

Chem340 Homework 9

P8.3) An ideal solution is formed by mixing liquids A and B at 298 K. The vapor pressure of pure A is 180. Torr and that of pure B is 82.1 Torr. If the mole fraction of A in the vapor is 0.450, what is the mole fraction of A in the solution?

The mol fraction of A in the ideal solution of liquids A and B is given by:

$$x_A = \frac{y_A p_B^*}{p_A^* + (p_B^* - p_A^*) y_A} = \frac{0.450 \times 82.1 \text{ Torr}}{180 \text{ Torr} + (82.1 \text{ Torr} - 180 \text{ Torr}) \times 0.450} = \underline{0.272}$$

P8.4) A and B form an ideal solution. At a total pressure of 0.900 bar, $y_A = 0.450$ and $x_A = 0.650$. Using this information, calculate the vapor pressure of pure A and of pure B.

$$P_{total} = x_A P_a^* + y_B P_{total}$$

$$P_a^* = \frac{P_{total} - y_B P_{total}}{x_A} = \frac{0.900 \text{ bar} \times 0.450}{0.650} = 0.623 \text{ bar}$$

$$x_A = \frac{y_A P_B^*}{P_a^* + (P_B^* - P_a^*) y_A}$$

$$0.650 = \frac{0.450 P_B^*}{P_a^* + 0.450 (P_B^* - P_a^*)}$$

$$\frac{P_B^*}{P_a^*} = \frac{0.650 \times (1 - 0.450)}{0.450 \times (1 - 0.650)} = 2.27$$

$$P_B^* = 1.414 \text{ bar}$$

P8.5) A and B form an ideal solution at 298 K, with $x_A = 0.600$, $P_A^* = 105 \text{ Torr}$, and

$$P_B^* = 63.5 \text{ Torr}.$$

a. Calculate the partial pressures of A and B in the gas phase.

b. A portion of the gas phase is removed and condensed in a separate container.

Calculate the partial pressures of A and B in equilibrium with this liquid sample at

298 K.

a) Calculate the partial pressures of A and B in the gas phase.

$$P_A = x_A P_A^* = 0.600 \times 105 \text{ Torr} = 63.0 \text{ Torr}$$

$$P_B = (1 - x_A) P_B^* = 0.400 \times 63.5 \text{ Torr} = 25.4 \text{ Torr}$$

b) A portion of the gas phase is removed and condensed in a separate container.

Calculate the partial pressures of A and B in equilibrium with this liquid sample at 298 K.

The composition of the initial gas is given by

$$y_A = \frac{P_A}{P_A + P_B} = \frac{63.0 \text{ Torr}}{88.4 \text{ Torr}} = 0.713; \quad y_B = 0.287$$

For the portion removed, the new x_A and x_B values are the previous y_A and y_B values.

$$P_A = x_A P_A^* = 0.713 \times 105 \text{ Torr} = 74.9 \text{ Torr}$$

$$P_B = (1 - x_A) P_B^* = 0.287 \times 63.5 \text{ Torr} = 18.2 \text{ Torr}$$

P8.7) Assume that 1-bromobutane and 1-chlorobutane form an ideal solution. At 273 K,

$P_{chloro}^* = 3790 \text{ Pa}$ and $P_{bromo}^* = 1394 \text{ Pa}$. When only a trace of liquid is present at 273 K,

$$y_{chloro} = 0.75.$$

a. Calculate the total pressure above the solution.

b. Calculate the mole fraction of 1-chlorobutane in the solution.

c. What value would Z_{chloro} have in order for there to be 4.86 mol of liquid and 3.21 mol of gas at a total pressure equal to that in part (a)? [Note: This composition is different from that of part (a).]

a) Calculate the total pressure above the solution.

$$y_{\text{chloro}} = \frac{P_{\text{chloro}}^* P_{\text{total}} - P_{\text{chloro}}^* P_{\text{bromo}}^*}{P_{\text{total}} (P_{\text{chloro}}^* - P_{\text{bromo}}^*)}$$

$$0.75 = \frac{3790 \text{ Pa} \times P_{\text{total}} - 3790 \text{ Pa} \times 1394 \text{ Pa}}{P_{\text{total}} \times (3790 \text{ Pa} - 1394 \text{ Pa})}$$

$$P_{\text{total}} = \frac{3790 \text{ Pa} \times 1394 \text{ Pa}}{3790 \text{ Pa} - 0.75 \times (3790 \text{ Pa} - 1394 \text{ Pa})} = 2651 \text{ Pa}$$

b) Calculate the mole fraction of 1-chlorobutane in the solution.

