# CHAPTER 8
# PHYSICAL EQUILIBRIA

**8.2**  The volume of the supply room (neglecting any contents of the room) is

$3.0 \text{ m} \times 2.0 \text{ m} \times 2.0 \text{ m} = 12 \text{ m}^3$ or $12 \text{ m}^3 \times 1000 \text{ L} \cdot \text{m}^{-3} = 12\ 000 \text{ L}$. The

ideal gas law can be used to calculate the mass of mercury present:

$PV = nRT$

let $m$ = mass of mercury

$$\left( \frac{0.227 \text{ Pa}}{1.01325 \times 10^5 \text{ Pa} \cdot \text{atm}^{-1}} \right) (12\ 000 \text{ L})$$

$$= \left( \frac{m}{200.59 \text{ g} \cdot \text{mol}^{-1}} \right) (0.082\ 06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})$$

$$m = \frac{(0.227 \text{ Pa})(12\ 000 \text{ L})(200.59 \text{ g} \cdot \text{mol}^{-1})}{(1.0135 \times 10^5 \text{ Pa} \cdot \text{atm}^{-1})(0.082\ 06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}$$

$m = 0.22 \text{ g}$

**8.4**  (a) about 72°C;   (b) about 58°C

**8.6**  (a) The quantities of $\Delta H°_{vap}$ 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 that, for pressure, is $P$ divided by the reference state of 1 atm so that the quantity inside the ln term is dimensionless.

$$8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times \ln \frac{67 \text{ Torr}}{760 \text{ Torr}} = -\frac{\Delta H°_{\text{vap}}}{273.2 \text{ K}} + \Delta S°_{\text{vap}}$$

$$8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times \ln \frac{222 \text{ Torr}}{760 \text{ Torr}} = -\frac{\Delta H°_{\text{vap}}}{298.2 \text{ K}} + \Delta S°_{\text{vap}}$$

which give, upon combining terms,

$$-20.19 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.003\ 660 \text{ K}^{-1} \times \Delta H°_{\text{vap}} + \Delta S°_{\text{vap}}$$

$$-10.23 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.003\ 353 \text{ K}^{-1} \times \Delta H°_{\text{vap}} + \Delta S°_{\text{vap}}$$

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

$\Delta H°_{\text{vap}}$ :

$$-9.96 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.000\ 307 \times \Delta H°_{\text{vap}}$$

$$\Delta H°_{\text{vap}} = +32.4 \text{ kJ} \cdot \text{mol}^{-1}$$

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

$$-20.19 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.003\ 660 \text{ K}^{-1} \times (+32\ 400 \text{ J} \cdot \text{mol}^{-1}) + \Delta S°_{\text{vap}}$$

$$\Delta S°_{\text{vap}} = 98.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$-10.23 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.003\ 353 \text{ K}^{-1} \times (+32\ 400 \text{ J} \cdot \text{mol}^{-1}) + \Delta S°_{\text{vap}}$$

$$\Delta S°_{\text{vap}} = 98.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

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

$$\Delta G°_{\text{r}} = +32.4 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(98.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1})$$

$$\Delta G°_{\text{r}} = +3.08 \text{ kJ} \cdot \text{mol}^{-1}$$

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

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

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

$$T_B = \frac{32.4 \text{ kJ} \cdot \text{mol}^{-1} \times 1000 \text{ J} \cdot \text{kJ}^{-1}}{98.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} = 329 \text{ K or } 56°\text{C}$$

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.

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

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

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 that, for pressure, is $P$ divided by the reference state of 1 atm so that the quantity inside the ln term is dimensionless.

$$8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times \ln 1 = -\frac{\Delta H°_{vap}}{326.1 \text{ K}} + \Delta S°_{vap}$$

$$8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times \ln \frac{96 \text{ Torr}}{760 \text{ Torr}} = -\frac{\Delta H°_{vap}}{273.2 \text{ K}} + \Delta S°_{vap}$$

which give, upon combining terms,

$$0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.003\ 067 \text{ K}^{-1} \times \Delta H°_{vap} + \Delta S°_{vap}$$
$$-17.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.003\ 660 \text{ K}^{-1} \times \Delta H°_{vap} + \Delta S°_{vap}$$

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

$$+17.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = +0.000\ 593 \text{ K}^{-1} \times \Delta H°_{vap}$$
$$\Delta H°_{vap} = +29.0 \text{ kJ} \cdot \text{mol}^{-1}$$

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

$$0 = -0.003\ 066\ \text{K}^{-1} \times (+29\ 000\ \text{J} \cdot \text{mol}^{-1}) + \Delta S°_{vap}$$

$$\Delta S°_{vap} = 88.9\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$-17.2\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.003\ 660\ \text{K}^{-1} \times (+29\ 000\ \text{J} \cdot \text{mol}^{-1}) + \Delta S°_{vap}$$

$$\Delta S°_{vap} = 88.9\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

(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:

$$\ln \frac{P_{\text{at 35°C}}}{1\ \text{atm}} = -\frac{29\ 000\ \text{J} \cdot \text{mol}^{-1}}{8.314\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}\left[\frac{1}{308\ \text{K}} - \frac{1}{326.1\ \text{K}}\right]$$

$$P_{\text{at 35°C}} = 0.63\ \text{atm or } 4.8 \times 10^2\ \text{Torr}$$

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

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

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 that, for pressure, is $P$ divided by the reference state of 1 atm so that the quantity inside the ln term is dimensionless.

$$8.314\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times \ln \frac{155\ \text{Torr}}{760\ \text{Torr}} = -\frac{\Delta H°_{vap}}{250.40\ \text{K}} + \Delta S°_{vap}$$

$$8.314\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times \ln \frac{485\ \text{Torr}}{760\ \text{Torr}} = -\frac{\Delta H°_{vap}}{273.2\ \text{K}} + \Delta S°_{vap}$$

which give, upon combining terms,

$-13.22 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.003\ 994 \text{ K}^{-1} \times \Delta H°_{\text{vap}} + \Delta S°_{\text{vap}}$

$-3.734 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.003\ 660 \text{ K}^{-1} \times \Delta H°_{\text{vap}} + \Delta S°_{\text{vap}}$

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

$-9.49 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.000\ 334 \text{ K}^{-1} \times \Delta H°_{\text{vap}}$

$\Delta H°_{\text{vap}} = +28.4 \text{ kJ} \cdot \text{mol}^{-1}$

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

$-13.22 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.003\ 994 \text{ K}^{-1} \times (+28\ 400 \text{ J} \cdot \text{mol}^{-1}) + \Delta S°_{\text{vap}}$

$\Delta S°_{\text{vap}} = 1.00 \times 10^2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

$-3.734 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.003\ 660 \text{ K}^{-1} \times (+28\ 400 \text{ J} \cdot \text{mol}^{-1}) + \Delta S°_{\text{vap}}$

$\Delta S°_{\text{vap}} = 1.00 \times 10^2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

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

$\Delta G°_{\text{r}} = +28.4 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(100 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1})$

$\Delta G°_{\text{r}} = -1.4 \text{ kJ} \cdot \text{mol}^{-1}$

Notice that the standard $\Delta G°_{\text{r}}$ is negative, so the vaporization of $ClO_2$ is spontaneous as expected; under those conditions it is a gas at room temperature.

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

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

$\Delta H°_{\text{vap}} = T_{\text{B}}\Delta S°_{\text{vap}} \text{ or } T_{\text{B}} = \dfrac{\Delta H°_{\text{vap}}}{\Delta S°_{\text{vap}}}$

$T_{\text{B}} = \dfrac{28.4 \text{ kJ} \cdot \text{mol}^{-1} \times 1000 \text{ J} \cdot \text{kJ}^{-1}}{100 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} = 284 \text{ K or } 11°C$

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

Here, we would substitute, in one of the known pressure points, the value

of the enthalpy of vaporization and the condition that $P = 1$ atm at the normal boiling point.

**8.12** (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 that, for pressure, is $P$ divided by the reference state of 1 atm so that the quantity inside the ln term is dimensionless.

$$8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times \ln 1 = -\frac{\Delta H°_{vap}}{311.6 \text{ K}} + \Delta S°_{vap}$$

$$8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times \ln \frac{13 \text{ Torr}}{760 \text{ Torr}} = -\frac{\Delta H°_{vap}}{227.94 \text{ K}} + \Delta S°_{vap}$$

which give, upon combining terms,

$$0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.003\,209 \text{ K}^{-1} \times \Delta H°_{vap} + \Delta S°_{vap}$$

$$-33.9 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.004\,387\,1 \text{ K}^{-1} \times \Delta H°_{vap} + \Delta S°_{vap}$$

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

$$+33.9 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = +0.001\,178 \text{ K}^{-1} \times \Delta H°_{vap}$$

$$\Delta H°_{vap} = +28.8 \text{ kJ} \cdot \text{mol}^{-1}$$

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

$$0 = -0.003\ 209\ \text{K}^{-1} \times (+28\ 800\ \text{J}\cdot\text{mol}^{-1}) + \Delta S^\circ_{\text{vap}}$$

$$\Delta S^\circ_{\text{vap}} = 92.4\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$-33.9\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -0.004\ 387\ 1\ \text{K}^{-1} \times (+28\ 800\ \text{J}\cdot\text{mol}^{-1}) + \Delta S^\circ_{\text{vap}}$$

$$\Delta S^\circ_{\text{vap}} = 92.4\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

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

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

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

$$\ln \frac{P_{\text{at }15.0°C}}{1\ \text{atm}} = -\frac{28\ 800\ \text{J}\cdot\text{mol}^{-1}}{8.314\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}\left[\frac{1}{288.2\ \text{K}} - \frac{1}{311.6\ \text{K}}\right]$$

$$P_{\text{at }25.0°C} = 0.41\ \text{atm or }3.1\times10^2\ \text{Torr}$$

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

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

$$\ln \frac{P_{215\ \text{K}}}{1} = -\frac{23\ 400\ \text{J}\cdot\text{mol}^{-1}}{8.314\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}\left[\frac{1}{215\ \text{K}} - \frac{1}{239.7\ \text{K}}\right]$$

$$P_{215\ \text{K}} = 0.26\ \text{atm or }2.0\times10^2\ \text{Torr}$$

**8.16** (a) solid; (b) vapor; (c) liquid; (d) equilibrium between solid, liquid, and vapor (triple point)

**8.18** (a) close to $10^5$ atm; (b) approximately 3600 K; (c) approximately $10^5$ atm; (d) The phase diagram indicates that diamonds are not thermodynamically stable (see Chapter 6) under normal conditions; they appear to be so because the rate of conversion is very slow. We say that diamonds are *kinetically inert*.

