{\text{solute}} = \frac{ik_{\text{b}}m_{\text{solute}}}{(\text{kg solvent})(\Delta T_{\text{b}})} = \frac{(1)(4.95 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1})(0.30 \text{ g})}{(0.0300 \text{ kg})(0.65 \text{ K})}$$

$$= 76 \text{ g} \cdot \text{mol}^{-1}$$

8.103 $\Delta T = k_{\text{f}}m, \ m = \dfrac{n_{\text{solute}}}{\text{mass}_{\text{solvent(kg)}}}, \ n_{\text{solute}} = \dfrac{\text{mass}_{\text{solute}}}{M_{\text{solute}}}$

or

$$\Delta T = k_{\text{f}} \frac{\text{mass}_{\text{solute}}}{M_{\text{solute}} \times \text{mass}_{\text{solvent(kg)}}}$$

Solving for M_{solute},

$$M_{\text{solute}} = \frac{k_{\text{f}} \times \text{mass}_{\text{solute}}}{\Delta T_{\text{f}} \times \text{mass}_{\text{solvent(kg)}}}$$

(a) If mass$_{\text{solute}}$ appears greater, M_{solute} appears greater than actual molar mass, as mass$_{\text{solute}}$ occurs in the numerator above. Also, the ΔT measured will be smaller because less solute will actually be dissolved. This has the same effect as increasing the apparent M_{solute}.

(b) Because the true mass$_{\text{solvent}} = d \times V$, if d_{solvent} is less than 1.00 g·cm^{-3}, then the true mass$_{\text{solvent}}$ will be less than the assumed mass. M_{solute} is inversely proportional to mass$_{\text{solvent}}$, so an artificially high mass$_{\text{solvent}}$ will lead to an artificially low M_{solute}.

(c) If true freezing point is higher than the recorded freezing point, true $\Delta T <$ assumed ΔT, or assumed $\Delta T >$ true ΔT, and M_{solute} appears less than actual M_{solute}, as ΔT occurs in the denominator.

(d) If not all solute dissolved, the true mass$_{\text{solute}} <$ assumed mass$_{\text{solute}}$ or assumed mass$_{\text{solute}} >$ true mass$_{\text{solute}}$, and M_{solute} appears greater than the actual M_{solute}, as mass$_{\text{solute}}$ occurs in the numerator.

8.105 The water Coleridge referred to was seawater. The boards shrank due to osmosis (a net movement of water from the cells of the wood to the saline water). You can't drink seawater: osmosis would cause a net flow of water from the cells of the body to the saline-enriched surround solution and the cells would die.

8.107 When a drop of aqueous solution containing $Ca(HCO_3)_2$ seeps through a cave ceiling, it encounters a situation where the partial pressure of CO_2 is reduced and the reaction $Ca(HCO_3)_2(aq) \rightarrow CaCO_2(s) + CO_2(g) + H_2O(l)$ occurs. The concentration of CO_2 decreases as the CO_2 escapes as a gas, with $CaCO_3$ precipitating and forming a column that extends downward from the ceiling to form a stalacite. Stalagmite formation is similar, except the drops fall to the floor and the precipitate grows upward.

8.109 (a) The 5.22 cm or 52.2 mm rise for an aqueous solution must be converted to Torr or mmHg in order to be expressed into consistent units.

$$52.2 \text{ mm} \times \frac{0.998 \text{ g} \cdot \text{cm}^{-3}}{13.6 \text{ g} \cdot \text{cm}^{-3}} = 3.83 \text{ mmHg or } 3.83 \text{ Torr}$$

The molar mass can be calculated using the osmotic pressure equation:

$\Pi = iRT \times \text{molarity}$

Assume that the protein is a nonelectrolyte with $i = 1$ and that the amount of protein added does not significantly affect the volume of the solution.