$$P_{\text{total}} = x_{\text{chloro}} P_{\text{chloro}}^* + (1 - x_{\text{chloro}}) P_{\text{bromo}}^*$$

$$x_{\text{chloro}} = \frac{P_{\text{total}} - P_{\text{bromo}}^*}{P_{\text{chloro}}^* - P_{\text{bromo}}^*} = \frac{2651 \text{ Pa} - 1394 \text{ Pa}}{3790 \text{ Pa} - 1394 \text{ Pa}} = 0.525$$

c) What value would Z_{chloro} have in order that there are 4.86 moles of liquid and 3.21 moles of gas at a total pressure equal to that in part a)? (This composition is different than that in part a.)

$$y_{\text{chloro}} = \frac{P_{\text{chloro}}^* P_{\text{total}} - P_{\text{chloro}}^* P_{\text{bromo}}^*}{P_{\text{total}} (P_{\text{chloro}}^* - P_{\text{bromo}}^*)}$$

$$= \frac{3790 \text{ Pa} \times 2651 \text{ Pa} - 3790 \text{ Pa} \times 1394 \text{ Pa}}{2651 \text{ Pa} \times (3790 \text{ Pa} - 1394 \text{ Pa})} = 0.750$$

$$x_{\text{chloro}} = \frac{y_{\text{chloro}} P_{\text{bromo}}^*}{P_{\text{chloro}}^* + (P_{\text{bromo}}^* - P_{\text{chloro}}^*) y_{\text{chloro}}}$$

$$= \frac{0.750 \times 1394 \text{ Pa}}{3790 \text{ Pa} + (1394 \text{ Pa} - 3790 \text{ Pa}) \times 0.750} = 0.525$$

$$n_{\text{liq}}^{\text{tot}} (Z_{\text{chloro}} - x_{\text{chloro}}) = n_{\text{vapor}}^{\text{tot}} (y_{\text{chloro}} - Z_{\text{chloro}})$$

$$Z_{\text{chloro}} = \frac{n_{\text{vapor}}^{\text{tot}} y_{\text{chloro}} + n_{\text{liq}}^{\text{tot}} x_{\text{chloro}}}{n_{\text{vapor}}^{\text{tot}} + n_{\text{liq}}^{\text{tot}}} = \frac{3.21 \text{ mol} \times 0.750 + 4.86 \text{ mol} \times 0.525}{3.21 \text{ mol} + 4.86 \text{ mol}} = 0.614$$

P8.10) At -31.2°C , pure propane and *n*-butane have vapor pressures of 1200 and 200

Torr, respectively.

- a. Calculate the mole fraction of propane in the liquid mixture that boils at -31.2°C at a pressure of 760 Torr.

b. Calculate the mole fraction of propane in the vapor that is in equilibrium with the liquid of part (a).

a) At the boiling point the vapor pressure of the mixture is equal to the external pressure:

$$p_{\text{tot}} = p_{\text{ext}} = 760 \text{ Torr}$$

Again, solving $p_{\text{tot}} = x_{\text{prop}}p_{\text{prop}}^* + (1 - x_{\text{prop}})p_{\text{but}}^*$ for x_A yields for the mol fraction of propane in the solution:

$$x_{\text{prop}} = \frac{(p_{\text{tot}} - p_{\text{but}}^*)}{(p_{\text{prop}}^* - p_{\text{but}}^*)} = \frac{(760 \text{ Torr} - 200 \text{ Torr})}{(1200 \text{ Torr} - 200 \text{ Torr})} = 0.560$$

b) The mol fraction of propane in the gas phase is:

$$y_{\text{but}} = \frac{p_{\text{but}}^*p_{\text{tot}} - p_{\text{but}}^*p_{\text{prop}}^*}{p_{\text{tot}}(p_{\text{but}}^* - p_{\text{prop}}^*)} = \frac{(200 \text{ Torr}) \times (760 \text{ Torr}) - (200 \text{ Torr}) \times (1200 \text{ Torr})}{(760 \text{ Torr}) \times ((200 \text{ Torr}) - (1200 \text{ Torr}))} = 0.116$$

$$y_{\text{prop}} = 1 - y_{\text{but}} = 0.884$$

P8.18) The partial molar volumes of water and ethanol in a solution with $x_{H_2O} = 0.60$ at 25°C are 17.0 and 57.0 cm³ mol⁻¹, respectively. Calculate the volume change on mixing sufficient ethanol with 2 mol of water to give this concentration. The densities of water and ethanol are 0.997 and 0.7893 g cm⁻³, respectively, at this temperature.

$$V = n_{H_2O} \bar{V}_{H_2O} + n_{Et} \bar{V}_{Et}$$

$$\bar{V}_{H_2O} = 17.0 \text{ cm}^3 \text{ mol}^{-1} \text{ and } \bar{V}_{Et} = 57.0 \text{ cm}^3 \text{ mol}^{-1}$$

$$n_{H_2O} = 2.00 \text{ and } x_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{Et}} = 0.600$$

$$\frac{2 \text{ mol}}{2 \text{ mol} + n_{Et}} = 0.600; \quad n_{Et} = 1.333$$

The total mixed volume is given by

$$V_{\text{mixed}} = n_{H_2O} \bar{V}_{H_2O} + n_{Et} \bar{V}_{Et}$$

$$\begin{aligned} &= 2.00 \text{ mol} \times 17.0 \text{ cm}^3 \text{ mol}^{-1} + 1.333 \text{ mol} \times 57.0 \text{ cm}^3 \text{ mol}^{-1} \\ &= 109.98 \text{ cm}^3 \end{aligned}$$

$$\begin{aligned}
V_{unmixed} &= n_{H_2O} \frac{M_{H_2O}}{\rho_{H_2O}} + n_{Et} \frac{M_{Et}}{\rho_{Et}} \\
&= 2.00 \text{ mol} \times 18.02 \text{ g mol}^{-1} \times \frac{1 \text{ cm}^3}{0.997 \text{ g}} \\
&\quad + 1.333 \text{ mol} \times 46.07 \text{ g mol}^{-1} \times \frac{1 \text{ cm}^3}{0.7873 \text{ g}} \\
&= 36.15 \text{ cm}^3 + 78.00 \text{ cm}^3 \\
&= 114.15 \text{ cm}^3 \\
\Delta V &= V_{mixed} - V_{unmixed} = 109.98 \text{ cm}^3 - 114.15 \text{ cm}^3 = -4.2 \text{ cm}^3
\end{aligned}$$

P8.20) The heat of fusion of water is $6.008 \times 10^3 \text{ J mol}^{-1}$ at its normal melting point of 273.15 K. Calculate the freezing point depression constant K_f .

$$\begin{aligned}
K_f &= \frac{RM_{\text{solvent}} T_{\text{fusion}}^2}{\Delta H_{\text{fusion}}} = -\frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 18.02 \times 10^{-3} \text{ kg mol}^{-1} \times (273.15 \text{ K})^2}{6.008 \times 10^3 \text{ J mol}^{-1}} \\
K_f &= 1.86 \text{ K kg mol}^{-1}
\end{aligned}$$

P8.22) A sample of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) of mass 1.25 g is placed in a test tube of radius 1.00 cm. The bottom of the test tube is a membrane that is semipermeable to water. The tube is partially immersed in a beaker of water at 298 K so that the bottom of the test tube is only slightly below the level of the water in the beaker. The density of water at this temperature is 997 kg m^{-3} . After equilibrium is reached, how high is the water level of the water in the tube above that in the beaker? What is the value of the osmotic pressure?