**8.20** (a) graphite $\longrightarrow$ diamond $\longrightarrow$ liquid;   (b) The diamond/graphite interface line has a positive slope; hence diamond is denser than graphite. The diamond/liquid line has a negative slope, hence diamond is less dense than liquid carbon. The order is graphite < diamond < liquid.

**8.22** (a)
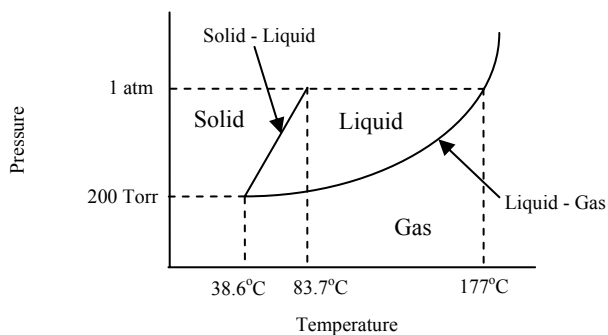


(b) The cooling curve for a sample of this material will resemble this sketch (not to scale):
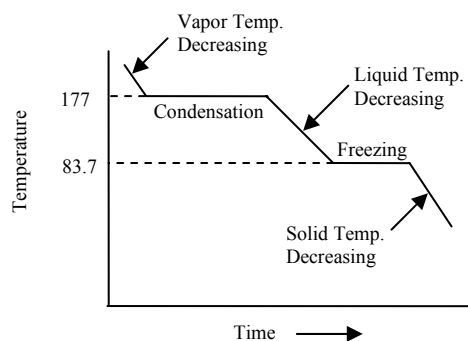


**8.24** In the previous problem, we are given the relationship:

$$\frac{dP}{dT} = \frac{\Delta H_{fus}}{T \cdot \Delta V}$$

Therefore, substituting in the values given in the problem:

$$\frac{317 \times 10^5 \text{ Pa}}{1.7 \text{ K}} = \frac{2290 \text{ J} \cdot \text{mol}^{-1}}{235.4 \text{ K} \cdot \Delta V}$$

Solving for $\Delta V$ we find $\Delta V = -5.217 \times 10^{-7}$ m$^3 \cdot$mol$^{-1}$ or $-0.5217$ cm$^3 \cdot$mol$^{-1}$. Converting to a per gram quantity:

$$\frac{-0.5217 \text{ cm}^3 \cdot \text{mol}^{-1}}{200.6 \text{ g} \cdot \text{mol}^{-1}} = -2.60 \times 10^{-3} \text{ cm}^3 \cdot \text{g}^{-1}$$

Given the density of liquid mercury, the volume of one gram of liquid mercury is

$$\frac{1 \text{ g}}{13.60 \text{ g} \cdot \text{cm}^{-3}} = 0.07353 \text{ cm}^3$$

The volume of 1 g of solid mercury under the conditions given is then:

$0.07353 \text{ cm}^3 - 2.60 \times 10^{-3} \text{ cm}^3 = 0.07093 \text{ cm}^3$

giving a density for the solid:

$$\frac{1 \text{ g}}{0.07093 \text{ cm}^3} = 14.1 \text{ g} \cdot \text{cm}^{-3}$$

**8.26**   (a) water, (b) water, (c) tetrachloromethane

**8.28**   (a) hydrophilic, hydrogen bonding;   (b) hydrophobic, nonpolar;   (c) hydrophilic, hydrogen bonding, and dipole-dipole interactions;   (d) Cl could be hydrophilic because of possible dipole-dipole interactions (depending on the electronegativity of the atom to which the Cl atom is bonded, as well as the symmetry or asymmetry of the molecule in which it is found). Otherwise, London forces would predominate and Cl would be hydrophobic.

**8.30**   (a)  The solubility of air in water is $7.9 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \cdot \text{atm}^{-1}$ and the molar mass of air (average) $= 28.97 \text{ g} \cdot \text{mol}^{-1}$ (see Table 5.1).

solubility $= k_{\text{H}} \times P$

solubility

$(\text{g} \cdot \text{L}^{-1}) = 1.0 \text{ atm} \times 7.9 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \cdot \text{atm}^{-1}$
$\qquad \times 28.97 \text{ g} \cdot \text{mol}^{-1} \times 10^3 \text{ mg} \cdot \text{g}^{-1}$
$\qquad = 23 \text{ mg} \cdot \text{L}^{-1}$

(b)  The solubility of He is $3.7 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \cdot \text{atm}^{-1}$.

solubility

$$(g \cdot L^{-1}) = 1.0 \text{ atm} \times 3.7 \times 10^{-4} \text{ mol} \cdot L^{-1} \cdot \text{atm}^{-1}$$
$$\times 4.00 \text{ g} \cdot \text{mol}^{-1} \times 10^3 \text{ mg} \cdot \text{g}^{-1}$$
$$= 1.48 \text{ mg} \cdot L^{-1}$$

(c) solubility

$$(g \cdot L^{-1}) = \frac{25 \text{ kPa}}{101.325 \text{ kPa} \cdot \text{atm}^{-1}} \times 3.7 \times 10^{-4} \text{ mol} \cdot L^{-1} \cdot \text{atm}^{-1} \times 4.00 \text{ g} \cdot \text{mol}^{-1}$$

$$\times 10^3 \text{ mg} \cdot \text{g}^{-1} = 0.37 \text{ mg}$$

**8.32** This answer can be calculated from the solubility data, which will give an answer in $\text{mol} \cdot L^{-1}$. We then use the solution component of the blood volume to determine the total number of moles present, which can be converted to volume using the ideal gas expression:

volume of plasma $= 0.45 \times 6.00$ L

$$S = k_{\text{H}} \times P = 5.8 \times 10^{-4} \text{ mol} \cdot L^{-1} \cdot \text{atm}^{-1} \times 10.00 \text{ atm}$$

$$n_{N_2} = S \times 2.7 \text{ L}$$

$$PV = nRT \text{ or } V = \frac{nRT}{P}$$

$$V_{N_2} = (5.8 \times 10^{-4} \text{ mol} \cdot L^{-1} \cdot \text{atm}^{-1})(10.0 \text{ atm})(0.45)(6.00 \text{ L})$$

$$\times \frac{(0.082\,06 \text{ L} \cdot \text{atm} \cdot K^{-1} \cdot \text{mol}^{-1})(310 \text{ K})}{1 \text{ atm}}$$

$$= 0.40 \text{ L}$$

**8.34** $CO_2(g) \longrightarrow CO_2(aq) + \text{heat}$    (exothermic reaction)

(a) If the pressure of $CO_2$ is increased, more $CO_2(g)$ will be forced into solution under pressure (Henry's law). The concentration of $CO_2$ in solution will thus increase. The factor by which the concentration will increase cannot be predicted, however, because the amount of $CO_2$ present above the solution is unknown, as is the amount of water.   (b) If the temperature is raised, the concentration of $CO_2$ in solution will decrease; the heat added will favor the escape of $CO_2$ from solution—the reverse process is exothermic. Further, addition of heat increases the speed and

energy of the $CO_2$ molecules, allowing more of them to break out into the gas phase.

**8.36** (a) endothermically: a positive enthalpy of solution means enthalpy is absorbed by the system during the dissolution process; (b) $NH_4NO_3(s) +$ heat $\rightleftharpoons NH_4^+(aq) + NO_3^-(aq)$; (c) Given that $\Delta H_L + \Delta H_{hydration} = \Delta H$ of solution, the endothermic values of solution enthalpy result from systems with lattice enthalpies greater than their enthalpies of hydration. Therefore, we expect that for $NH_4NO_3$ the lattice enthalpy will be greater than the enthalpy of hydration.

**8.38** The molar enthalpies of solution are given in Table 8.6. Multiplying these numbers by the number of moles of solid dissolved will give the amount of heat released. The change in temperature will be given by dividing the heat released by the specific heat capacity of the solution.

(a) enthalpy of solution of $KCl = +17.2 \text{ kJ} \cdot \text{mol}^{-1}$

$$\Delta T = -\frac{\dfrac{10.0 \text{ g KCl}}{74.55 \text{ g} \cdot \text{mol}^{-1} \text{ KCl}} \times (+17\ 200 \text{ J} \cdot \text{mol}^{-1})}{(4.18 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1})(100.0 \text{ g})} = -5.52 \text{ K or } -5.52°C$$

(b) enthalpy of solution of $MgBr_2 = -185.6 \text{ kJ} \cdot \text{mol}^{-1}$

$$\Delta T = -\frac{\dfrac{10.0 \text{ g MgBr}_2}{184.13 \text{ g} \cdot \text{mol}^{-1} \text{ MgBr}_2} \times (-185\ 600 \text{ J} \cdot \text{mol}^{-1})}{(4.18 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1})(100.0 \text{ g})}$$
$$= +24.1 \text{ K or } +24.1°C$$

(c) enthalpy of solution of $KNO_3 = +34.9 \text{ kJ} \cdot \text{mol}^{-1}$

$$\Delta T = -\frac{\dfrac{10.0 \text{ g KNO}_3}{101.11 \text{ g} \cdot \text{mol}^{-1} \text{ KNO}_3} \times (+34\ 900 \text{ J} \cdot \text{mol}^{-1})}{(4.18 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1})(100.0 \text{ g})}$$
$$= -8.26 \text{ K or } -8.26°C$$

(d) enthalpy of solution of $NaOH = -44.5 \text{ kJ} \cdot \text{mol}^{-1}$

$$\Delta T = -\frac{\dfrac{10.0 \text{ g NaOH}}{40.00 \text{ g} \cdot \text{mol}^{-1} \text{ NaOH}} \times (-44\,500 \text{ J} \cdot \text{mol}^{-1})}{(4.18 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1})(100.0 \text{ g})}$$

$$= +26.6 \text{ K or } +26.6°\text{C}$$

**8.40** The data for the heats of solution are (in $kJ \cdot mol^{-1}$) NaF, $1.9 \text{ kJ} \cdot \text{mol}^{-1}$; NaCl, $+3.9 \text{ kJ} \cdot \text{mol}^{-1}$; NaBr, $-0.6$; NaI, $-7.5$. $\Delta H_{soln} = \Delta H_L + \Delta H_{hyd}$. As the size of the anion increases, $\Delta H_L$ decreases (see Table 6.3), but $\Delta H_{hyd}$ increases (becomes less negative, Table 8.8), so $\Delta H_{sol}$ would be expected to decrease, as the data partly indicate. The decrease in $\Delta H_L$ outweighs the increase in $\Delta H_{hyd}$, and $\Delta H_{sol}$ generally does decrease on proceeding down the group of halides. The exception to the trend, NaF, has an unusually high $\Delta H_L$, indicating a reluctance to dissolve. It is difficult to say precisely why ionic size has a slightly greater effect on $\Delta H_L$ than on $\Delta H_{hyd}$. We are effectively taking the difference of two large quantities (recall $\Delta H_{hyd}$ is negative), and that difference cannot be precisely related to ionic size.