$$\Pi = 1 \times 0.082\,06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 293 \text{ K} \times \frac{\left(\dfrac{0.010 \text{ g}}{M_{\text{protein}}}\right)}{0.010 \text{ L}} = \frac{3.83 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}}$$

$$M_{\text{protein}} = \frac{1 \times 0.082\,06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 293 \text{ K} \times 0.010 \text{ g} \times 760 \text{ Torr} \cdot \text{atm}^{-1}}{0.010 \text{ L} \times 3.83 \text{ Torr}}$$

$$M_{\text{protein}} = 4.8 \times 10^3 \text{ g} \cdot \text{mol}^{-1}$$

(b) The freezing point can be calculated using the relationship $\Delta T_{\text{f}} = i k_{\text{f}} m$

$$\Delta T_{\text{f}} = i k_{\text{f}} m$$

$$= 1 \times 1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \frac{\left(\dfrac{0.010 \text{ g}}{4.8 \times 10^3 \text{ g} \cdot \text{mol}^{-1}}\right)}{\left(\dfrac{10 \text{ mL} \times 1.00 \text{ g} \cdot \text{mL}^{-1}}{1000 \text{ g} \cdot \text{kg}^{-1}}\right)}$$

$$= 3.9 \times 10^{-4} \text{ K or } 3.9 \times 10^{-4}\,^{\circ}\text{C}$$

The freezing point will be $0.00^{\circ}\text{C} - 3.9 \times 10^{-4}\,^{\circ}\text{C} = -3.9 \times 10^{-4}\,^{\circ}\text{C}.$

(c) The freezing point change is so small that it cannot be measured accurately, so osmotic pressure would be the preferred method for measuring the molecular weight.

8.111 (a) The vapor pressure data can be used to obtain the concentration of the solution in terms of mole fraction, which in turn can be converted to molarity and used to calculate the osmotic pressure. Because 80.1°C is the boiling point of benzene, the vapor pressure of pure benzene at that temperature will be 760 Torr.

$$P_{\text{solution}} = x_{\text{solvent}} \times P_{\text{pure solvent}}$$

$$740 \text{ Torr} = x_{\text{solvent}} \times 760 \text{ Torr}$$

$$x_{\text{solvent}} = 0.974$$

The mole fraction of solute is, therefore, $1 - 0.974 = 0.026$. This means that there will be 0.026 moles of solute and 0.974 moles of benzene. From this we can calculate the molarity:

$$\text{molarity} = \frac{0.026 \text{ mol}}{\left(\dfrac{0.974 \text{ mol benzene} \times 78.11 \text{ g} \cdot \text{mol}^{-1} \text{ benzene}}{0.88 \text{ g} \cdot \text{mL}^{-1} \times 1000 \text{ mL} \cdot \text{L}^{-1}} \right)} = 0.30 \text{ mol} \cdot \text{L}^{-1}$$

The osmotic pressure is given by $\Pi = iRT \times \text{molarity}$. Assume $i = 1$.

$\Pi = 1 \times 0.082\,06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 293 \text{ K} \times 0.30 \text{ mol} \cdot \text{L}^{-1} = 7.2 \text{ atm}$

(b) As in (a), the freezing point will be used to calculate the molality of the solution, which will be converted to molarity for the osmotic pressure calculation.

$\Delta T_{\text{f}} = 5.5°\text{C} - 5.4°\text{C} = 0.1°\text{C or } 0.1 \text{ K}$

$\Delta T_{\text{f}} = i k_{\text{f}} m$

$0.1 \text{ K} = 1 \times 5.12 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \text{molality}$

$\text{molality} = 0.02 \text{ mol} \cdot \text{kg}^{-1}$

A $0.02 \text{ mol} \cdot \text{kg}^{-1}$ solution will contain 0.02 mol of solute and 1 kg of solvent. The volume of the solvent will be

$1000 \text{ g} \div 0.88 \text{ g} \cdot \text{mL}^{-1} = 1.1 \times 10^{3} \text{ mL}$ or 1.1 L. The molar concentration

will thus be $\dfrac{0.02 \text{ mol}}{1.1 \text{ L}} = 0.02 \text{ M}$.