You may find the approximation $\ln \frac{1}{1+x} \approx -x$ useful.

$$\pi V_m^* + RT \ln x_{\text{solvent}} = \pi V_m^* + RT \ln \frac{n_{\text{solvent}}}{n_{\text{solvent}} + n_{\text{sucrose}}} = 0$$

$$\rho gh V_m^* + RT \ln \frac{\frac{\rho Ah}{M}}{\frac{\rho Ah}{M} + n_{\text{sucrose}}} = \rho gh V_m^* + RT \ln \frac{1}{1 + \frac{n_{\text{sucrose}} M}{\rho Ah}} = 0$$

Expanding the argument of the logarithmic term in a Taylor series, $\ln \frac{1}{1+x} \approx -x$

$$\rho gh V_m^* - RT \frac{n_{\text{sucrose}} M}{\rho Ah} = 0$$

$$h = \sqrt{\frac{RT n_{\text{sucrose}} M}{\rho^2 A g V_m^*}} = \sqrt{\frac{RT n_{\text{sucrose}}}{\rho A g}}$$

$$= \sqrt{\frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \frac{1.25 \times 10^{-3} \text{ kg}}{0.18016 \text{ kg mol}^{-1}}}{997 \text{ kg m}^{-3} \times 3.14 \times 10^{-4} \text{ m}^2 \times 9.81 \text{ ms}^{-2}}} = 2.37 \text{ m}$$

$$\pi = \rho gh = 997 \text{ kg m}^{-3} \times 9.81 \text{ ms}^{-2} \times 2.37 \text{ m} = 2.32 \times 10^4 \text{ Pa}$$

P8.24) To extend the safe diving limit, both oxygen and nitrogen must be reduced in the breathing mixture. One way to do this is to mix oxygen with helium. Assume a mixture of 10.% oxygen and 90.0% helium. Assuming Henry's law behavior, calculate the levels of oxygen and helium in the blood of a diver at 100 m. Assume $T = 298 \text{ K}$.

$$p = \rho gh + 101325 \text{ Pa} = 1000 \text{ kg} \cdot \text{m}^{-3} \cdot 9.81 \text{ m} \cdot \text{s}^{-2} \cdot 100 \text{ m} + 101325 \text{ Pa} = 1.081 \times 10^6 \text{ Pa}$$

$$p_{\text{O}_2} = 10\% \times 1.081 \times 10^6 \text{ Pa} = 1.08 \times 10^5 \text{ Pa}$$

$$x_{\text{O}_2} = \frac{P_{\text{O}_2}}{k_H^{\text{O}_2}} = \frac{1.08 \times 10^5 \text{ Pa}}{4.95 \times 10^4 \text{ bar} \times 10^5 \text{ Pa} / \text{bar}} = 2.18 \times 10^{-5}$$

P8.32) Calculate the activity and activity coefficient for CS_2 at $x_{\text{CS}_2} = 0.7220$ using the

data in Table 8.3 for both a Raoult's law and a Henry's law standard state.

$$a_{\text{CS}_2}^R = \frac{P_{\text{CS}_2}}{P_{\text{CS}_2}^*} = \frac{446.9 \text{ Torr}}{512.3 \text{ Torr}} = 0.8723$$

$$\gamma_{\text{CS}_2}^R = \frac{a_{\text{CS}_2}^R}{x_{\text{CS}_2}} = \frac{0.8723}{0.7220} = 1.208$$

$$a_{CS_2}^H = \frac{P_{CS_2}}{k_{H,CS_2}} = \frac{446.9 \text{ Torr}}{2010 \text{ Torr}} = 0.2223$$

$$\gamma_{CS_2}^H = \frac{a_{CS_2}^H}{x_{CS_2}} = \frac{0.2223}{0.7220} = 0.3079$$

P8.36) Assume sucrose and water form an ideal solution. What is the equilibrium vapor pressure of a solution of 2.0 grams of sucrose (molecular weight 342 g mol^{-1}) at $T = 293 \text{ K}$ if the vapor pressure of pure water at 293 K is 17.54 Torr . What is the osmotic pressure of the sucrose solution versus pure water? Assume 100.0 g of water.