**8.42** (a) $m_{KOH} = \dfrac{\left(\dfrac{13.72 \text{ g KOH}}{56.11 \text{ g} \cdot \text{mol}^{-1} \text{ KOH}}\right)}{0.0750 \text{ kg}} = 3.26 \ m$

(b) $\dfrac{\left(\dfrac{\text{mass}_{\text{ethylene glycol}}}{62.07 \text{ g} \cdot \text{mol}^{-1}}\right)}{1.5 \text{ kg}} = 0.44 \ m$

$\text{mass}_{\text{ethylene glycol}} = 41 \text{ g}$

(c) 1.00 kg of solution will contain 38.9 g HCl and 961.1 g $H_2O$.

$\dfrac{\left(\dfrac{38.9 \text{ g HCl}}{36.46 \text{ g} \cdot \text{mol}^{-1} \text{ HCl}}\right)}{0.9611 \text{ kg}} = 1.11 \ m$

**8.44** (a) $\dfrac{\left(\dfrac{13.63 \text{ g sucrose}}{342.29 \text{ g} \cdot \text{mol}^{-1} \text{ sucrose}}\right)}{0.612 \text{ kg}} = 0.0650 \ m$

(b) 1 kg of 10.00% CsCl will contain 100.0 g CsCl and 900.0 g $H_2O$.

$\dfrac{\left(\dfrac{100.0 \text{ g CsCl}}{168.36 \text{ g} \cdot \text{mol}^{-1} \text{ CsCl}}\right)}{0.9000 \text{ kg}} = 0.6600 \ m$

(c) The solution contains 0.235 mol of acetone for 0.765 mol $H_2O$.

$\dfrac{0.197 \text{ mol acetone}}{(0.765 \text{ mol H}_2\text{O})(18.02 \text{ g} \cdot \text{mol}^{-1})\left(\dfrac{1 \text{ kg}}{1000 \text{ g}}\right)} = 14.3 \ m$

**8.46** (a) If $x_{\text{FeCl}_3}$ is 0.0205, then there are 0.0205 mol $FeCl_3$ for every 0.9795 mol $H_2O$. The mass of water will be

$18.02 \text{ g} \cdot \text{mol}^{-1} \times 0.9795 \text{ mol} = 17.65 \text{ g or } 0.01765 \text{ kg}.$

$m_{\text{OH}^-} = \dfrac{\left(\dfrac{3 \text{ Cl}^-}{\text{FeCl}_3}\right)(0.0205 \text{ mol FeCl}_3)}{0.01765 \text{ kg solvent}} = 3.48 \ m$

(b) $m_{\text{Cl}^-} = \dfrac{\left(\dfrac{2 \text{ mol OH}^-}{1 \text{ mol Ba(OH)}_2}\right)\left(\dfrac{9.25 \text{ g Ba(OH)}_2}{171.36 \text{ g} \cdot \text{mol}^{-1} \text{ Ba(OH)}_2}\right)}{0.183 \text{ kg solvent}} = 0.590 \ m$

(c) 1.000 L of 12.00 M $NH_3$(aq) will contain 12.00 mol with a mass of $12.00 \times 17.03 \text{ g} \cdot \text{mol}^{-1} = 204.4 \text{ g}$. The density of the 1.000 L of solution is $0.9519 \text{ g} \cdot \text{cm}^{-3}$, so the total mass in the solution is 951.9 g. This leaves $951.9 \text{ g} - 204.4 \text{ g} = 747.5 \text{ g}$ as water.

$\dfrac{12.00 \text{ mol NH}_3}{0.7475 \text{ kg solvent}} = 16.05 \ m$

**8.48** (a) $X \times 1.07 \text{ g} \cdot \text{cm}^{-3} \times \dfrac{0.100 \text{ g H}_2\text{SO}_4}{1 \text{ g}} = 8.37 \text{ g H}_2\text{SO}_4$

$$X = \dfrac{8.37 \text{ g } H_2SO_4}{1.07 \text{ g} \cdot \text{cm}^{-3} \times \dfrac{0.100 \text{ g } H_2SO_4}{1 \text{ g}}}$$

$$= 78.2 \text{ mL}$$

(b) 100 g of solution contains 10.0 g of $H_2SO_4$ and 90.0 g of water.

$10.0 \text{ g} \div 98.07 \text{ g} \cdot \text{mol}^{-1} = 0.102 \text{ mol } H_2SO_4$. 90.0 g equals 0.0900 kg of solvent,

$$\text{so molality} = \dfrac{0.102 \text{ mol}}{0.0900 \text{ kg}} = 1.13 \text{ mol} \cdot \text{kg}^{-1}$$

(c)

$$250 \text{ mL} \times 1.07 \text{ g} \cdot \text{cm}^{-3} \times 0.100 \text{ g } H_2SO_4 \cdot (\text{g solution})^{-1} = 26.8 \text{ g } H_2SO_4$$

**8.50** (a) The vapor pressure of water at 80°C is 355.26 Torr. If the mole fraction of glucose is 0.050, then the mole fraction of the solvent water will be $1.000 - 0.050 = 0.950$.

$$P = x_{\text{solvent}} \times P_{\text{pure solvent}}$$
$$P = 0.950 \times 355.26 \text{ Torr} = 338 \text{ Torr}$$

(b) At 25°C, the vapor pressure of water is 23.76 Torr. The molality of the urea solution must be converted to mole fraction. A 0.10 *m* solution will contain 0.10 mol urea per 1000 g $H_2O$.

$$x_{H_2O} = \dfrac{n_{H_2O}}{n_{H_2O} + n_{\text{urea}}} = \dfrac{\dfrac{1000 \text{ g}}{18.02 \text{ g} \cdot \text{mol}^{-1}}}{\dfrac{1000 \text{ g}}{18.02 \text{ g} \cdot \text{mol}^{-1}} + 0.10 \text{ mol}} = 0.9982$$

$$P = 0.9982 \times 23.76 \text{ Torr} = 23.72 \text{ Torr}$$

**8.52** (a) The vapor pressure of pure water at 40°C is 55.34 Torr. If the mole fraction of fructose in solutions is 0.11, then the mole fraction of the solvent will be 0.81.

$$P = x_{\text{solvent}} \times P_{\text{pure solvent}}$$
$$P = 0.81 \times 55.34 \text{ Torr} = 45 \text{ Torr}$$

$\Delta P = 55.34\ \text{Torr} - 45\ \text{Torr} = 10\ \text{Torr.}$

(b) The vapor pressure of pure water at $20°C$ is 17.54 Torr. When $MgF_2$ dissolves, we will assume it dissociates completely into $Mg^{+2}$ and $F^-$ ions:
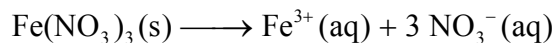
$$MgF_2(s) \longrightarrow Mg^{2+}(aq) + 2\ F^-(aq)$$
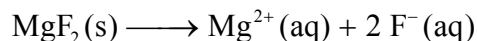
Note that the $F^-$ ion concentration will be $2 \times$ that of the $Mg^{2+}$ concentration:

$$x_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{Mg^{2+}} + n_{F^-}}$$

$$= \frac{\dfrac{100\ \text{g}}{18.02\ \text{g}\cdot\text{mol}^{-1}}}{\dfrac{100\ \text{g}}{18.02\ \text{g}\cdot\text{mol}^{-1}} + \dfrac{0.008\ \text{g}}{62.31\ \text{g}\cdot\text{mol}^{-1}} + \left(2 \times \dfrac{0.008\ \text{g}}{62.31\ \text{g}\cdot\text{mol}^{-1}}\right)}$$

$$\approx 1.00$$

$P = 1.00 \times 17.54\ \text{Torr} = 17.5\ \text{Torr}$

(c) The vapor pressure of pure water is 4.58 Torr at $0°C$.

Assume that the $Fe(NO_3)_3$ undergoes complete dissociation is solution:

$$Fe(NO_3)_3(s) \longrightarrow Fe^{3+}(aq) + 3\ NO_3^-(aq)$$

The concentration must be converted from molality to mole fraction:

$$x_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{Fe^{3+}} + n_{NO_3^-}}$$

$$= \frac{\dfrac{1000\ \text{g}}{18.02\ \text{g}\cdot\text{mol}^{-1}}}{\dfrac{1000\ \text{g}}{18.02\ \text{g}\cdot\text{mol}^{-1}} + 0.025\ \text{mol} + (3 \times 0.025\ \text{mol})}$$

$$\approx 1.00$$

$P = 1.00 \times 4.58\ \text{Torr} = 4.58\ \text{Torr}$

**8.54** (a) From the relationship $P = x_{solvent} \times P_{pure\ solvent}$ we can calculate the mole fraction of the solvent, making use of the fact that at its normal boiling point, the vapor pressure of any liquid will be 760.00 Torr:

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

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

The mole fraction of the unknown compound will be

$1.000 - 0.974 = 0.026$.