The osmotic pressure is given by $\Pi = iRT \times \text{molarity}$. Assume $i = 1$.

$\Pi = 1 \times 0.082\,06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 283 \text{ K} \times 0.02 \text{ mol} \cdot \text{L}^{-1} = 0.5 \text{ atm}$

(c) The height of the rise of the solution is inversely proportional to the density of that solution. Mercury with a density of $13.6 \text{ g} \cdot \text{cm}^{-3}$ would produce a rise of $0.5 \text{ atm} \times 760 \text{ mmHg} \cdot \text{atm}^{-1}$ or 380 mmHg. For the benzene solution with a density of $0.88 \text{ g} \cdot \text{cm}^{-3}$, we would obtain

$$0.5 \text{ atm} \times \frac{760 \text{ mm}}{1 \text{ atm}} \times \frac{13.6 \text{ g} \cdot \text{cm}^{-3}}{0.88 \text{ g} \cdot \text{cm}^{-3}} = 6 \times 10^{3} \text{ mm or 6 m}$$

8.113 (a) $\Delta T_{f} = 1.72 \text{ K} = i \cdot k_{f} \cdot m = \left(1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \right) \dfrac{n_{aa}}{0.95 \text{ kg}}$

where n_{aa} are the moles of acetic acid in solution.
Assuming $i = 1$:

$$n_{aa} = \frac{(1.72 \text{ K})(0.95 \text{ kg})}{(1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1})} = 0.878 \text{ mol}$$

Experimentally, the molar mass of acetic acid is, therefore:

$$\frac{50 \text{ g}}{0.878 \text{ mol}} = 56.9 \text{ g} \cdot \text{mol}^{-1}$$

This experimental molar mass of acetic acid is less than the known molecular mass of the acid ($60.0 \text{ g} \cdot \text{mol}^{-1}$) indicating that the acid is dissociating in solution giving an $i > 1$.

(b)   As in part (a) the experimental molar mass is first found:

$$\Delta T_f = 2.32 \text{ K} = i \cdot k_f \cdot m = (5.12 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}) \frac{n_{aa}}{0.95 \text{ kg}}$$

where n_{aa} are the moles of acetic acid in solution.

Assuming $i = 1$:

$$n_{aa} = \frac{(2.32 \text{ K})(0.95 \text{ kg})}{(5.12 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1})} = 0.430 \text{ mol}$$

Experimentally, the molar mass of acetic acid is, therefore:

$$\frac{50 \text{ g}}{0.43 \text{ mol}} = 116 \text{ g} \cdot \text{mol}^{-1}$$

This experimental molar mass of acetic acid is significantlyhigher than the known molecular mass of the acid ($60.0 \text{ g} \cdot \text{mol}^{-1}$) indicating that the acid is dissociating in solution giving an $i < 1$. A van't Hoff factor less than 1 indicates that acetic acid is not completely dissolved in the benzene, or acetic acid molecules are agregating together in solution.

8.115 (a) The data in Appendix 2A can be used to calculate the change in enthalpy and entropy for the vaporization of methanol:
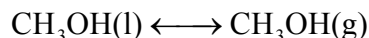
$$CH_3OH(l) \longleftrightarrow CH_3OH(g)$$

$$\Delta H°_{vap} = \Delta H°_f (CH_3OH, g) - \Delta H°_f (CH_3OH, l)$$
$$= (-200.66 \text{ kJ} \cdot \text{mol}^{-1}) - (-238.86 \text{ kJ} \cdot \text{mol}^{-1})$$
$$= 38.20 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta S°_{vap} = S°_m (CH_3OH(g)) - S°_m (CH_3OH(l))$$
$$= 239.81 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - 126.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$
$$= 113.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

