

SOLUTIONS

PROBLEM SET 6

CHM 3400, Dr. Chatfield

- 5.18** The solubility of N_2 in blood at $37^\circ C$ and a partial pressure of 0.80 atm is $5.6 \times 10^{-4} \text{ mol L}^{-1}$. A deep-sea diver breathes compressed air with a partial pressure of N_2 equal to 4.0 atm . Assume that the total volume of blood in the body is 5.0 L . Calculate the amount of N_2 gas released (in liters) when the diver returns to the surface of water, where the partial pressure of N_2 is 0.80 atm .

Assuming N_2 is an ideal gas, the volume of N_2 released can be readily calculated from the number of moles of N_2 released, which in turn is related to the number of moles of N_2 dissolved in blood when the partial pressures of N_2 are 4.0 atm and 0.80 atm , respectively.

According to Henry's law, the solubility of a substance is proportional to the applied pressure. Therefore,

$$\frac{\text{Solubility of } N_2 \text{ when } P_{N_2} \text{ is } 4.0 \text{ atm}}{\text{Solubility of } N_2 \text{ when } P_{N_2} \text{ is } 0.80 \text{ atm}} = \frac{4.0 \text{ atm}}{0.80 \text{ atm}} = 5.0$$

$$\text{Solubility of } N_2 \text{ when } P_{N_2} \text{ is } 4.0 \text{ atm} = 5.0 \left(5.6 \times 10^{-4} \text{ mol L}^{-1} \right) = 2.80 \times 10^{-3} \text{ mol}$$

When $P_{N_2} = 0.80 \text{ atm}$,

$$\text{Number of moles of } N_2 \text{ in blood} = \left(5.6 \times 10^{-4} \text{ mol L}^{-1} \right) (5.0 \text{ L}) = 2.80 \times 10^{-3} \text{ mol}$$

When $P_{N_2} = 4.0 \text{ atm}$,

$$\text{Number of moles of } N_2 \text{ in blood} = \left(2.80 \times 10^{-3} \text{ mol L}^{-1} \right) (5.0 \text{ L}) = 1.40 \times 10^{-2} \text{ mol}$$

When the diver returns to the surface of water,

$$\text{Number of moles of } N_2 \text{ released} = 1.40 \times 10^{-2} \text{ mol} - 2.80 \times 10^{-3} \text{ mol} = 1.12 \times 10^{-2} \text{ mol}$$

and therefore,

$$\text{Volume of } N_2 \text{ released} = \frac{(1.12 \times 10^{-2} \text{ mol}) (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) (310 \text{ K})}{0.80 \text{ atm}} = 0.36 \text{ L}$$

- 5.28** A common antifreeze for car radiators is ethylene glycol, $\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$. How many milliliters of this substance would you add to 6.5 L of water in the radiator if the coldest day in winter is -20°C ? Would you keep this substance in the radiator in the summer to prevent the water from boiling? (The density and boiling point of ethylene glycol are 1.11 g cm^{-3} and 470 K , respectively.)

The molality of ethylene glycol that can depress the freezing point by 20°C or 20 K is

$$m_2 = \frac{\Delta T}{K_f} = \frac{20\text{ K}}{1.86\text{ K mol}^{-1}\text{ kg}} = 10.75\text{ mol kg}^{-1}$$

Assuming the density of water is 1 kg L^{-1} , the mass of water in the radiator is 6.5 kg , which, together with the molality of ethylene glycol, gives the number of moles of ethylene glycol.

$$\text{Number of moles of ethylene glycol} = (10.75\text{ mol kg}^{-1})(6.5\text{ kg}) = 69.88\text{ mol}$$

which corresponds to a volume of

$$V = \frac{(69.88\text{ mol})(62.07\text{ g mol}^{-1})}{1.11\text{ g cm}^{-3}} = 3.91 \times 10^3\text{ cm}^3 = 3.91 \times 10^3\text{ mL}$$

Since it has a higher boiling point, ethylene glycol can also elevate the boiling point of water. With a 10.75 m solution, the boiling point of water will be elevated by

$$\Delta T_b = K_b m_2 = (0.51\text{ K mol}^{-1}\text{ kg})(10.75\text{ mol kg}^{-1}) = 5.5\text{ K}$$

Therefore, keeping ethylene glycol in the radiator in the summer will increase the boiling point by 5.5°C .

- 5.30** The tallest trees known are the redwoods in California. Assuming the height of a redwood to be 105 m (about 350 ft), estimate the osmotic pressure required to push water up from the roots to the treetop.

