## Chapter 19 Problems: Real Solutions

1. A solution of solvent A and solute B has relative forces A-A, B-B < A-B. Are the activity coefficients for the solvent less than one or greater than one?

*Answer*: The A-B forces are favorable giving negative deviations from ideality and $\gamma_A < 1$ for the solvent. We always assume a Raoult's Law standard state for the solvent.

2. The partial pressure of acetone over a solution of acetone in ether at 30°C is 0.120 bar at $x_{acetone} = 0.200$. The partial pressure of ether at this same concentration is 0.713 bar. Calculate the activity coefficients for ether and acetone given that vapor pressure of pure acetone is 0.377 bar and of pure ether is 0.861 bar.

*Answer*: On a Raoult's Law standard state basis, Eqs. 19.1.5 and 19.1.7, with $P^*_{acetone} = 0.377$ bar and $P^*_{ether} = 0.861$ bar, the activities are:

$$a_A = P_A/P^*_A = 0.120/0.377 = 0.318 \qquad\qquad \gamma_A = a_A/x_A = 0.318/0.200 = 1.59$$

$$a_E = P_E/P^*_E = 0.713/0.861 = 0.828 \qquad\qquad \gamma_E = a_E/x_E = 0.828/0.800 = 1.04$$

3. The pure vapor pressure of substance A is 28.2 torr. The mole fraction of A in the vapor above a solution is 0.0432 while the mole fraction of A in the solution is 0.672. Calculate the activity coefficient for A in this solution on a Raoult's Law basis. The total vapor pressure is 760.0 torr.

*Answer*: The plan is to use Dalton's Law to find the partial vapor pressure of A and then $a_A = P_A/P^*_A$.
   Dalton's Law gives the partial vapor pressure of A in the gas phase:

$$P_A = y_A P = 0.0432 \ (760 \ torr) = 32.8 \ torr$$

On a Raoult's Law standard state basis, Eqs. 19.1.5 and 19.1.7 give:

$$a_A = P_A/P^*_A = 32.8/28.2 = 1.16 \qquad\qquad \gamma_A = a_A/x_A = 1.16/0.672 = 1.73$$

Vapor phase composition data is easily obtained using gas-phase UV or IR absorption spectroscopy or gas chromatography.

4. Under what circumstances can the activity coefficient of the solvent be greater than one, but in the same solution, the activity coefficient of the solute be less than one (or visa versa)?

*Answer*: The situation is likely when a Raoult's Law standard state is used for the solvent and a Henry's Law standard state is used for the solute. For example, if the solvent activity coefficient is greater than one, the solution has positive deviations from ideality, as in the figure below.
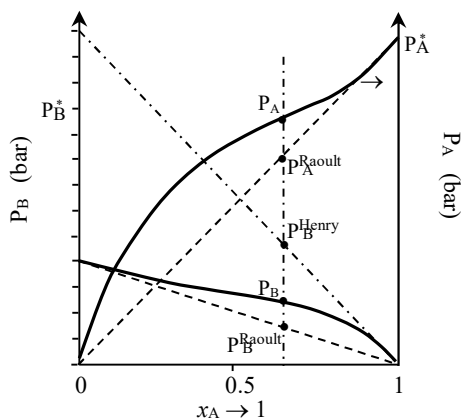


From the figure, for the solvent A, $P_A > P_A^{Raoult}$ giving $\gamma_A > 1$. For the solute B, $P_B < P_B^{Henry}$ giving $\gamma_B < 1$. At intermediate concentration, the behavior of <u>each</u> component is intermediate between Raoult's Law (for example, positive deviations) and Henry's Law (corresponding negative deviations).