To derive the general equation, we start with the expression that
$\Delta G^\circ_{vap} = -RT \ln P$, where P is the vapor pressure of the solvent. Because
$\Delta G^\circ_{vap} = \Delta H^\circ_{vap} - T\Delta S^\circ_{vap}$, this is the relationship to use to determine the
temperature dependence of $\ln P$:

$$\Delta H^\circ_{vap} - T\Delta S^\circ_{vap} = -RT \ln P$$

This equation can be rearranged to give

$$\ln P = -\frac{\Delta H^\circ_{vap}}{R} \cdot \frac{1}{T} + \frac{\Delta S^\circ_{vap}}{R}$$

To create an equation specific to methanol, we can plug in the actual
values of R, ΔH°_{vap}, and ΔS°_{vap} :

$$\ln P = -\frac{38\,200 \text{ J} \cdot \text{mol}^{-1}}{8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} \cdot \frac{1}{T} + \frac{113.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}{8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$$

$$= -\frac{4595 \text{ K}}{T} + 13.59$$

(b) The relationship to plot is $\ln P$ versus $\frac{1}{T}$. This should result in a

straight line whose slope is $-\frac{\Delta H^\circ_{vap}}{R}$ and whose intercept is $\frac{\Delta S^\circ_{vap}}{R}$. The

pressure must be given in atm for this relationship, because atm is the
standard state condition.

(c) Because we have already determined the equation, it is easiest to
calculate the vapor by inserting the value of $0.0°C$ or 273.2 K :

$$\ln P = -\frac{4595 \text{ K}}{T} + 13.59 = -\frac{4595 \text{ K}}{273.2 \text{ K}} + 13.59 = -16.82 + 13.59 = -3.23$$

$P = 0.040$ atm or 30 Torr

(d) As in (c) we can use the equation to find the point where the vapor
pressure of methanol $= 1$ atm.

$$\ln P = \ln 1 = 0 = -\frac{4595 \text{ K}}{T} + 13.59$$

$T = 338.1 \text{ K}$

8.117 The plot of the data is shown below. On this plot, the slope $= -\dfrac{\Delta H^\circ_{vap}}{R}$

and the intercept $= \dfrac{\Delta S^\circ_{vap}}{R}$.

Temp. (K)	T^{-1} (K^{-1})	Vapor pressure (Torr)	V.P. (atm)	$\ln P$
190	0.005 26	3.2	0.0042	−5.47
228	0.004 38	68	0.089	−2.41
250	0.004 00	240	0.316	−1.15
273	0.003 66	672	0.884	−0.123

From the curve fitting program:

$y = -3358.714x + 12.247$

(b) $-\dfrac{\Delta H^\circ_{vap}}{R} = -3359$

$\Delta H^\circ_{vap} = (3359)(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 28 \text{ kJ} \cdot \text{mol}^{-1}$

(c) $\dfrac{\Delta S^\circ_{vap}}{R} = 12.25$

$\Delta S^\circ_{vap} = (12.25)(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 1.0 \times 10^2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

(d) The normal boiling point will be the temperature at which the vapor pressure $= 1$ atm or at which the $\ln 1 = 0$. This will occur when $T^{-1} = 0.0036$ or $T = 2.7 \times 10^2$ K. This is most easily done by using an equation derived from ΔH°_{vap} and ΔS°_{vap} :

$\ln P = -\dfrac{\Delta H^\circ_{vap}}{R} \cdot \dfrac{1}{T} + \dfrac{\Delta S^\circ_{vap}}{R}$

$\ln \dfrac{15 \text{ Torr}}{760 \text{ Torr}} = -\dfrac{28\,000 \text{ J} \cdot \text{mol}^{-1}}{8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} \cdot \dfrac{1}{T} + \dfrac{100 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}{8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$

$T = 2.1 \times 10^2$ K

8.119 The critical temperatures are

Compound T_C (°C)

CH$_4$ −82.1

C$_2$H$_6$ 32.2

C$_3$H$_8$ 96.8

C$_4$H$_{10}$ 152

The critical temperatures increase with increasing mass, showing the influence of the stronger London forces.