Assume that the density of water is $1 \times 10^3\text{ kg m}^{-3}$.

$$\begin{aligned} \pi &= h\rho g \quad (\text{See Example 5.6 in text.}) \\ &= (105\text{ m})(1 \times 10^3\text{ kg m}^{-3})(9.81\text{ m s}^{-2}) \\ &= (1.030 \times 10^6\text{ N m}^{-2}) \left(\frac{1\text{ atm}}{1.013 \times 10^5\text{ N m}^{-2}} \right) = 10.2\text{ atm} \end{aligned}$$

- 5.34 Lysozyme extracted from chicken egg white has a molar mass of $13,930 \text{ g mol}^{-1}$. Exactly 0.1 g of this protein is dissolved in 50 g of water at 298 K . Calculate the vapor pressure lowering, the depression in freezing point, the elevation of boiling point, and the osmotic pressure of this solution. The vapor pressure of pure water at 298 K is 23.76 mmHg .

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First calculate the mole fraction, molality, and molarity of lysozyme.

$$\text{Number of moles of lysozyme} = \frac{0.1 \text{ g}}{13930 \text{ g mol}^{-1}} = 7.17875 \times 10^{-6} \text{ mol}$$

$$\text{Number of moles of water} = \frac{50 \text{ g}}{18.02 \text{ g mol}^{-1}} = 2.7747 \text{ mol}$$

$$x_{\text{lysozyme}} = \frac{7.17875 \times 10^{-6} \text{ mol}}{7.17875 \times 10^{-6} \text{ mol} + 2.7747 \text{ mol}} = 2.5872 \times 10^{-6}$$

$$m = \frac{7.17875 \times 10^{-6} \text{ mol}}{50 \times 10^{-3} \text{ kg}} = 1.43575 \times 10^{-4} \text{ mol kg}^{-1}$$

For a dilute aqueous solution, the molality and molarity are numerically the same (see Problem 5.6). Therefore, $M = 1.43575 \times 10^{-4} \text{ mol L}^{-1}$.

Vapor pressure lowering:

$$\Delta P = x_{\text{lysozyme}} P_{\text{H}_2\text{O}}^* = (2.5872 \times 10^{-6})(23.76 \text{ mmHg}) = 6.147 \times 10^{-5} \text{ mmHg}$$

Depression in freezing point:

$$\Delta T_f = K_f m = (1.86 \text{ K m}^{-1})(1.43575 \times 10^{-4} \text{ m}) = 2.67 \times 10^{-4} \text{ K}$$

Elevation of boiling point:

$$\Delta T_b = K_b m = (0.51 \text{ K m}^{-1})(1.43575 \times 10^{-4} \text{ m}) = 7.3 \times 10^{-5} \text{ K}$$

Osmotic pressure:

$$\begin{aligned} \pi &= MRT = (1.43575 \times 10^{-4} \text{ M})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(298 \text{ K}) \\ &= 3.51 \times 10^{-3} \text{ atm} \left(\frac{760 \text{ torr}}{1 \text{ atm}} \right) = 2.67 \text{ torr} \end{aligned}$$

Note that the only property that is readily measurable is the osmotic pressure.

5.48 The following data give the pressures for carbon disulfide–acetone solutions at 35.2° C. Calculate the activity coefficients of both components based on deviations from Raoult's law and Henry's law. (*Hint*: First determine Henry's law constants graphically.)

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x_{CS_2}	0	0.20	0.45	0.67	0.83	1.00
$P_{\text{CS}_2}/\text{torr}$	0	272	390	438	465	512
$P_{\text{C}_3\text{H}_6\text{O}}/\text{torr}$	344	291	250	217	180	0