The equilibrium water pressure is given by:

$$\frac{p_{\text{solvent}}}{p_{\text{solvent}}^*} = x_{\text{solvent}} = 1 - x_{\text{solute}} = 1 - \frac{n_{\text{solute}}}{(n_{\text{solute}} + n_{\text{solvent}})}$$

$$p_{\text{solvent}} = p_{\text{solvent}}^* \left(1 - \frac{n_{\text{solute}}}{(n_{\text{solute}} + n_{\text{solvent}})} \right) = p_{\text{solvent}}^* \left(1 - \frac{(m_{\text{sucrose}} / M_{\text{sucrose}})}{[(m_{\text{water}} / M_{\text{water}}) + (m_{\text{sucrose}} / M_{\text{sucrose}})]} \right)$$

$$= (17.54 \text{ Torr}) \times \left(1 - \frac{(2.0 \text{ g} / 342 \text{ g mol}^{-1})}{[(100 \text{ g} / 18.02 \text{ g mol}^{-1}) + (2.0 \text{ g} / 342 \text{ g mol}^{-1})]} \right) = 17.52 \text{ Torr}$$

The osmotic pressure is:

$$\pi = \frac{n_{\text{solute}} RT}{V} = \frac{(2.0 \text{ g} / 342 \text{ g mol}^{-1}) \times (8.314472 \text{ J K mol}^{-1}) \times (293 \text{ K})}{(0.0001 \text{ m}^3)} = 142464.3 \text{ Pa} = 1068.57 \text{ Torr}$$

P8.45) The concentrations in moles per kilogram of water for the dominant salts in sea water are:

Ion	Cl^-	Na^+	Mg^{2+}	SO_4^{2-}	Ca^{2+}
Mol kg^{-1}	0.546	0.456	0.053	0.028	0.010

Calculate the osmotic pressure exerted by sea water at $T = 298 \text{ K}$. Suppose sea water is separated from pure water by a membrane that is permeable to water but impermeable to the ions in sea water. Assuming the density of sea water is about equal to pure water at $T = 298 \text{ K}$, calculate the column of sea water that would be supported by osmotic pressure.

For 1 kg of sea water (1 L) the osmotic pressure is:

$$\pi = \frac{n_{\text{solutes}} RT}{V} = \frac{(0.546 + 0.456 + 0.053 + 0.028 + 0.010) \text{ mol} \times (8.314472 \text{ J K mol}^{-1}) \times (298 \text{ K})}{(0.001 \text{ m}^3)}$$

$$= 2708139.93 \text{ Pa} = 27.08 \text{ bar}$$

The column of sea water that would be supported by this osmotic pressure can be calculated as follows:

$$\pi = p = 1 \text{ atm} + \rho g h$$

$$h = \frac{(\pi - 1 \text{ atm})}{\rho g} = \frac{(2708139.93 \text{ Pa} - 101325 \text{ Pa})}{(1000 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2})} = 265.73 \text{ m} = 0.266 \text{ km}$$

Q1 (modified from P8.15)

The data in the Table below shows the vapor pressure of water (component A) and methanol (B) at 39.9°C.

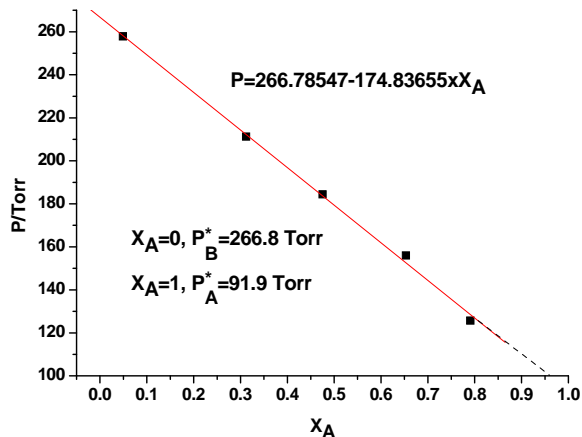
x_A	y_A	P (Torr)
0.0490	0.0175	257.9
0.3120	0.1090	211.3
0.4750	0.1710	184.4
0.6535	0.2550	156.0
0.7905	0.3565	125.7

(a) Plot P vs X_A . By fitting the data to a linear curve, obtain P_A^* and P_B^* assuming that the solution is an ideal solution.

(b) The actual vapor pressure of pure water is 55.03 Torr and that of methanol is 255.6 Torr at 39.9 °C. Using the vapor pressures and the data from the table above, calculate the activity coefficients for both components using a Raoult's law standard state. Make a table.