8.121 (a) If sufficient chloroform and acetone are available, the pressures in the flasks will be the equilibrium vapor pressures at that temperature. We can calculate these amounts using the ideal gas equation:

$$\left(\frac{195 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}} \right)(1.00 \text{ L}) =$$

$$\left(\frac{m_{\text{chloroform}}}{119.37 \text{ g} \cdot \text{mol}^{-1} \text{ chloroform}} \right)(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})$$

$$m_{\text{chloroform}} = 1.25 \text{ g}$$

$$\left(\frac{225 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}} \right)(1.00 \text{ L}) =$$

$$\left(\frac{m_{\text{acetone}}}{58.08 \text{ g} \cdot \text{mol}^{-1} \text{ acetone}} \right)(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})$$

$$m_{\text{acetone}} = 0.703 \text{ g}$$

In both cases, sufficient compound is available to achieve the vapor pressure; flask A will have a pressure of 195 Torr and flask B will have a pressure of 222 Torr.

(b) When the stopcock is opened, some chloroform will move into flask B and acetone will move into flask A to restore the equilibrium vapor pressure. Additionally, however, some acetone vapor will dissolve in the liquid chloroform and vice versa. Ultimately the system will reach an equilibrium state in which the compositions of the liquid phases in both flasks are the same and the gas phase composition is uniform. The gas phase and liquid phase compositions will be established by Raoult's law. It is conceptually most convenient for this calculation to start by putting all the material into one liquid phase. Such a solution would have the following composition:

$$\chi_{acetone} = \cfrac{\cfrac{35.0\ g}{58.08\ g\cdot mol^{-1}\ acetone}}{\cfrac{35.0\ g}{58.08\ g\cdot mol^{-1}\ acetone} + \cfrac{35.0\ g}{119.37\ g\cdot mol^{-1}\ chloroform}}$$

$$\chi_{acetone} = 0.67$$

$$\chi_{chloroform} = \cfrac{\cfrac{35.0\ g}{119.37\ g\cdot mol^{-1}\ chloroform}}{\cfrac{35.0\ g}{58.08\ g\cdot mol^{-1}\ acetone} + \cfrac{35.0\ g}{119.37\ g\cdot mol^{-1}\ chloroform}}\ or\ 1 - \chi_{acetone}$$

$$\chi_{chloroform} = 0.33$$

This gives the composition of the liquid phase. The composition of the gas phase will be determined from the pressures of the gases:

$$P_{acetone} = \chi_{acetone,\ liquid} \cdot P^{\circ}_{acetone} = (0.67)(222\ Torr) = 149\ Torr$$

$$P_{chloroform} = \chi_{chloroform,\ liquid} \cdot P^{\circ}_{chloroform} = (0.33)(195\ Torr) = 64\ Torr$$

$$\chi_{acetone,\ gas} = \frac{P_{acetone}}{P_{acetone} + P_{chloroform}}$$

$$\chi_{acetone,\ gas} = \frac{149\ Torr}{149\ Torr + 64\ Torr} = 0.70$$

$$\chi_{chloroform,\ gas} = 1 - \chi_{acetone,\ gas} = 0.30$$

The gas phase composition will, therefore, be slightly richer in acetone than in chloroform. The total pressure in the flask will be 213 Torr.

(c) The solution shows negative deviation from Raoult's law. This means that the molecules of acetone and chloroform attract each other slightly more than molecules of the same kind. Under such circumstances, the vapor pressure is lower than expected from the ideal calculation. This will give rise to a high-boiling azeotrope. The gas phase composition will also be slightly different from that calculated from the ideal state, but whether acetone or chloroform would be richer in the gas phase depends on which side of the azeotrope the composition lies. Because we are not given the composition of the azeotrope, we cannot state which way the values will vary.