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

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

$$0.974 = \frac{\dfrac{100 \text{ g}}{46.07 \text{ g} \cdot \text{mol}^{-1}}}{\dfrac{100 \text{ g}}{46.07 \text{ g} \cdot \text{mol}^{-1}} + \dfrac{9.15 \text{ g}}{M_{\text{unknown}}}}$$

$$M_{\text{unknown}} = \frac{9.15 \text{ g}}{\left[ \left( \dfrac{100 \text{ g}}{46.07 \text{ g} \cdot \text{mol}^{-1}} \right) \Big/ 0.974 \right] - \left( \dfrac{100 \text{ g}}{46.07 \text{ g} \cdot \text{mol}^{-1}} \right)} = 158 \text{ g} \cdot \text{mol}^{-1}$$

**8.56**  (a)  $\Delta T_b = ik_b m$

For $CaCl_2$, $i = 3$

$\Delta T_b = 3 \times 0.51 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times 0.22 \text{ mol} \cdot \text{kg}^{-1} = 0.34 \text{ K or } 0.34°\text{C}$

The boiling point will be $100.00°\text{C} + 0.34°\text{C} = 100.34°\text{C}$.

(b)  $\Delta T_b = ik_b m$

For $Li_2CO_3$, $i = 3$

$$\Delta T_b = 3 \times 0.51 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \frac{\left( \dfrac{0.72 \text{ g}}{73.89 \text{ g} \cdot \text{mol}^{-1}} \right)}{0.100 \text{ kg}} = 0.15 \text{ K or } 0.15°\text{C}$$

The boiling point will be $100.00°\text{C} + 0.15°\text{C} = 100.15°\text{C}$.

(c)  $\Delta T_b = ik_b m$

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

A 1.7% solution of urea will contain 1.7 g of urea per 98.3 g of water.

$$\Delta T_b = 0.51 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \frac{\left(\dfrac{1.7 \text{ g}}{60.06 \text{ g} \cdot \text{mol}^{-1}}\right)}{0.0983 \text{ kg}} = 0.15 \text{ K or } 0.15°\text{C}$$

The boiling point will be $100.00°\text{C} + 0.15°\text{C}$ or $100.15°\text{C}$.

**8.58**  (a) The molality of the solution can be calculated, knowing the freezing point; this value can, in turn, be used to calculate the boiling point.

$$\Delta T_f = k_f m$$

Because the solvent is water with a normal freezing point of $0°\text{C}$, the freezing point of the solution is also the $\Delta T_f$.

$$1.04 \text{ K} = 1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \text{molality}$$
$$\text{molality} = 0.559 \text{ mol} \cdot \text{kg}^{-1}$$

$$\Delta T_b = k_b m$$
$$= 0.51 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times 0.559 \text{ mol} \cdot \text{kg}^{-1}$$
$$= 0.29 \text{ K or } 0.29°\text{C}$$

$$\text{boiling point} = 100.00°\text{C} + 0.29°\text{C} = 100.29°\text{C}$$

(b)  $\Delta T_f = k_f m$

$$\Delta T_f = 5.5°\text{C} - 2.0°\text{C} = 3.5°\text{C or } 3.5 \text{ K}$$
$$3.5 \text{ K} = 5.12 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \text{molality}$$
$$\text{molality} = 0.68 \text{ mol} \cdot \text{kg}^{-1}$$

$$\Delta T_b = k_b m$$
$$= 2.53 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times 0.68 \text{ mol} \cdot \text{kg}^{-1}$$
$$= 1.7 \text{ K or } 1.7°\text{C}$$

$$\text{boiling point} = 80.1°\text{C} + 1.7°\text{C} = 81.8°\text{C}$$

**8.60**  $\Delta T_b = 0.481°\text{C}$ or $0.481 \text{ K}$

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

$0.481 \text{ K} = 2.79 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \text{molality}$

$$0.481 \text{ K} = 2.79 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \frac{\left(\dfrac{2.25 \text{ g}}{M_{\text{unknown}}}\right)}{0.150 \text{ kg}}$$

$$\frac{0.150 \text{ kg} \times 0.481 \text{ K}}{2.79 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}} = \frac{2.25 \text{ g}}{M_{\text{unknown}}}$$

$$M_{\text{unknown}} = \frac{2.25 \text{ g} \times 2.79 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}}{0.150 \text{ kg} \times 0.481 \text{ K}} = 87.0 \text{ g} \cdot \text{mol}^{-1}$$

**8.62**   (a)  $\Delta T_{\text{f}} = i k_{\text{f}} m$

For $CaCl_2$, $i = 3$

$\Delta T_{\text{f}} = 3 \times 1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times 0.22 \text{ mol} \cdot \text{kg}^{-1} = 1.2 \text{ K or } 1.2°\text{C}$

The freezing point will be $0.00°\text{C} - 1.2°\text{C} = -1.2°\text{C}$.

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

For $Li_2CO_3$, $i = 3$

$$\Delta T_{\text{f}} = 3 \times 1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \frac{\left(\dfrac{0.001\,54 \text{ g}}{73.89 \text{ g} \times \text{mol}^{-1}}\right)}{0.100 \text{ kg}}$$

$$= 1.16 \times 10^{-3} \text{ K or } 1.16 \times 10^{-3}°\text{C}$$

The boiling point will be $0.00°\text{C} - 1.16 \times 10^{-3}°\text{C} = -1.16 \times 10^{-3}°\text{C}$.

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

Because urea is a nonelectrolyte, $i = 1$

A 1.7% solution of urea will contain 1.7 g of urea per 98.3 g of water.

$$\Delta T_{\text{f}} = 1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \frac{\left(\dfrac{1.7 \text{ g}}{60.06 \text{ g} \cdot \text{mol}^{-1}}\right)}{0.0983 \text{ kg}} = 0.54 \text{ K or } 0.54°\text{C}$$

The freezing point will be $0.00°\text{C} - 0.54°\text{C}$ or $-0.54°\text{C}$.

**8.64**   $\Delta T_{\text{f}} = k_{\text{f}} m$

$$1.454 \text{ K} = (7.27 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}) \, m$$

$$1.454 \text{ K} = (7.27 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}) \frac{\left(\dfrac{1.32 \text{ g}}{M_{\text{unknown}}}\right)}{0.0500 \text{ kg}}$$

$$\frac{0.0500 \text{ kg} \times 1.454 \text{ K}}{7.27 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}} = \frac{1.32 \text{ g}}{M_{\text{unknown}}}$$

$$M_{\text{unknown}} = \frac{1.32 \text{ g} \times 7.27 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}}{0.0500 \text{ kg} \times 1.454 \text{ K}} = 132 \text{ g} \cdot \text{mol}^{-1}$$

**8.66** (a) We use the vapor pressure to calculate the mole fraction of benzene and then convert this quantity to molality, which in turn is used to calculate the freezing point depression.

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

(Remember that the vapor pressure of a liquid at its boiling point is 760 Torr by definition.)

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

Because the absolute amount of solvent is not important here, we can assume that the total number of moles = 1.

$$x_{\text{solvent}} = 0.974 = \frac{n_{\text{solvent}}}{n_{\text{solvent}} + n_{\text{solute}}} = \frac{n_{\text{solvent}}}{1}$$

$$n_{\text{solvent}} = 0.974, \; n_{\text{solute}} = 0.026$$

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

$$\Delta T_{\text{f}} = k_{\text{f}} m$$
$$= 5.12 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times 0.34 \text{ mol} \cdot \text{kg}^{-1} = 1.7°\text{C}$$

The freezing point will be $5.12°\text{C} - 1.7°\text{C} = 3.4°\text{C}$.

(b) $\Delta T_f = k_f m$

$4.02\ \text{K} = 1.86\ \text{K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \text{molality}$

$4.02\ \text{K} = 1.86\ \text{K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \dfrac{n_{CO(NH_2)_2}}{\text{kg solvent}} = 1.86\ \text{K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \dfrac{n_{CO(NH_2)_2}}{1.200\ \text{kg}}$

$n_{CO(NH_2)_2} = 2.59\ \text{mol}$

$$\Delta T_f = k_f m$$

$$\Delta T_f = 1.86\ \text{K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \dfrac{n_{protein}}{\text{kg solvent}}$$

$$= 1.86\ \text{K} \cdot \text{kg} \cdot \text{mol}^{-1} \times \dfrac{\left(\dfrac{1.0\ \text{g}}{1.0 \times 10^5\ \text{g} \cdot \text{mol}^{-1}}\right)}{1.0\ \text{kg}}$$

$$= 1.9 \times 10^{-5}\ \text{K or } 1.9 \times 10^{-5}\ ^\circ\text{C}$$

(c) freezing point $\approx 0.0\ ^\circ\text{C}$

**8.68** (a) A 1.00% aqueous solution of $MgSO_4$ will contain 1.00 g of $MgSO_4$ for 99.0 g of water. To use the freezing point depression equation, we need the molality of the solution.

$$\text{molality} = \dfrac{\left(\dfrac{1.00\ \text{g}}{120.37\ \text{g} \cdot \text{mol}^{-1}}\right)}{0.0990\ \text{kg}} = 0.0839\ \text{mol} \cdot \text{kg}^{-1}$$

$\Delta T_f = i k_f m$

$\Delta T_f = i\ (1.86\ \text{K} \cdot \text{kg} \cdot \text{mol}^{-1})(0.0839\ \text{mol} \cdot \text{kg}^{-1}) = 0.192\ \text{K}$

$i = 1.23$

(b) molality of all solute species (undissociated $MgSO_4(aq)$ plus $Mg^{2+}(aq)$ + $SO_4^{2-}(aq)$) $= 1.23 \times 0.0839\ \text{mol} \cdot \text{kg}^{-1} = 0.103\ \text{mol} \cdot \text{kg}^{-1}$

(c) If all the $MgSO_4$ had dissociated, the total molality in solution would have been $0.168\ \text{mol} \cdot \text{kg}^{-1}$, giving an $i$ value equal to 2. If no dissociation had taken place, the molality in solution would have equaled $0.0839\ \text{mol} \cdot \text{kg}^{-1}$.

$$MgSO_4(aq) \rightleftharpoons Mg^{2+}(aq) + SO_4^{2-}(aq)$$

$0.0839\ \text{mol} \cdot \text{kg}^{-1} - x \qquad x \qquad\qquad x$

$0.0839 \ \text{mol} \cdot \text{kg}^{-1} - x + x + x = 0.103 \ \text{mol} \cdot \text{kg}^{-1}$

$0.0839 \ \text{mol} \cdot \text{kg}^{-1} + x = 0.103 \ \text{mol} \cdot \text{kg}^{-1}$

$x = 0.019 \ \text{mol} \cdot \text{kg}^{-1}$

$\% \ \text{dissociation} = \dfrac{0.019 \ \text{mol} \cdot \text{kg}^{-1}}{0.0839 \ \text{mol} \cdot \text{kg}^{-1}} \times 100 = 23\%$

**8.70**  First calculate the van't Hoff $i$ factor:

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

$0.423 \ \text{K} = i \times 1.86 \ \text{K} \cdot \text{kg} \cdot \text{mol}^{-1} \times 0.124 \ \text{mol} \cdot \text{kg}^{-1}$

$i = 1.83$

The molality of all solute species (undissociated $CCl_3COOH(aq)$ plus

$CCl_3COO^-(aq) + H^+(aq)) = 1.83 \times 0.124 \ \text{mol} \cdot \text{kg}^{-1} = 0.227 \ \text{mol} \cdot \text{kg}^{-1}$

If all the $CCl_3COOH(aq)$ had dissociated, the total molality in solution

would have been $0.248 \ \text{mol} \cdot \text{kg}^{-1}$, giving an $i$ value equal to 2. If no

dissociation had taken place, the molality in solution would have equaled

$0.124 \ \text{mol} \cdot \text{kg}^{-1}$.