(a) Plot P vs. X_A , extrapolate to $X_A=0$, $P_B^*=266.8$ Torr and

$X_A=1$, $P_A^*=91.9$ Torr.



(b)

$$a_A = \frac{P_A}{P_A^*} = \frac{y_A \times P_{total}}{P_A^*} = \frac{0.0175 \times 257.9 \text{ Torr}}{55.03 \text{ Torr}} = 0.0820$$

For example, $X_A=0.0490$, , the

$$\gamma_A = \frac{a_A}{x_A} = \frac{0.0820}{0.0490} = 1.67$$

same calculation can be performed to get activity coefficients of water and ethanol at different compositions. The results are shown below.

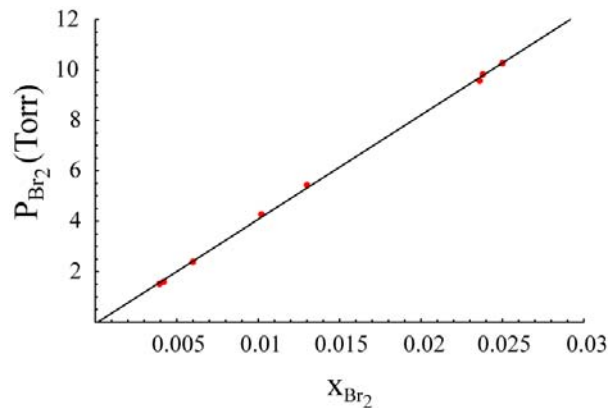
x_A	y_A	P (Torr)
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0.3120	0.1090	211.3
0.4750	0.1710	184.4
0.6535	0.2550	156.0
0.7905	0.3565	125.7

x_A	y_A	P (Torr)	a_A	a_B	γ_A	γ_B
0.0490	0.0175	257.9	0.082	0.991	1.67	1.04
0.3120	0.1090	211.3	0.419	0.737	1.34	1.07
0.4750	0.1710	184.4	0.573	0.598	1.21	1.14
0.6535	0.2550	156.0	0.723	0.455	1.11	1.31
0.7905	0.3565	125.7	0.814	0.316	1.03	1.55

P8.16) The partial pressures of Br_2 above a solution containing CCl_4 as the solvent at 25°C are found to have the values listed in the following table as a function of the mole fraction of Br_2 in the solution [G. N. Lewis and H. Storch, *J. American Chemical Society* 39 (1917), 2544]. Use these data and a graphical method to determine the Henry's law constant for Br_2 in CCl_4 at 25°C .

x_{Br_2}	P (Torr)	x_{Br_2}	P (Torr)
0.00394	1.52	0.0130	5.43
0.00420	1.60	0.0236	9.57

0.00599	2.39	0.0238	9.83
0.0102	4.27	0.0250	10.27



The best fit line in the plot is $P_{Br_2} \text{ (Torr)} = 413 x_{Br_2} - 0.063$. Therefore, the Henry's law constant in terms of mole fraction is 413 Torr.

P9.1) Calculate $\Delta H_{reaction}^\circ$ and $\Delta G_{reaction}^\circ$ for the reaction $AgNO_3(aq) + KCl(aq) \rightarrow AgCl(s) + KNO_3(aq)$.

$\Delta H_{reaction}^\circ$ and $\Delta G_{reaction}^\circ$ are given by:

$$\begin{aligned} \Delta H_{reaction}^\circ &= \Delta H_f^\circ(AgCl(s)) + \Delta H_f^\circ(K^+(aq)) + \Delta H_f^\circ(NO_3^-(aq)) \\ &\quad - \Delta H_f^\circ(K^+(aq)) - \Delta H_f^\circ(Cl^-(aq)) - \Delta H_f^\circ(Ag^+(aq)) - \Delta H_f^\circ(NO_3^-(aq)) \\ \Delta H_{reaction}^\circ &= (-127.0 \text{ kJ mol}^{-1}) + (-252.4 \text{ kJ mol}^{-1}) + (-207.4 \text{ kJ mol}^{-1}) \\ &\quad - (-252.4 \text{ kJ mol}^{-1}) - (-167.2 \text{ kJ mol}^{-1}) - (105.6 \text{ kJ mol}^{-1}) - (-207.4 \text{ kJ mol}^{-1}) \\ &= \underline{-65.4 \text{ kJ mol}^{-1}} \\ \Delta G_{reaction}^\circ &= \Delta G_f^\circ(AgCl(s)) + \Delta G_f^\circ(K^+(aq)) + \Delta G_f^\circ(NO_3^-(aq)) \\ &\quad - \Delta G_f^\circ(K^+(aq)) - \Delta G_f^\circ(Cl^-(aq)) - \Delta G_f^\circ(Ag^+(aq)) - \Delta G_f^\circ(NO_3^-(aq)) \end{aligned}$$