8.123 (a) The vapor pressure above the sucrose solution will be lower than the vapor pressure of the pure solvent. This results in an imbalance in the

system that causes pure ethanol to condense into the sucrose solution. As this happens, the sucrose solution becomes more dilute and its vapor pressure would approach that of pure ethanol if there were sufficient pure ethanol. In this case, however, the process will stop once all the pure ethanol has transferred to the solution. This will result in a solution that has $1/2$ the original concentration, or $7.5\ m$. (b) The vapor pressure of this solution will be given by

$$P = \chi_{ethanol} \times P^{\circ}_{\ ethanol} = \chi_{ethanol} \times 60\ \text{Torr}$$

We need to convert the molality of the solution to mole fraction. A $7.5\ m$ solution will contain 7.5 mol sucrose for 1.0 kg solvent. The molar mass of ethanol is $46.07\ \text{g}\cdot\text{mol}^{-1}$, so 1.0 kg represents 22 mol of ethanol. The mole fraction of ethanol will be given by

$$\chi_{ethanol} = \frac{22\ \text{mol}}{22\ \text{mol} + 7.5\ \text{mol}} = 0.75$$

$$P = 0.75 \times 60\ \text{Torr} = 45\ \text{Torr}$$

8.125 The vapor pressure is more sensitive if ΔH_{vap} is small. The fact that ΔH_{vap} is small indicates that it takes little energy to volatilize the sample, which means that the intermolecular forces are weaker. Hence we expect the vapor pressure to be more dramatically affected by small changes in temperature.

8.127 (a) $\Pi = iRT \times \text{molarity}$

Assuming $i = 1$

$$0.0112\ \text{atm} = \left(0.0821\ \text{L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}\right)\left(298\ \text{K}\right)\frac{\left(3.16\ \text{g}\middle/ X\right)}{0.500\ \text{L}}$$

$$X = 13\ 800\ \text{g}\cdot\text{mol}^{-1} = \text{molar mass of the polymer}$$

(b) The molecular mass of CH_3CHCH_2 is $42.08\ \text{g}\cdot\text{mol}^{-1}$. Dividing the molar mass of the polymer by the molar mass of the

monomer, $13800 \text{ g} \cdot \text{mol}^{-1} / 42.08 \text{ g} \cdot \text{mol}^{-1} = 328$, indicates that there are approximately 328 monomers in the average polymer.

(c) $(308 \text{ pm} \cdot \text{monomer}^{-1})(328 \text{ monomers}) = 101000 \text{ pm}$ or 101 nm

8.129 The initial information tells us that the detector is more responsive to A than to B. Under these conditions, the response is

$5.44 \text{ cm}^2 \div 0.52 \text{ mgA} = 11 \text{ cm}^2 \cdot \text{mg}^{-1}$ A whereas the response for B is

$8.72 \text{ cm}^2 \div 2.30 \text{ mg} = 3.79 \text{ cm}^2 \cdot \text{mg}^{-1}$ B. The detector is thus

$11 \text{ cm}^2 \cdot \text{mg}^{-1} \div 3.79 \text{ cm}^2 \cdot \text{mg}^{-1} = 2.9$ times more sensitive for A than B. Because the conditions are different for determining the unknown amount of A present, we cannot use the area ratios directly to determine the quantity of A. Instead, we use the standard B as a reference.

$(X = \text{mg A})$

$$\frac{3.52 \text{ cm}^2}{X} \div \frac{7.58 \text{ cm}^2}{2.00 \text{ mg (B)}} = 2.9$$

$$X = \frac{3.52 \text{ cm}^2}{2.9} \times \frac{2.00 \text{ mg}}{7.58 \text{ cm}^2}$$

$X = 0.32 \text{ mg A}$

8.131 $\Pi = iRT \times \text{molarity}$

Assuming $i = 1$

$7.7 \text{ atm} = (0.0821 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(310 \text{ K})(M)$

$M = 0.303 \text{ mol} \cdot \text{L}^{-1}$

If 0.500 L of solution is needed:

$(0.303 \text{ mol} \cdot \text{L}^{-1})(0.500 \text{ L}) = 0.151 \text{ mol of glucose}$