<u>5</u>. (a). Calculate the activity coefficient for B at $x_B$ =0.667 with a Raoult's Law <u>and</u> a Henry's Law standard state. (b). Characterize the relative forces, $\varepsilon_{AB}$ versus $(\varepsilon_{AA} + \varepsilon_{BB})/2$. (c). Find the vapor pressure of pure B and the Henry's Law constant for B from the plot. Find the Raoult's Law and Henry's Law predictions for the vapor pressure of B at $x_B$ =0.667.
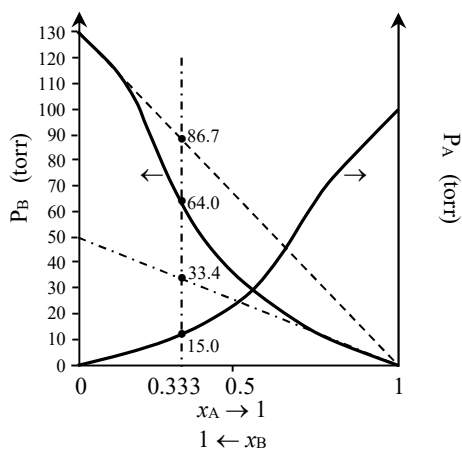


*Answer*: The plan is to note that $P_A$ = 15.0 torr, $P_B$ = 64.0 torr, $P_B^{Raoult}$ = 86.7 torr, and $P_B^{Henry}$ = 33.4 torr at $x_B = 1 - x_A = 0.667$.

(a). Using Eq. 19.1.9 for a Raoult's Law standard state gives:

$$\gamma_B = P_B/P_B^{Raoult} = 64.0/86.7 = 0.738$$

Using Eq. 19.1.16 for a Henry's Law standard state gives:

$$\gamma_B = P_B/P_B^{Henry} = 64.0/33.4 = 1.92$$

At this intermediate concentration, the behavior of B is intermediate between Raoult's Law (with negative deviations) and Henry's Law (with positive deviations), as expected.

(b). Because the vapor pressures are less than the Raoult's Law predictions, this solution shows negative deviations from ideality; $|\varepsilon_{AB}| > |(\varepsilon_{AA} + \varepsilon_{BB})/2|$.

   It is best to deal with magnitudes, since the forces are all attractive, $\varepsilon_{AB}, \varepsilon_{AA}, \varepsilon_{BB} < 0$. Using simple solution theory, noting Eq. 19.6.4, then $\varepsilon_{AB}$ is more favorable than $(\varepsilon_{AA} + \varepsilon_{BB})$ so that $\varepsilon_{AB} < (\varepsilon_{AA} + \varepsilon_{BB})/2$ gives $\Delta_{sol}G < 0$.

(c). Visually, the vapor pressure of B at $x_B = 1$ is $P_B^* = 130.$ torr. The Raoult's Law prediction is:

$$P_B^{Raoult} = x_B\, P_B^* = 0.667(130.\text{ torr}) = 86.7\text{ torr} \qquad \text{as shown in the figure.}$$

Visually, from the intersection of the Henry's Law line at $x_B = 1$, $k_{H,B} = 50.0$ torr. The Henry's Law prediction is:

$$P_B^{Henry} = x_B\, k_{H,B} = 0.667(50.0\text{ torr}) = 33.4\text{ torr} \qquad \text{as shown in the figure.}$$

6. The partial vapor pressure of heptane above a solution of heptane and 1-bromobutane was 0.0885 bar for a heptane mole fraction of 0.4164. The vapor pressure of pure heptane is 0.187 bar. The Henry's Law constant for heptane was determined in Problem 18.13 to be $k_{H}$,heptane = 0.265 bar. Calculate the activity coefficients on both a Raoult's Law and Henry's Law basis.

*Answer*:  On a Raoult's Law standard state basis, Eqs. 19.1.5 and 19.1.7 give:

$$a_A = P_A/p_A^* = 0.0885/0.187 = 0.473 \qquad\qquad \gamma_A = {}^{a_A}\!/_{x_A} = 0.473/0.4164 = 1.14$$

The solution has positive deviations from ideality, overall. On a Henry's Law standard state basis, using Eq. 19.1.14 for heptane as the solute B:

$$a_B = {}^{P_B}\!/_{k_{H,B}} = 0.0885/0.265 = 0.334 \qquad\qquad \gamma_B = {}^{a_B}\!/_{x_B} = 0.334/0.4164 = 0.802$$

The vapor pressure of heptane is less than that predicted from the dilute solution environment. The behavior of heptane is intermediate between Raoult's Law (positive deviations) and Henry's Law (negative deviations) as you might expect since the solution is intermediate in concentration.