$$\begin{aligned}\Delta G_{\text{reaction}}^{\circ} &= (-109.8 \text{ kJ mol}^{-1}) + (-283.3 \text{ kJ mol}^{-1}) + (-111.3 \text{ kJ mol}^{-1}) \\ &- (-283.3 \text{ kJ mol}^{-1}) - (-131.2 \text{ kJ mol}^{-1}) - (77.1 \text{ kJ mol}^{-1}) - (-111.3 \text{ kJ mol}^{-1}) \\ &= \underline{-55.7 \text{ kJ mol}^{-1}}\end{aligned}$$

P9.2) Calculate $\Delta H_{\text{reaction}}^{\circ}$ and $\Delta G_{\text{reaction}}^{\circ}$ for the reaction $\text{Ba}(\text{NO}_3)_2(\text{aq}) + 2\text{KCl}(\text{aq}) \rightarrow \text{BaCl}_2(\text{s}) + 2\text{KNO}_3(\text{aq})$.

$$\Delta G_{\text{reaction}}^{\circ} = \Delta G_f^{\circ}(\text{BaCl}_2, \text{s}) + 2 \Delta G_f^{\circ}(\text{K}^+, \text{aq}) + 2 \Delta G_f^{\circ}(\text{NO}_3^-, \text{aq}) - \Delta G_f^{\circ}(\text{Ba}^{2+}, \text{aq})$$

$$-2 \Delta G_f^{\circ}(\text{NO}_3^-, \text{aq}) - 2 \Delta G_f^{\circ}(\text{K}^+, \text{aq}) - 2 \Delta G_f^{\circ}(\text{Cl}^-, \text{aq})$$

$$\Delta G_{\text{reaction}}^{\circ} = \Delta G_f^{\circ}(\text{BaCl}_2, \text{s}) - \Delta G_f^{\circ}(\text{Ba}^{2+}, \text{aq}) - 2 \Delta G_f^{\circ}(\text{Cl}^-, \text{aq})$$

$$\Delta G_{\text{reaction}}^{\circ} = -806.7 \text{ kJ mol}^{-1} + 560.8 \text{ kJ mol}^{-1} + 2 \times 131.2 \text{ kJ mol}^{-1} = 16.5 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{reaction}}^{\circ} = \Delta H_f^{\circ}(\text{BaCl}_2, \text{s}) - \Delta H_f^{\circ}(\text{Ba}^{2+}, \text{aq}) - 2 \Delta H_f^{\circ}(\text{Cl}^-, \text{aq})$$

$$\Delta H_{\text{reaction}}^{\circ} = -855.0 \text{ kJ mol}^{-1} + 537.6 \text{ kJ mol}^{-1} + 2 \times 167.2 \text{ kJ mol}^{-1} = 17.0 \text{ kJ mol}^{-1}$$

P9.4) Calculate $\Delta S_{\text{reaction}}^{\circ}$ for the reaction $\text{Ba}(\text{NO}_3)_2(\text{aq}) + 2\text{KCl}(\text{aq}) \rightarrow \text{BaCl}_2(\text{s}) + 2\text{KNO}_3(\text{aq})$.

$$\Delta S_{\text{reaction}}^{\circ} = S^{\circ}(\text{BaCl}_2, \text{s}) - S^{\circ}(\text{Ba}^{2+}, \text{aq}) - 2 \times S^{\circ}(\text{Cl}^-, \text{aq})$$

$$\Delta S_{\text{reaction}}^{\circ} = 123.7 \text{ J K}^{-1} \text{ mol}^{-1} - 9.6 \text{ J K}^{-1} \text{ mol}^{-1} - 2 \times 56.5 \text{ J K}^{-1} \text{ mol}^{-1} = 1.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