$CCl_3COOH(aq) \quad \rightleftharpoons \quad H^+(aq) \ + \ CCl_3COO^-(aq)$

$0.124 \ \text{mol} \cdot \text{kg}^{-1} - x \qquad\qquad x \qquad\qquad\quad x$

$0.124 \ \text{mol} \cdot \text{kg}^{-1} - x + x + x = 0.227 \ \text{mol} \cdot \text{kg}^{-1}$

$0.124 \ \text{mol} \cdot \text{kg}^{-1} + x = 0.227 \ \text{mol} \cdot \text{kg}^{-1}$

$x = 0.103 \ \text{mol} \cdot \text{kg}^{-1}$

$\% \ \text{ionization} = \dfrac{0.103 \ \text{mol} \cdot \text{kg}^{-1}}{0.124 \ \text{mol} \cdot \text{kg}^{-1}} \times 100 = 83.1\%$

**8.72**  First, calculate the osmotic pressure of each solution from

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

(a) KCl is an ionic compound that dissociates into 2 ions, so $i = 2$.

$\Pi = 2 \times 0.082 \ 06 \ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 323 \ \text{K} \times 0.10 \ \text{mol} \cdot \text{L}^{-1}$

$\quad = 5.3 \ \text{atm}$

(b) urea, $CO(NH_2)_2$ is a nonelectrolyte, so $i = 1$.

$$\Pi = 1 \times 0.082\ 06\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 323\ \text{K} \times 0.60\ \text{mol} \cdot \text{L}^{-1}$$
$$= 15.9\ \text{atm}$$

(c) $K_2SO_4$ is an ionic solid that dissolves in solution to produce 3 ions, so $i = 3$.

$$\Pi = 3 \times 0.082\ 06\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 323\ \text{K} \times 0.30\ \text{mol} \cdot \text{L}^{-1}$$
$$= 24\ \text{atm}$$

Solution (c) has the highest osmotic pressure.

**8.74** Insulin is a nonelectrolyte, so $i = 1$.

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

$$\Pi = \frac{2.30\ \text{Torr}}{760\ \text{Torr} \cdot \text{atm}^{-1}} = 1 \times 0.082\ 06\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\times\ 298\ \text{K} \times \frac{\left(\dfrac{0.10\ \text{g}}{M_{\text{unknown}}}\right)}{0.200\ \text{L}}$$

$$M_{\text{unknown}} = \frac{0.082\ 06\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}{2.30\ \text{Torr} \times 0.200\ \text{L}}$$

$$\times\ \frac{293\ \text{K} \times 0.10\ \text{g} \times 760\ \text{Torr} \cdot \text{atm}^{-1}}{2.30\ \text{Torr} \times 0.200\ \text{L}}$$

$$= 4.0 \times 10^3\ \text{g} \cdot \text{mol}^{-1}$$

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

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

$$\Pi = \frac{0.582\ \text{Torr}}{760\ \text{Torr} \cdot \text{atm}^{-1}} = 1 \times 0.082\ 06\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\times\ 293\ \text{K} \times \frac{\left(\dfrac{0.50\ \text{g}}{M_{\text{unknown}}}\right)}{0.200\ \text{L}}$$

$$M_{unknown} = \frac{0.082\ 06\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 293\ \text{K} \times}{0.582\ \text{Torr} \times 0.200\ \text{L}}$$

$$\times \frac{0.50\ \text{g} \times 760\ \text{Torr} \cdot \text{atm}^{-1}}{0.582\ \text{Torr} \times 0.200\ \text{L}}$$

$$= 7.8 \times 10^4\ \text{g} \cdot \text{mol}^{-1}$$

**8.78** (a) Assume that $C_6H_{12}O_6$ is a nonelectrolyte, so $i = 1$.

$\Pi = iRT \times$ molarity

$\quad = 1 \times 0.082\ 06\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 293\ \text{K} \times 3.0 \times 10^{-3}\ \text{mol} \cdot \text{L}^{-1}$

$\quad = 0.072\ \text{atm}$

(b) $CaCl_2$ is an ionic compound that will dissolve in solution to give 3 ions, so $i = 3$.

$\Pi = iRT \times$ molarity

$\quad = 3 \times 0.082\ 06\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 293\ \text{K} \times 2.0 \times 10^{-3}\ \text{mol} \cdot \text{L}^{-1}$

$\quad = 0.14\ \text{atm}$

(c) $K_2SO_4$ is an ionic compound that will dissolve into 3 ions in solution, $i = 3$.

$\Pi = iRT \times$ molarity

$\quad = 3 \times 0.082\ 06\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 293\ \text{K} \times 0.010\ \text{mol} \cdot \text{L}^{-1}$

$\quad = 0.72\ \text{atm}$

**8.80** 5% glucose $= \dfrac{5.0\ \text{g glucose}}{1.0 \times 10^2\ \text{g solution}}$

assume the solution density $\approx 1\ \text{g} \cdot \text{mL}^{-1}$

Then $\left(\dfrac{5.0\ \text{g glucose}}{1.0 \times 10^2\ \text{mL}}\right)\left(\dfrac{1\ \text{mL}}{10^{-3}\ \text{L}}\right)\left(\dfrac{1\ \text{mol glucose}}{180.16\ \text{g} \cdot \text{mol}^{-1}}\right) = 0.28\ \text{mol} \cdot \text{L}^{-1}$

and

$\Pi = iRTM = (1)(0.082\ 06\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(310\ \text{K})(0.28\ \text{mol} \cdot \text{L}^{-1})$

$\quad = 7.1\ \text{atm}$

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

$$x_{hexane} = \frac{0.25 \text{ mol}}{0.25 \text{ mol} + 0.65 \text{ mol}} = 0.28$$

$$x_{cyclohexane} = 1 - x_{hexane} = 0.72$$

$$P_{total} = (0.28 \times 151 \text{ Torr}) + (0.72 \times 98 \text{ Torr}) = 113 \text{ Torr}$$

The vapor phase composition will be given by

$$x_{hexane \text{ in vapor phase}} = \frac{P_{hexane}}{P_{total}} = \frac{0.28 \times 151 \text{ Torr}}{113 \text{ Torr}} = 0.37$$

$$x_{cyclohexane \text{ in vapor phrase}} = 1 - 0.37 = 0.63$$

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

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

$$n_{hexane} = \frac{10.0 \text{ g}}{86.18 \text{ g} \cdot \text{mol}^{-1}} = 0.116$$

$$n_{cyclohexane} = \frac{10.0 \text{ g}}{84.16 \text{ g} \cdot \text{mol}^{-1}} = 0.119$$

$$x_{hexane} = \frac{0.116 \text{ mol}}{0.116 \text{ mol} + 0.119 \text{ mol}} = 0.494$$

$$x_{cyclohexane} = 1 - x_{hexane} = 0.506$$

$$P_{total} = (0.494 \times 151 \text{ Torr}) + (0.506 \times 98 \text{ Torr}) = 124 \text{ Torr}$$

The vapor phase composition will be given by

$$x_{hexane \text{ in vapor phase}} = \frac{P_{hexane}}{P_{total}} = \frac{0.494 \times 151 \text{ Torr}}{124 \text{ Torr}} = 0.602$$

$$x_{cyclohexane \text{ in vapor phase}} = 1 - 0.602 = 0.398$$

**8.84** We are given the following information:

$$P_{butanone, \text{ pure}} = 100. \text{ Torr at } 25°\text{C}, 350.0\text{g} \quad (72.107 \text{ g} \cdot \text{mol}^{-1} \quad \text{M.W.})$$

$$P_{propanone, \text{ pure}} = 222 \text{ Torr at } 25°\text{C} \quad (58.080 \text{ g} \cdot \text{mol}^{-1} \quad \text{M.W.})$$

$$P_{total} = 135 \text{ Torr}$$

and Raoult's Law states:

$$P_{\text{total}} = X_{\text{butanone}} P_{\text{butanone, pure}} + X_{\text{propanone}} P_{\text{propanone, pure}}$$

$$= \frac{n_{\text{butanone}}}{n_{\text{total}}} P_{\text{butanone, pure}} + \frac{n_{\text{propanone}}}{n_{\text{total}}} P_{\text{propanone, pure}}$$

given $n_{\text{tot}}al = n_{\text{butanone}} + n_{\text{propanone}}$ we can write:

$$P_{\text{tot}} = \frac{n_{\text{butanone}}}{n_{\text{total}}} P_{\text{butanone, pure}} + \frac{n_{\text{total}} - n_{\text{butanone}}}{n_{\text{total}}} P_{\text{propanone, pure}}$$

Rearranging to solve for $n_{\text{total}}$:'

$$n_{\text{total}} = \frac{\left(n_{\text{butanone}} \cdot P_{\text{butanone, pure}}\right) - \left(n_{\text{butanone}} \cdot P_{\text{propanone, pure}}\right)}{P_{\text{total}} - P_{\text{propanone, pure}}}$$

$$= \frac{\left(4.8539 \text{ mol} \cdot 100. \text{ Torr}\right) - \left(4.8539 \text{ mol} \cdot 222 \text{ Torr}\right)}{135 \text{ Torr} - 222 \text{ Torr}}$$

$$= 6.81 \text{ mol}$$

Therefore,

$$n_{\text{propanone}} = n_{\text{total}} - n_{\text{butanone}} = 6.81 \text{ mol} - 4.85 \text{ mol} = 1.95 \text{ mol}$$

and

$$mass_{\text{propanone}} = 1.95 \text{ mol} \cdot 58.080 \text{ g} \cdot \text{mol}^{-1} = 113 \text{ g}$$

**8.86** Raoult's Law applies to the vapor pressure of the mixture, so a 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 HBr and $H_2O$, the possibility of intermolecular hydrogen bonding between water and HBr would suggest that negative deviation would be observed, which is the case. HBr and $H_2O$ form an azeotrope that boils at $126\,^{\circ}\text{C}$, which is higher than the boiling point of either HBr ($-67°C$) or water.