7. The freezing point depression for a 10.00 % by weight solution of acetone in water is 3.29°C. Calculate the activity, activity coefficient, and osmotic coefficient. Calculate the osmotic pressure of the solution at 25°C assuming the activity coefficient and osmotic coefficient are constant over the given temperature range and the partial molar volume of the solvent is the pure molar volume. The molar mass of acetone is 58.05 g mol$^{-1}$. The enthalpy of fusion of water is 6.008 kJ mol$^{-1}$.

*Answer*: We follow Example 19.1.2. The mole fraction of the solvent, assuming 100.0 g of solution, is:

$$x_A = \frac{90.00 \text{ g}/\mathfrak{M}_A}{90.00 \text{ g}/\mathfrak{M}_A + 10.00 \text{ g}/\mathfrak{M}_B} = \frac{90.0 \text{ g}/18.0153 \text{ g mol}^{-1}}{90.0 \text{ g}/18.0153 \text{ g mol}^{-1} + 10.00 \text{ g}/58.05 \text{ g mol}^{-1}} =$$

0.96667

The molality of the solute, assuming 100.0 g of solution, is:

$$m_B = \frac{10.00 \text{ g}/\mathfrak{M}_B}{90.00 \text{ g } (1 \text{ kg}/1000 \text{ g})} = \frac{10.0 \text{ g}/58.05 \text{ g mol}^{-1}}{90.0 \text{ g } (1 \text{ kg}/1000 \text{ g})} = 1.914 \text{ m}$$

Using Eq. 19.1.4 with the melting point of the solution, T = 273.15 K – 3.29 K = 269.86 K, and assuming a constant enthalpy of fusion:

$$\ln a_A = -\frac{\Delta_{fus}H_A}{R}\left(\frac{1}{T} - \frac{1}{T_m^*}\right) = -\frac{6.008\text{x}10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\left(\frac{1}{269.86 \text{ K}} - \frac{1}{273.15 \text{ K}}\right) = -0.032252$$

$$a_A = 0.96826$$

The activity coefficient is $\gamma_A = a_A/x_A = 0.96826/0.96667 = 1.00164$.
The osmotic coefficient is given by Eq. 19.1.20 or directly using Eq. 19.1.23:

$$\phi = -(55.51 \text{ mol kg}^{-1} \ln a_A)/m_B = \frac{\Delta_{fus}H_A}{R \, m_B/(55.51 \text{ mol kg}^{-1})}\left(\frac{1}{T} - \frac{1}{T_m^*}\right)$$

$$= -55.51(-0.032252)/1.914 \text{ m}$$

$$= 0.93538$$

The osmotic coefficient has a larger difference from one than the activity coefficient, as designed.

The pure molar volume of water is $V_A^* = \mathfrak{M}_A/d_{A,pure} = 18.069 \text{ mL} = 0.018069 \text{ L}$. The osmotic pressure can be calculated from Eq. 18.4.23[†] with the activity substituted or Eq. 19.1.24 using the osmotic coefficient:

$$\pi \, \bar{V}_A = -RT \ln a_A = -0.083145 \text{ bar L K}^{-1} \text{ mol}^{-1}(298.15 \text{ K})(-0.032252) \quad \text{giving}$$
$$\pi = 44.25 \text{ bar} \qquad \text{alternatively:}$$

$$\pi \, \bar{V}_A = RT \, \phi \, m_B/(55.51 \text{ mol kg}^{-1}) \qquad \text{giving} \quad \pi = 44.25 \text{ bar}$$

The ideal prediction using Eq. 18.4.26[†] is 46.5 bar, which corresponds to a 5% error neglecting the activity coefficient. Electrolyte solutions show much larger deviations from ideality.


<u>8</u>. The freezing point depression for a 10.00 % by weight solution of $MgCl_2$ in water is 7.91°C. Calculate the activity, activity coefficient, and osmotic coefficient. Calculate the osmotic pressure of the solution at 25°C assuming the activity coefficient and osmotic coefficient are constant over the given temperature range and the partial molar volume of the solvent is the pure molar volume. The molar mass of $MgCl_2$ is 95.23 g mol$^{-1}$. The enthalpy of fusion of water is 6.008 kJ mol$^{-1}$.