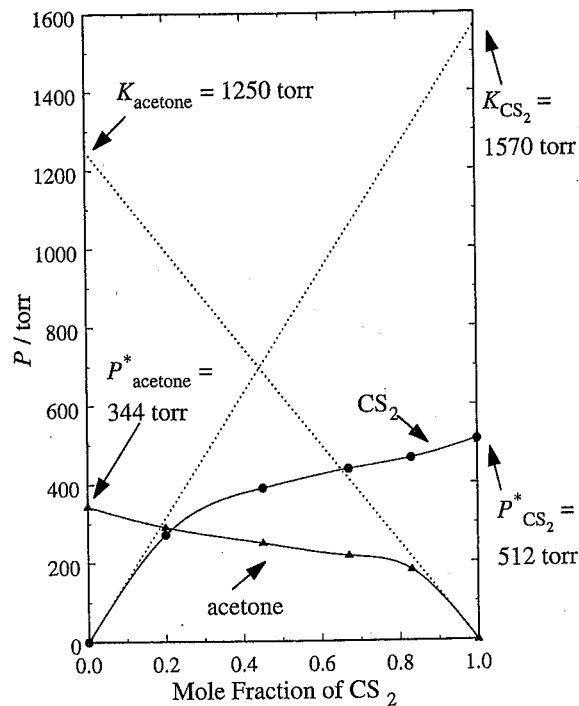
From a graph of the vapor pressure data, Henry's law constants may be obtained from the limiting slopes of the curves as they approach their respective infinite dilution (mole fraction equals zero) limits. (Note that the graph pictured is scaled to show the $x = 1$ intercept of each Henry's law line. In making the actual determination of the limiting slopes it is better to use an expanded scale that shows the limiting behavior in detail.) The Henry's law constants obtained from these data are $K_{\text{CS}_2} = 1570$ torr and $K_{\text{C}_3\text{H}_6\text{O}} = 1250$ torr. The activity coefficient of the i^{th} component accounts for deviations from Henry's law as

$$P_i = K_i \gamma_i x_i$$

or

$$\gamma_i = \frac{P_i}{K_i x_i}$$

The necessary data to find the Henry's law activity coefficients, $\gamma_i(\text{H})$ are in the table. (Note that $x_{\text{C}_3\text{H}_6\text{O}} = 1 - x_{\text{CS}_2}$.)



x_{CS_2}	0	0.20	0.45	0.67	0.83	1.00
$P_{\text{CS}_2}/\text{torr}$	0	272	390	438	465	512
$P_{\text{C}_3\text{H}_6\text{O}}/\text{torr}$	344	291	250	217	180	0
$\gamma_{\text{CS}_2}(\text{H})$	1.00	0.87	0.55	0.42	0.36	0.33
$\gamma_{\text{C}_3\text{H}_6\text{O}}(\text{H})$	0.28	0.29	0.36	0.53	0.85	1.00

$$P_i = \gamma_i x_i P_i^*$$

or

$$\gamma_i = \frac{P_i}{x_i P_i^*}$$

The tabulated data are used once again, noting that the vapor pressures of the pure components are included, namely $P_{\text{CS}_2}^* = 512$ torr and $P_{\text{C}_3\text{H}_6\text{O}}^* = 344$ torr. The Raoult's law activity is denoted $\gamma_i(\text{R})$, and is not defined at zero mole fraction.

x_{CS_2}	0	0.20	0.45	0.67	0.83	1.00
$P_{\text{CS}_2}/\text{torr}$	0	272	390	438	465	512
$P_{\text{C}_3\text{H}_6\text{O}}/\text{torr}$	344	291	250	217	180	0
$\gamma_{\text{CS}_2}(\text{R})$	—	2.66	1.69	1.28	1.09	1.00
$\gamma_{\text{C}_3\text{H}_6\text{O}}(\text{R})$	1.00	1.06	1.32	1.91	3.08	—

The activities determined from the two laws differ because the standard state is chosen differently in the two cases.

5.53 Express the mean activity, mean activity coefficient, and mean molality in terms of the individual ionic quantities (a_+ , a_- , γ_+ , γ_- , m_+ , and m_-) for the following electrolytes: KI, SrSO_4 , CaCl_2 , Li_2CO_3 , $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$.

	ν_+	ν_-	ν	a_{\pm}	γ_{\pm}	m_{\pm}
KI	1	1	2	$(a_+ a_-)^{1/2}$	$(\gamma_+ \gamma_-)^{1/2}$	$(m_+ m_-)^{1/2}$
SrSO_4	1	1	2	$(a_+ a_-)^{1/2}$	$(\gamma_+ \gamma_-)^{1/2}$	$(m_+ m_-)^{1/2}$
CaCl_2	1	2	3	$(a_+ a_-^2)^{1/3}$	$(\gamma_+ \gamma_-^2)^{1/3}$	$(m_+ m_-^2)^{1/3}$
Li_2CO_3	2	1	3	$(a_+^2 a_-)^{1/3}$	$(\gamma_+^2 \gamma_-)^{1/3}$	$(m_+^2 m_-)^{1/3}$
$\text{K}_3\text{Fe}(\text{CN})_6$	3	1	4	$(a_+^3 a_-)^{1/4}$	$(\gamma_+^3 \gamma_-)^{1/4}$	$(m_+^3 m_-)^{1/4}$
$\text{K}_4\text{Fe}(\text{CN})_6$	4	1	5	$(a_+^4 a_-)^{1/5}$	$(\gamma_+^4 \gamma_-)^{1/5}$	$(m_+^4 m_-)^{1/5}$

5.54 Calculate the ionic strength and the mean activity coefficient for the following solutions at 298 K: (a) 0.10 *m* NaCl, (b) 0.010 *m* MgCl₂, and (c) 0.10 *m* K₄Fe(CN)₆.