(b)  Because formic acid is a very polar molecule with hydrogen bonding and benzene is nonpolar, we would expect a positive deviation, which is observed. Benzene and formic acid form an azeotrope that boils

at $71°C$, which is well below the boiling point of either benzene $(80.1°C)$ or formic acid $(101°C)$.

(c) Because cyclohexane and cyclopentane are both nonpolar hydrocarbons of similar size and with similar intermolecular forces, we would expect them to form an ideal solution.

**8.88**  (a) Given:

$P_{A,\ pure} = 1.55$ atm,  $P_{B,\ pure} = 0.650$ atm,  and $P_{total} = 1.00$ atm

Raoult's Law states:

$P_{tot} = X_A P_{A,\ pure} + X_B P_{B,\ pure}$

To solve for the mole fractions of A and B we use:

$X_A + X_B = 1$, and therefore: $X_B = 1 - X_A$.

Substituting into the equation above we obtain:

$P_{tot} = X_A P_{A,\ pure} + (1 - X_A) P_{B,\ pure}$.

Solving for $X_A$ :

$$X_A = \frac{P_{tot} - P_{B,\ pure}}{P_{A,\ pure} - P_{B,\ pure}} = \frac{1.00\ \text{atm} - 0.650\ \text{atm}}{1.55\ \text{atm} - 0.650\ \text{atm}} = 0.389$$

and $X_B = 1 - X_A = 1 - 0.389 = 0.611$

(b) The gas-phase mole fraction is given by:

$P_A = X_{A,\ liquid} P_{A,\ pure} = 0.389 \cdot 1.55\ \text{atm} = 0.603\ \text{atm}$

$P_B = X_{B,\ liquid} P_{B,\ pure} = 0.611 \cdot 0.650\ \text{atm} = 0.397\ \text{atm}$

$P_{tot} = P_A + P_B = 0.603\ \text{atm} + 0.397\ \text{atm} = 1.00\ \text{atm}$

and

$$X_{A,\ gas} = \frac{0.603\ \text{atm}}{1.00\ \text{atm}} = 0.603,  \quad X_{B,\ gas} = \frac{0.397\ \text{atm}}{1.00\ \text{atm}} = 0.397$$

(c) Qualitatively, as the boiling proceeds, the liquid becomes enriched in component B, the less volatile component. The gas phase, on the other hand, starts out highly enriched in the more volatile component, component A, but will slowly gain more of component B as the boiling process proceeds.

**8.90**   $H_2O_2$ has a greater molar mass than $H_2O$, which allows for greater London forces. Hydrogen bonding should occur for both molecules.

**8.92**   (a)  Vapor pressure increases due to the increased kinetic energy of the molecules at higher temperatures.   (b)  No effect on the vapor pressure as such, which is determined only by the temperature, but the rate of evaporation increases.   (c)  No effect on the vapor pressure, which is determined only by the temperature, but additional liquid evaporates.   (d) Very little effect. Adding air above the liquid could increase the external pressure on the liquid, but pressure changes have only a small and usually negligible effect on vapor pressure.

**8.94**   (a)  At $0°C$ and 2 atm, the system exists at the ice/liquid boundary. Decreased pressure brings it to the ice/vapor boundary, when the solid sublimes. Sublimation is complete upon further pressure decrease: the system now contains the vapor alone.   (b)  At $50°C$, water begins in the liquid phase. The vapor pressure of water at $50°C$ is greater than 5 Torr (between 55 and 150 Torr). As the pressure is lowered to 5 Torr, the water will begin to boil.

**8.96**   (a)  In a sense, nothing (the air mass simply warms up and the percent humidity is reduced).   (b)  It condenses to fog or freezes to frost.

**8.98**    Partial pressure of $H_2O = \dfrac{64\% \times 39.90 \text{ Torr}}{100\%} = 26 \text{ Torr}$

The vapor pressure of $H_2O$ at $25°C$ is 23.76 Torr; therefore, fog or dew will form.

**8.100**  Boiling point elevation and freezing point depression both arise because dissolving a solute in a solvent increases the entropy of the solvent, thereby decreasing its free energy. For the vapor pressure curve, the lines

representing the free energies of the liquid solution and the vapor intersect at a higher temperature than for the pure solvent, so the boiling point is higher in the presence of a solute (see Fig. 8.33b). Similarly for freezing point depression, the lines representing the free energies of the liquid and solid phases of the solvent intersect at a lower temperature than for the pure solvent, so the freezing point is lower in the presence of the solute (see Fig. 8.34). This is explained in detail in section 8.17.

**8.102** (a) $\Delta T_{\mathrm{f}} = 1.20°C - 5.5°C = -4.3°C$

$$\Delta T_{\mathrm{f}} = i k_f m = i k_f \frac{\left(\dfrac{m_{\mathrm{solute}}}{M_{\mathrm{solute}}}\right)}{\mathrm{kg\ solvent}}$$

$$M_{\mathrm{solute}} = \frac{i k_f m_{\mathrm{solute}}}{(\mathrm{kg\ solvent})(\Delta T_{\mathrm{f}})} = \frac{(1)(5.12\ \mathrm{K \cdot kg \cdot mol^{-1}})(10.0\ \mathrm{g})}{(0.0800\ \mathrm{kg})(4.3°C)}$$

$$= 1.5 \times 10^2\ \mathrm{g \cdot mol^{-1}}$$

(b) The empirical formula mass $= 73.4\ \mathrm{g \cdot mol^{-1}}$; the experimental formula mass is roughly double this value, so the molecular formula is $C_6H_4Cl_2$.

(c) molar mass $= 146.99\ \mathrm{g \cdot mol^{-1}}$

**8.104** (a) The elemental analysis yields the following:

| element | % by mass | mol in 100 g | ratio to smallest moles (0.542 for N) |
|---------|-----------|--------------|----------------------------------------|
| C | 59.0 | 4.91 | 9.04 |
| O | 26.2 | 1.64 | 3.02 |
| H | 7.10 | 7.04 | 13.0 |
| N | 7.60 | 0.542 | 1 |

The empirical formula is $C_9H_{13}O_3N$ (formula mass $\sim 183\ \mathrm{g \cdot mol^{-1}}$).

(b) and (c)

$$\Delta T_{\mathrm{f}} = i k_f m = i k_f \frac{\left(\dfrac{\mathrm{mass}_{\mathrm{solute}}}{M_{\mathrm{solute}}}\right)}{\mathrm{kg\ solvent}}$$

$$M_{\mathrm{solute}} = \frac{i k_f \mathrm{mass}_{\mathrm{solute}}}{(\mathrm{kg\ solvent})(\Delta T_{\mathrm{f}})} = \frac{(1)(5.12\ \mathrm{K\cdot kg\cdot mol^{-1}})(0.64\ \mathrm{g})}{(0.036\ \mathrm{kg})(0.50°C)}$$

$$= 1.8 \times 10^2\ \mathrm{g\cdot mol^{-1}}$$

The molecular formula is the same as the empirical formula, $C_9H_{13}O_3N$.

Molar mass of epinephrine $=183.20\ \mathrm{g\cdot mol^{-1}}$.


**8.106** (a) The partial pressure remains the same. Some of the ethanol will

condense to return the ethanol(l) $\rightleftharpoons$ ethanol(g) reaction to the equilibrium

point.   (b) The total pressure will be the sum of the pressures due to the

ethanol vapor and to the air. The air will not condense, so its pressure

should follow the ideal gas law. If the total pressure initially is 750 Torr

and 58.9 Torr is due to ethanol vapor, the 750 Torr – 58.9 Torr = 691 Torr

will be due to the air. If the volume is halved at constant temperature, then

the pressure due to the air will be doubled, or $2 \times 691$ Torr

$= 1.38 \times 10^3$ Torr. The total pressure will then be

$1.38 \times 10^3$ Torr + 58.9 Torr $= 1.44 \times 10^3$ Torr.