Molecular mass of glucose is $81.158 \text{ g} \cdot \text{mol}^{-1}$

$(0.151 \text{ mol})(81.158 \text{ g} \cdot \text{mol}^{-1}) = 27.3 \text{ g}$

8.133 First, calculate the weight % of acetic acid in a solution with $x_{\text{acetic acid}} = 0.15$:

If you have 1 mol total of a solution with $x_{\text{acetic acid}} = 0.15$ and

$x_{\text{H}_2\text{O}} = 0.85,$ you would have 0.15 mol of acetic acid (60.053 g·mol⁻¹)

in 0.85 mol of H_2O (18.015 g·mol⁻¹). The weight % of acetic acid in

such a solution is:

$(0.15 \text{ mol})(60.053 \text{ g}\cdot\text{mol}^{-1}) = 9.01$ g of acetic acid

$(0.85 \text{ mol})(18.015 \text{ g}\cdot\text{mol}^{-1}) = 15.3$ g of H_2O

$\dfrac{9.01 \text{ g}}{9.01 \text{ g} + 15.3 \text{ g}}(100\%) = 37.0\%$ acetic acid by weight

If a solution with $x_{\text{acetic acid}} = 0.15$ is 37.0% acetic acid by weight,

30 g of such a solution will contain:

$(30 \text{ g})(0.370) = 11.1$ g acetic acid

$\dfrac{11.1 \text{ g}}{60.053 \text{ g}\cdot\text{mol}^{-1}} = 0.185$ mol of acetic acid

given that acetic acid is a monoprotic acid which will react

in a 1:1 fashion with NaOH, 0.185 mol of NaOH will completely

react with 0.185 mol of acetic acid. The volume of a 0.010 M

solution of NaOH needed to completely consume the acetic acid

is: $\dfrac{0.185 \text{ mol}}{0.010 \text{ mol}\cdot\text{L}^{-1}} = 18.5$ L

8.135 (a) Assume 100 g of compound:
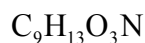
$(0.590)(100 \text{ g}) = 59 \text{ g C} \rightarrow 4.912$ mol C

$(0.262)(100 \text{ g}) = 26.2 \text{ g O} \rightarrow 1.638$ mol O

$(0.0710)(100 \text{ g}) = 7.10 \text{ g H} \rightarrow 7.044$ mol H

$(0.0760)(100 \text{ g}) = 7.60 \text{ g N} \rightarrow 0.5424$ mol N

Dividing by 0.5424 mol and rounding to the

nearest whole number we find the C:O:H:N ratio

to be 9:3:13:1, giving an empirical formula of

$C_9H_{13}O_3N$

(b) Molar mass may be found using the freezing point depression:

$\Delta T_f = i \cdot k_f \cdot m$, assuming $i = 1$:

$$0.50 \text{ K} = \left(5.12 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}\right) \dfrac{\left(\dfrac{0.64 \text{ g}}{X \text{ g} \cdot \text{mol}^{-1}}\right)}{0.0360 \text{ kg}}$$

$X = 182 \text{ g} \cdot \text{mol}^{-1}$

The molar mass of the compound will be an integral multiple of the molar mass of the empirical formula:

$n((9 \cdot 12.011 \text{ g} \cdot \text{mol}^{-1}) + (3 \cdot 16.00 \text{ g} \cdot \text{mol}^{-1}) + (13 \cdot 1.0079 \text{ g} \cdot \text{mol}^{-1})$

$+(14.01 \text{ g} \cdot \text{mol}^{-1})) = 182 \text{ g} \cdot \text{mol}^{-1}$

$n = 1$

Therefore, the molecular formula is $C_{9*n} H_{13*n} O_{3*n} N_n = C_9 H_{13} O_3 N$

8.137 The non-polar chains of both the surfactant and pentanol will interact to form a hydrophobic region with the heads of the two molecules pointing away from this region towards the aqueous solution. To prevent the heads of the shorter pentanol molecules from winding up in the hydrophobic region, the layered structure might be comprised of a water region, a surfactant layer (heads pointing toward the water) a pentanol layer (with tails pointing toward the hydrophobic tails of the surfactant) and back to an aqueous region.