The ionic strength can be obtained from the equation

$$I = \frac{1}{2} \sum_i m_i z_i^2$$

and subsequently the mean activity from the Debye-Hückel limiting law

$$\log \gamma_{\pm} = -0.509 |z_+ z_-| \sqrt{I}$$

(a) 0.10 *m* NaCl: $z_+ = 1$, $z_- = -1$, $m_+ = 0.10$ *m*, $m_- = 0.10$ *m*

$$I = \frac{1}{2} [(0.10 \text{ m}) (1)^2 + (0.10 \text{ m}) (-1)^2] = 0.10 \text{ m}$$

$$\log \gamma_{\pm} = -0.509 |(1) (-1)| \sqrt{0.10} = -0.161$$

$$\gamma_{\pm} = 0.69$$

(b) 0.010 *m* MgCl₂: $z_+ = 2$, $z_- = -1$, $m_+ = 0.010$ *m*, $m_- = 0.020$ *m*

$$I = \frac{1}{2} [(0.010 \text{ m}) (2)^2 + (0.020 \text{ m}) (-1)^2] = 0.030 \text{ m}$$

$$\log \gamma_{\pm} = -0.509 |(2) (-1)| \sqrt{0.030} = -0.176$$

$$\gamma_{\pm} = 0.67$$

(c) 0.10 *m* K₄Fe(CN)₆: $z_+ = 1$, $z_- = -4$, $m_+ = 0.40$ *m*, $m_- = 0.10$ *m*

$$I = \frac{1}{2} [(0.40 \text{ m}) (1)^2 + (0.10 \text{ m}) (-4)^2] = 1.0 \text{ m}$$

$$\log \gamma_{\pm} = -0.509 |(1) (-4)| \sqrt{1.0} = -2.04$$

$$\gamma_{\pm} = 9.1 \times 10^{-3}$$

5.64 The osmotic pressure of poly(methyl methacrylate) in toluene has been measured at a series of concentrations at 298 K. Determine graphically the molar mass of the polymer.

π / atm	8.40×10^{-4}	1.72×10^{-3}	2.52×10^{-3}	3.23×10^{-3}	7.75×10^{-3}
$c / \text{g} \cdot \text{L}^{-1}$	8.10	12.31	15.00	18.17	28.05

In the limit of a dilute solution, where all virial coefficients except the second may be ignored, the osmotic pressure π is given by

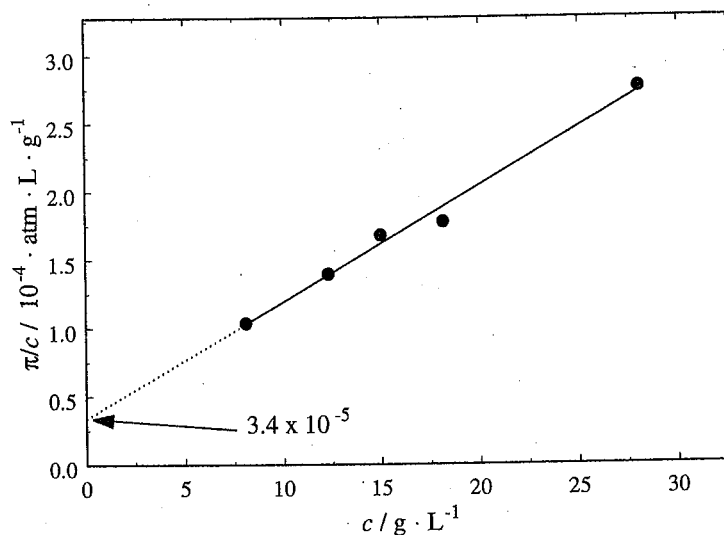
$$\frac{\pi}{c} = \frac{RT}{\mathcal{M}} (1 + Bc)$$

Thus, a graph of π/c vs. c will extrapolate to a y intercept of $\frac{RT}{\mathcal{M}}$, where \mathcal{M} is the molar mass of the solute.

The data for the graph is given in the table below.