**8.108** (a) Given $d = 1.00\ \mathrm{g\cdot cm^{-3}} = 1.00\ \mathrm{g\cdot mL^{-1}}$,

$$\therefore \frac{1.54\ \mathrm{g}}{100\ \mathrm{mL\ solution}} = 15.4\ \mathrm{g\cdot L^{-1}}$$

$$15.4\ \mathrm{g\cdot L^{-1}} \times \frac{1\ \mathrm{mol\ Li_2CO_3}}{73.89\ \mathrm{g\ Li_2CO_3}} = 0.208\ \mathrm{mol\cdot L^{-1}}$$

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

$$= 3 \times 0.082\,06\ \mathrm{L\cdot atm\cdot K^{-1}\cdot mol^{-1}} \times 273\ K \times 0.208\ \mathrm{mol\cdot L^{-1}} = 14.0\ \mathrm{atm}$$

(b) $P_{\mathrm{solution}} = x_{\mathrm{solvent}} \times P_{\mathrm{pure\ solvent}}$

$751\ \mathrm{Torr} = x_{\mathrm{solvent}} \times 760\ \mathrm{Torr}$

$x_{solvent} = 0.988$

$x_{solute} = 1 - 0.988 = 0.012$

Consider a solution of 0.012 mol solute in 0.988 mol $H_2O$. Assume that the volume of solution equals the volume of $H_2O$. Then

$$V = 0.988 \text{ mol } H_2O \times \frac{18.02 \text{ g } H_2O}{1.00 \text{ mol } H_2O} \times \frac{1.00 \text{ mL } H_2O}{1.00 \text{ g } H_2O}$$

$$= 17.8 \text{ mL} = 0.0178 \text{ L}$$

$$\text{molarity of solution} = \frac{0.012 \text{ mol}}{0.0178 \text{ L}} = 0.67 \text{ mol} \cdot L^{-1}$$

Assuming that $i = 1$,

$$\Pi = 1 \times 0.082\,06 \text{ L} \cdot \text{atm} \cdot K^{-1} \cdot \text{mol}^{-1} \times 373 \text{ K} \times 0.67 \text{ mol} \cdot L^{-1} = 21 \text{ atm}$$

(c) $\Delta T = ik_b \times \text{molality}$, assume $i = 1$, then

$$\text{molality} = \frac{\Delta T_b}{k_b} = \frac{1 \text{ K}}{0.51 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}} = 2.0 \text{ mol} \cdot \text{kg}^{-1}$$

Given that $d_{solution} = d_{water} = 1.00 \text{ g} \cdot \text{cm}^{-3} = 1.00 \text{ g} \cdot \text{mL}^{-1}$, we have

$$2.0 \text{ mol} \cdot \text{kg}^{-1} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{1.00 \text{ g}}{1.00 \text{ mL}} \times \frac{1000 \text{ mL}}{1.00 \text{ L}} = 2.0 \text{ mol} \cdot L^{-1}$$

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

$$= 1 \times 0.082\,06 \text{ L} \cdot \text{atm} \cdot K^{-1} \cdot \text{mol}^{-1} \times 374 \text{ K} \times 2.0 \text{ mol} \cdot L^{-1}$$

$$= 61 \text{ atm}$$

**8.110** (a) Because the osmotic pressure is calculated from $\Pi = iRT \times \text{molarity}$ (both compounds are nonelectrolytes, so $i = 1$), the solution with the higher concentration will have the higher osmotic pressure, which in this case is the solution of urea, $CO(NH_2)_2$.

(b) The more concentrated solution, $CO(NH_2)_2$, will become more dilute with the passage of $H_2O$ molecules through the membrane.

(c) Pressure must be applied to the more concentrated solution, $CO(NH_2)_2$, to equilibrate the water flow.

(d) $\Pi = iRT \times \Delta M$ (where $\Delta M$ is the difference in molar concentration between the two solutions):

$$\Pi = 1 \times 0.082\,06\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 298\ \text{K} \times 0.038\ \text{mol} \cdot \text{L}^{-1} = 0.73\ \text{atm}$$

**8.112** As illustrated in example 8.8, the molar mass is determined by first finding the concentration of the prepared solution:

$$RTc = gdh,\ \text{and, therefore,}\ c = \frac{gdh}{RT}$$

$$= \frac{\left(9.80665\,\frac{\text{m}}{\text{s}^2}\right)\left(1000\,\frac{\text{cm}}{\text{m}}\right)\left(1000\,\frac{\text{cm}^3}{\text{L}}\right)\left(0.79\,\frac{\text{g}}{\text{cm}^3}\right)\left(\frac{1\ \text{kg}}{1000\ \text{g}}\right)(32.5\ \text{cm})}{\left(8.31447\,\frac{\text{kg m}^2}{\text{s}^2\ \text{K mol}}\right)\left(\frac{100\ \text{cm}}{\text{m}}\right)^2 (298\ \text{K})}$$
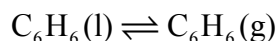
$$= 1.02 \times 10^{-3}\ \text{M}$$

The moles of protein in the solution is then:

$$n_{\text{protein}} = \left(1.02 \times 10^{-3}\ \text{M}\right)(0.010\ \text{L}) = 1.02 \times 10^{-5}\ \text{mol}$$

and the molar mass is:

$$\text{M.M.} = \frac{0.155\ \text{g}}{1.02 \times 10^{-5}\ \text{mol}} = 15300\,\frac{\text{g}}{\text{mol}}$$

**8.114** (a) The data in Table 6.2 can be used to obtain the heat of vaporization and boiling point of benzene.

$$C_6H_6(l) \rightleftharpoons C_6H_6(g)$$

$$\Delta H^\circ_{\text{vap}} = 30.8\ \text{KJ} \cdot \text{mol}^{-1}$$

The boiling point is 353.2 K or 80.0°C, at which the vapor pressure = 1 atm.

To derive the general equation, we start with the expression that

$$\Delta G^\circ_{\text{vap}} = -RT\ \ln P,\ \text{where } P \text{ is the vapor pressure of the solvent. Because}$$

$$\Delta G^\circ_{\text{vap}} = \Delta H^\circ_{\text{vap}} - T\Delta S^\circ_{\text{vap}},\ \text{this is the relationship to use to determine the}$$

temperature dependence of $\ln P$:

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

This equation can be rearranged to give:

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

Because we do not have enough data to calculate $\Delta S^\circ_{vap}$ from the table or appendix, we can use the alternate form of the equation, which relates the vapor pressure at two points to the corresponding temperatures. This equation is obtained by subtracting one specific point from another as shown:

$$\ln P_2 = -\frac{\Delta H^\circ_{vap}}{R} \times \frac{1}{T_2} + \frac{\Delta S^\circ_{vap}}{R}$$

$$-\left[ \ln P_1 = -\frac{\Delta H^\circ_{vap}}{R} \times \frac{1}{T_1} + \frac{\Delta S^\circ_{vap}}{R} \right]$$

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

Because we know $\Delta H^\circ_{vap}$ and one point, we can introduce those values:

$$\ln \frac{P}{1} = -\frac{30\,800 \text{ J}\cdot\text{mol}^{-1}}{8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}} \left[ \frac{1}{T} - \frac{1}{353.2 \text{ K}} \right]$$

$$\ln P = -\frac{3.70 \times 10^3 \text{ K}}{T} + 10.5$$

(b) The appropriate quantities to plot to get a straight line are $\ln P$ versus $\frac{1}{T}$.

(c) The solution will boil when the vapor pressure equals the external pressure.

Simply substitute the numbers once the equation has been derived:

$$\ln P = -\frac{3.70 \times 10^3 \text{ K}}{T} + 10.5$$

$$\ln 0.655 = -\frac{3.70 \times 10^3 \text{ K}}{T} + 10.5$$

$T = 339$ K or 66°C

(d) The equation of the line is written in such a form that the constant 10.5 is

equal to $\dfrac{\Delta S^\circ_{vap}}{R}$.

$\dfrac{\Delta S^\circ_{vap}}{R} = 10.5$

$\Delta S^\circ_{vap} = 10.5 \times 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 87.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

Because $\Delta S^\circ_{vap} = S^\circ_m (\text{benzene, g}) - S^\circ_m (\text{benzene, l})$

we can now calculate the standard molar entropy of benzene(g)

$87.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = S^\circ_m (\text{benzene, g}) - 173.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

$S^\circ_m (\text{benzene, g}) = 260.6 \text{ J} \cdot \text{K}^{-1} \text{ mol}^{-1}$


**8.116** The equation to give vapor pressure as a function of temperature is

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

$\ln P = -\dfrac{57\,814 \text{ J} \cdot \text{mol}^{-1}}{8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} \times \dfrac{1}{T} + \dfrac{124 \text{ J} \cdot \text{mol}^{-1}}{8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$

$\ln P = -\dfrac{6954 \text{ K}}{T} + 14.9$

In order for the substance to boil, we need to reduce the external pressure on the sample to its vapor pressure at that temperature. Thus, the problem becomes simply a matter of calculating the vapor pressure at $80°C$:

$\ln P = -\dfrac{6954 \text{ K}}{353 \text{ K}} + 14.9 = -4.80$

$P = 0.008\,23 \text{ atm or } 6.26 \text{ Torr}$

The pressure needs to be reduced to 6.26 Torr.


**8.118** The critical pressures and temperatures of the compounds are as follows:

| Compound | $T_C$ (°C) | $P_C$ (atm) |
|---|---|---|
| Methane, $CH_4$ | −82.1 | 45.8 |
| Methyl amine, $CH_3NH_2$ | 156.9 | 40.2 |
| Ammonia, $NH_3$ | 132.5 | 112.5 |
| Tetrafluoromethane, $CF_4$ | −45.7 | 41.4 |

In order to access the supercritical fluid state, we must have conditions in excess of the critical temperature and pressure. Given the rating of the autoclave, ammonia would not be suitable because one could not access the supercritical state due to the pressure limitation. Methylamine would not be suitable for a room temperature extraction because its $T_C$ is too high. Either methane or tetrafluoromethane would be suitable for this application.

**8.120** (a) If there is enough diethyl ether present, then the pressure will be due to the vapor pressure of diethyl ether at that temperature. If there is insufficient diethyl ether present, then it will all convert to gas and the pressure will be determined from the ideal gas law. We can calculate the amount of diethyl ether necessary to achieve the vapor pressure from the ideal gas equation, using the vapor pressure as the pressure of the gas.

$$\left(\frac{57 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}}\right)(1.00 \text{ L}) = \left(\frac{m_{\text{diethyl ether}}}{74.12 \text{ g} \cdot \text{mol}^{-1} \text{ diethyl ether}}\right)$$
$$(0.082\ 06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})\,(228 \text{ K})$$
$$m_{\text{diethyl ether}} = 0.297 \text{ g}$$

Because there are 1.50 g of diethyl ether, the vapor pressure will be achieved, so the answer to (a) is 57 Torr.