P9.5) Calculate $\Delta G_{\text{reaction}}^{\circ}$ in an aqueous solution for $\text{Cl}^-(\text{aq})$ using the Born model. The

radius of the Cl^- ion is $1.81 \times 10^{-10} \text{ m}$.

$$\Delta G_{\text{solvation}}^{\circ} = \frac{Z^2 e^2 N_A}{8\pi\epsilon_0 r} \left(\frac{1}{\epsilon_r} - 1 \right)$$

ϵ_r for water at 298 K is 78.5

For water at 25°C

$$\Delta G_{\text{solvation}}^{\circ} = -\frac{z^2}{(r/\text{pm})} \times (6.86 \times 10^4 \text{ kJ mol}^{-1})$$

Cl⁻ radius is 181 pm

$$\begin{aligned}\Delta G_{\text{solvation}}^{\circ} &= -\frac{1}{181} \times 6.86 \times 10^4 \text{ kJ mol}^{-1} \\ &= -379 \text{ kJ mol}^{-1}\end{aligned}$$

P9.8) Express a_{\pm} in terms of a_{+} and a_{-} for (a) Li₂CO₃, (b) CaCl₂, (c) Na₃PO₄, and (d) K₄Fe(CN)₆. Assume complete dissociation.

$$\text{a) Li}_2\text{CO}_3 \quad a_{\pm} = (a_{+}^{v_{+}} a_{-}^{v_{-}})^{\frac{1}{v}} = (a_{+}^2 a_{-})^{\frac{1}{3}}$$

$$\text{b) CaCl}_2 \quad a_{\pm} = (a_{+}^{v_{+}} a_{-}^{v_{-}})^{\frac{1}{v}} = (a_{+} a_{-}^2)^{\frac{1}{3}}$$

$$\text{c) Na}_3\text{PO}_4 \quad a_{\pm} = (a_{+}^{v_{+}} a_{-}^{v_{-}})^{\frac{1}{v}} = (a_{+}^3 a_{-})^{\frac{1}{4}}$$

$$\text{d) K}_4\text{Fe(CN)}_6 \quad a_{\pm} = (a_{+}^{v_{+}} a_{-}^{v_{-}})^{\frac{1}{v}} = (a_{+}^4 a_{-})^{\frac{1}{5}}$$

P9.9) Express γ_{\pm} in terms of γ_{+} and γ_{-} for (a) SrSO₄, (b) MgBr₂, (c) K₃PO₄, and (d) Ca(NO₃)₂. Assume complete dissociation.

$$\text{a) SrSO}_4 \quad \gamma_{\pm} = (\gamma_{+} \gamma_{-})^{\frac{1}{2}}$$

$$\text{b) MgBr}_2 \quad \gamma_{\pm} = (\gamma_{+} \gamma_{-}^2)^{\frac{1}{3}}$$

$$\text{c) K}_3\text{PO}_4 \quad \gamma_{\pm} = (\gamma_{+}^3 \gamma_{-})^{\frac{1}{4}}$$

$$\text{d) Ca(NO}_3)_2 \quad \gamma_{\pm} = (\gamma_{+} \gamma_{-}^2)^{\frac{1}{3}}$$

P9.14) Calculate the Debye–Hückel screening length $1/\kappa$ at 298 K in a 0.00100 *m* solution of NaCl.

For water, the screening length at 298 K in m^{-1} can be calculated as:

$$\kappa = 2.91 \times 10^{10} \sqrt{\frac{I/(\text{mol kg}^{-1})\rho_{\text{solvent}}}{\epsilon_r}} = 9.211 \times 10^8 \sqrt{\frac{(0.0010)0.997}{(78.54)}} \text{ m}^{-1} = 1.04 \times 10^8 \text{ m}^{-1}$$

$$\frac{1}{\kappa} = 9.65 \times 10^{-9} \text{ m} = \underline{9.65 \text{ nm}}$$