$(\pi/c) / \text{atm} \cdot \text{L} \cdot \text{g}^{-1}$	1.037×10^{-4}	1.397×10^{-4}	1.680×10^{-4}	1.778×10^{-4}	2.763×10^{-4}
$c / \text{g} \cdot \text{L}^{-1}$	8.10	12.31	15.00	18.17	28.05

As seen in the graph, the extrapolation to zero concentration gives an intercept of $3.4 \times 10^{-5} \text{ atm L g}^{-1}$.



Thus,

$$\begin{aligned}
 3.4 \times 10^{-5} \text{ atm L g}^{-1} &= \frac{RT}{\mathcal{M}} \\
 &= \frac{(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) (298 \text{ K})}{\mathcal{M}} \\
 \mathcal{M} &= 7.2 \times 10^5 \text{ g mol}^{-1}
 \end{aligned}$$

- 5.66 Suppose 2.6 moles of He at 0.80 atm and 25° C are mixed with 4.1 moles of Ne at 2.7 atm and 25° C. Calculate the Gibbs energy change for the process. Assume ideal behavior.

The expression $\Delta_{\text{mix}}G = nRT (x_1 \ln x_1 + x_2 \ln x_2)$ is valid only for mixing two gases originally at the same pressure and is not directly applicable here. G is a state function, however, so consider a path in which the two gases are first individually brought to the final pressure of the mixture and then mixed. The overall ΔG is the sum of the ΔG 's for the steps. The process is assumed to take place with the gases originally in two containers connected by a valve which is opened. The final volume of the mixture is then the sum of the original volumes. Since $V_{\text{He}} = \frac{n_{\text{He}}RT}{P_{\text{He}}}$, with a similar expression for Ne,

$$\begin{aligned} P_f &= \frac{n_{\text{total}}RT}{V_f} \\ &= \frac{(n_{\text{He}} + n_{\text{Ne}}) RT}{\frac{n_{\text{He}}RT}{P_{\text{He}}} + \frac{n_{\text{Ne}}RT}{P_{\text{Ne}}}} \\ &= \frac{n_{\text{He}} + n_{\text{Ne}}}{\frac{n_{\text{He}}}{P_{\text{He}}} + \frac{n_{\text{Ne}}}{P_{\text{Ne}}}} \\ &= \frac{2.6 \text{ mol} + 4.1 \text{ mol}}{\frac{2.6 \text{ mol}}{0.80 \text{ atm}} + \frac{4.1 \text{ mol}}{2.7 \text{ atm}}} \\ &= 1.41 \text{ atm} \end{aligned}$$

For the compression (expansion) of an ideal gas, $\Delta G = nRT \ln \frac{P_f}{P_i}$, so that

$$\Delta G_{\text{He}} = (2.6 \text{ mol}) \left(8.314 \text{ J K}^{-1} \text{ mol}^{-1} \right) (298 \text{ K}) \ln \frac{1.41 \text{ atm}}{0.80 \text{ atm}} = 3.65 \times 10^3 \text{ J}$$

$$\Delta G_{\text{Ne}} = (4.1 \text{ mol}) \left(8.314 \text{ J K}^{-1} \text{ mol}^{-1} \right) (298 \text{ K}) \ln \frac{1.41 \text{ atm}}{2.7 \text{ atm}} = -6.60 \times 10^3 \text{ J}$$

$$\begin{aligned} \Delta_{\text{mix}}G &= n_{\text{total}}RT (x_{\text{He}} \ln x_{\text{He}} + x_{\text{Ne}} \ln x_{\text{Ne}}) \\ &= (2.6 \text{ mol} + 4.1 \text{ mol}) \left(8.314 \text{ J K}^{-1} \text{ mol}^{-1} \right) (298 \text{ K}) \\ &\quad \times \left[\frac{2.6 \text{ mol}}{2.6 \text{ mol} + 4.1 \text{ mol}} \ln \left(\frac{2.6 \text{ mol}}{2.6 \text{ mol} + 4.1 \text{ mol}} \right) \right. \\ &\quad \left. + \frac{4.1 \text{ mol}}{2.6 \text{ mol} + 4.1 \text{ mol}} \ln \left(\frac{4.1 \text{ mol}}{2.6 \text{ mol} + 4.1 \text{ mol}} \right) \right] \\ &= -1.11 \times 10^4 \text{ J} \end{aligned}$$

$$\Delta G_{\text{total}} = \Delta G_{\text{He}} + \Delta G_{\text{Ne}} + \Delta_{\text{mix}}G = -1.4 \times 10^4 \text{ J} = -14 \text{ kJ}$$