(b)

$$\left(\frac{535 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}}\right)(1.00 \text{ L}) = \left(\frac{m_{\text{diethyl ether}}}{74.12 \text{ g} \cdot \text{mol}^{-1} \text{ diethyl ether}}\right)$$
$$(0.082\ 06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})$$
$$m_{\text{diethyl ether}} = 2.13 \text{ g}$$

In this case, there is not enough diethyl ether to achieve equilibrium so all of the ether will vaporize. The pressure will be

$$(P)(1.00 \text{ L}) = \left( \frac{1.50 \text{ g diethyl ether}}{74.12 \text{ g} \cdot \text{mol}^{-1} \text{ diethyl ether}} \right)$$

$$(0.082\,06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})$$

$P = 0.495$ atm or 376 Torr

(c) The system is at the same temperature as in (a) but the volume is now doubled. This volume will accommodate twice as much diethyl ether or $2 \times 0.297$ g $= 0.594$ g. There is still sufficient diethyl ether for this to occur so that the pressure will again be equal to the vapor pressure of diethyl ether, or 57 Torr.   (d) If flask B is cooled by liquid nitrogen, its temperature will approach $-196°C$. The vapor pressure of ether at that temperature is negligible and the ether will solidify in flask B. As the ether condenses in flask B, the liquid ether in flask A will continue to vaporize and will do so until all the ether has condensed in flask B. At the end of this, there will be no ether left in flask A and the pressure in the apparatus will be 0.

**8.122**

$$0.50 = \frac{\chi_{\text{pentane, liquid}} P°_{\text{pentane}}}{\chi_{\text{pentane, liquid}} P°_{\text{pentane}} + (1 - \chi_{\text{pentane, liquid}}) P°_{\text{hexane}}}$$

$$\chi_{\text{pentane, gas}} = 0.50 = \frac{\chi_{\text{pentane, liquid}} P°_{\text{pentane}}}{\chi_{\text{pentane, liquid}} P°_{\text{pentane}} + \chi_{\text{hexane, liquid}} P°_{\text{hexane}}}$$

$$0.50 = \frac{(\chi_{\text{pentane, liquid}})(512 \text{ Torr})}{(\chi_{\text{pentane, liquid}})(512 \text{ Torr}) + (1 - \chi_{\text{pentane, liquid}})(151 \text{ Torr})}$$

$\chi_{\text{pentane, liquid}} = 0.228; \; \chi_{\text{hexane, liquid}} = 0.772$

**8.124** (a) The vapor pressures over the two solutions are different. The volatile component, ethanol, will transfer from one solution to the other until the vapor pressures (and therefore concentrations) are equal. The vapor pressure is lower over the more concentrated solution so ethanol will condense on that side of the apparatus. As this takes place, there will be a

net transfer of ethanol from the less concentrated side to the more concentrated side of the apparatus.

(b)  The vapor pressure will be determined by the concentration of the solution (the solutions in both sides of the apparatus will have the same concentration) once the system reaches equilibrium.

For the 0.15 $m$ solution, there will be 0.15 mol sucrose $(342.29 \text{ g} \cdot \text{mol}^{-1})$ for 1000 g ethanol $(46.07 \text{ g} \cdot \text{mol}^{-1})$. This corresponds to 51 g of sucrose for a total solution mass of 1051 g.

In 15.0 g of solution there will be 0.73 g sucrose and 14.27 g of ethanol. Similarly, for the 0.050 $m$ solution, there will be 0.050 mol sucrose for 1000 g ethanol, corresponding to 17 g sucrose and a total solution mass of 1017 g. In 15.0 g of solution there will be 0.25 g sucrose and 14.75 g ethanol.

At equilibrium, the concentrations must be equal. In order to calculate the vapor pressure, we need to know the concentration in terms of mole fractions. The concentrations will be made equal by transferring some ethanol from one solution to the other. This can be expressed mathematically by the following relationship:

$$\frac{\left(\dfrac{0.73 \text{ g}}{342.29 \text{ g} \cdot \text{mol}^{-1}}\right)}{\left(\dfrac{14.27 + x \text{ g}}{46.07 \text{ g} \cdot \text{mol}^{-1}}\right) + \left(\dfrac{0.73 \text{ g}}{342.29 \text{ g} \cdot \text{mol}^{-1}}\right)}$$

$$= \frac{\left(\dfrac{0.25 \text{ g}}{342.29 \text{ g} \cdot \text{mol}^{-1}}\right)}{\left(\dfrac{14.75 - x \text{ g}}{46.07 \text{ g} \cdot \text{mol}^{-1}}\right) + \left(\dfrac{0.25 \text{ g}}{342.29 \text{ g} \cdot \text{mol}^{-1}}\right)}$$

Solving this equation gives $x = 7.3$ g. The mole fraction of sucrose for the solution will be 0.0045, and the mole fraction of ethanol will be $1 - 0.0045 = 0.9955$. The vapor pressure will be

$P = \chi_{\text{ethanol}} P°_{\text{ethanol}} = (0.9955)(60 \text{ Torr}) \cong 60 \text{ Torr}$. A 0.0045 mole fraction corresponds to a 0.098 $m$ solution of sucrose.

**8.126** (a) The polymer concentration is given by:

$$c = \frac{\Pi}{iRT} = \frac{0.325 \text{ atm}}{(1)(0.08206 \frac{\text{L atm}}{\text{K mol}})(298 \text{ K})} = 0.0133 \text{ M}$$

The moles of polymer in solution are:

$$n_{\text{polymer}} = (0.0133 \text{ M})(0.500 \text{ L}) = 0.00664 \text{ mol}$$

and the molar mass of the polymer is:

$$\text{M.M.} = \frac{47.7 \text{ g}}{0.00664 \text{ mol}} = 7180 \frac{\text{g}}{\text{mol}}$$

(b) If a monomer in the polymer is $-CH_2CH(CN)-$, then the molar mass of a monomer is 53.06 g/mol and the average number of monomers in a polymer is: $(7180 \text{g/mol})/(53.06 \text{ g/mol}) = 135$ monomers .

(c) The pressure of $H_2O(g)$ above the mixture is given by:

$$P_{H_2O} = X_{H_2O} \cdot P_{H_2O, \text{ pure}}$$

in 100 mL, $n_{H_2O} = \dfrac{(100 \text{ mL})(1.00 \frac{\text{g}}{\text{mL}})}{18.02 \frac{\text{g}}{\text{mol}}} = 5.55 \text{ mol}$

and, $n_{\text{polymer}} = (0.100 \text{ L})(0.01328 \frac{\text{mol}}{\text{L}}) = 0.00133$ mol.

Therefore,

$$X_{H_2O} = \frac{5.55 \text{ mol}}{5.55 \text{ mol} + 0.00133 \text{ mol}} = 0.9998 \quad \text{and}$$

$$P_{H_2O} = (0.9998)(23.76 \text{ Torr}) = 23.75 \text{ Torr}$$

(d) Measuring the change in osmotic pressure proves to be a better method in this case. The osmotic pressure developed by the resulting polymer solution is readily measured while the change in partial pressure of $H_2O(g)$ changes by less than 0.1 % upon addition of the polymer.

**8.128** Compound (a). The stationary phase is more polar than the liquid phase, so the more polar compound of (a) and (b) should be attracted more strongly to the stationary phase and should remain on the column longer. Because compound (a) has two carboxylic acid units (COOH), it will be more polar and will have the greater value of $k$.

**8.130** We can use the initial data to calculate an experimental freezing-point depression constant for naphthalene:

Freezing-point depression $= k_f \times$ molality

$$k_f = \frac{\text{Freezing-point depression}}{\text{molality}} = \frac{7.0 \text{ K}}{1 \text{ mol} \cdot \text{kg}^{-1}} = 7.0 \text{ K} \cdot \text{mol}^{-1} \cdot \text{kg}$$

The molecular weight of the $S_x$ is found using:

Freezing-point depression $= k_f \times$ molality

$$0.7 = \left(7.0 \text{ K} \cdot \text{mol}^{-1} \cdot \text{kg}\right) \left( \frac{\dfrac{14.8 \text{ g S}}{M_{S_x}}}{0.575 \text{ kg}} \right)$$

$$M_{S_x} = 257 \text{ g} \cdot \text{mol}^{-1}$$

The molecular formula for the sulfur compound is:

Freezing-point depression $= k_f \times$ molality

$$\frac{257 \text{ g S}_x \cdot \text{mol}^{-1}}{32.06 \text{ g S} \cdot \text{mol}^{-1}} = 8$$

Therefore, the molecular formula is $S_8$.

**8.132** All three molecules possess the same weak London forces holding them in the condensed phase. One would expect that neopentane would have the highest vapor pressure as the molecules are rigid and unable to "flex" to increase favorable intermolecular interactions. Octane would have the lowest vapor pressure as it is the most massive of the three options.

**8.134** (a) The molar mass of L-carnitine is found as in problem 8.130 above:

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

$$0.501 \text{ atm} = 1 \times 0.082\,06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 305.2 \text{ K} \times \left( \frac{\dfrac{0.322 \text{ g}}{M}}{0.100 \text{ kg}} \right)$$

$$M = 161 \text{ g} \cdot \text{mol}^{-1}$$

(b) The empirical formula is found first using the observed composition of the compound:

Assuming 100 g of compound:

$$C: \frac{52.16 \text{ g}}{12.011 \text{ g} \cdot \text{mol}^{-1}} = 4.343 \text{ mol} \qquad (7)$$

$$H: \frac{9.38 \text{ g}}{1.00794 \text{ g} \cdot \text{mol}^{-1}} = 9.31 \text{ mol} \qquad (15)$$

$$N: \frac{8.69 \text{ g}}{14.01 \text{ g} \cdot \text{mol}^{-1}} = 0.620 \text{ mol} \qquad (1)$$

$$O: \frac{29.78 \text{ g}}{15.9994 \text{ g} \cdot \text{mol}^{-1}} = 1.861 \text{ mol} \qquad (3)$$

(the whole numbers on the right were obtained by dividing the number of moles of each element by the moles of N present.)

The empirical formula is, therefore, $C_7H_{15}O_3N$.

The molecular mass of this formula is 161.2 g mol$^{-1}$, which matches the molecular mass determined using the osmotic pressure above indicating that $C_7H_{15}O_3N$ is the molecular formula for L-carnitine.

**8.136** (a) $CH_3OH$ will be more soluble as it has a polar –OH group, which gives this molecule some polar character; $CH_4$ is completely nonpolar. (b) KI would be more soluble as it is less polar than KCl, a highly polar molecule. (c) CsBr would be more soluble, again because CsBr is less polar than highly polar LiBr.