*Answer*: We follow Example 19.1.2 with $m_B = \nu m_{MgCl_2}$ and $\nu = 3$. The mole fraction of the solvent, assuming 100.0 g of solution, is:

$$x_A = \frac{90.00 \text{ g}/\mathfrak{M}_A}{90.00 \text{ g}/\mathfrak{M}_A + 3(10.00 \text{ g}/\mathfrak{M}_B)} = \frac{90.0 \text{ g}/18.0153 \text{ g mol}^{-1}}{90.0 \text{ g}/18.0153 \text{ g mol}^{-1} + 3(10.00 \text{ g}/95.23 \text{ g mol}^{-1})}$$
$$= 0.94068$$

The molality of the solute particles, assuming 100.0 g of solution, is:

$$m_B = 3\left(\frac{10.00 \text{ g}/\mathfrak{M}_B}{90.00 \text{ g } (1 \text{ kg}/1000 \text{ g})}\right) = 3\left(\frac{10.0 \text{ g}/95.23 \text{ g mol}^{-1}}{90.0 \text{ g } (1 \text{ kg}/1000 \text{ g})}\right) = 3.5003 \text{ m}$$

Using Eq. 19.1.4 with the melting point of the solution, $T = 273.15 \text{ K} - 7.91 \text{ K} = 265.24 \text{ K}$, and assuming a constant enthalpy of fusion:

$$\ln a_A = -\frac{\Delta_{fus}H_A}{R}\left(\frac{1}{T} - \frac{1}{T_m^*}\right) = -\frac{6.008 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\left(\frac{1}{265.24 \text{ K}} - \frac{1}{273.15 \text{ K}}\right) = -0.078891$$
$$a_A = 0.92414$$

The activity coefficient is $\gamma_A = a_A/x_A = 0.92414/0.94068 = 0.98242$.
The osmotic coefficient is given by Eq. 19.1.20 or directly using Eq. 19.1.23:

$$\phi = -(55.51 \text{ mol kg}^{-1} \ln a_A)/m_B = \frac{\Delta_{fus}H_A}{R \, m_B/(55.51 \text{ mol kg}^{-1})}\left(\frac{1}{T} - \frac{1}{T_m^*}\right)$$
$$= -55.51(-0.078891)/3.5003 \text{ m}$$
$$= 1.2511$$

The osmotic coefficient has a larger difference from one than the activity coefficient, as designed.

The pure molar volume of water is $V_A^* = \mathfrak{M}_A/d_{A,pure} = 18.069 \text{ mL} = 0.018069 \text{ L}$. The osmotic pressure can be calculated from Eq. 18.4.23[†] with the activity substituted or Eq. 19.1.24 using the osmotic coefficient:

$$\pi \, \overline{V}_A = -RT \ln a_A = -0.083145 \text{ bar L K}^{-1} \text{ mol}^{-1}(298.15 \text{ K})(-0.078891) \qquad \pi = 108.2 \text{ bar}$$
$$\pi \, \overline{V}_A = RT \, \phi \, m_B/(55.51 \text{ mol kg}^{-1}) \qquad\qquad\qquad \pi = 108.2 \text{ bar}$$

The ideal prediction using Eq. 18.4.26[†] is 83.9 bar, which corresponds to a 22% error neglecting the activity coefficient.

<u>9</u>. Eqs. 18.4.8[†], 18.4.15[†], and 19.1.4 assume the phase transition enthalpy of the solvent is constant. For careful determinations of the activity with large freezing point changes, the temperature dependence of the enthalpy of fusion should be taken into account: $\Delta_{fus}H_A(T) = \Delta_{fus}H_A(T_A^*) + \Delta_{fus}C_{p,A}(T - T_A^*)$. Use this temperature dependence to find a better approximation to Eq. 19.1.4 by completing the following steps.
(a). At equilibrium for a solid-liquid phase transition, the equivalence of the chemical potentials gives $\mu_A^*(s) = \mu_A^*(l) + RT \ln x_A$, which is the analog to Eq. 18.4.2[†]. Convert the last equation into the corresponding equation for a real solution. The Gibbs energy of fusion for the pure solvent is $\Delta_{fus}G_A = \mu_A^*(l) - \mu_A^*(s)$. Use the Gibbs-Helmholtz relationship, Eq. 16.3.12, to show:

$$\left(\frac{\partial \ln a_A}{\partial T}\right)_P = \frac{\Delta_{fus}H_A}{RT^2}$$

(b). Use the temperature dependence of the enthalpy to integrate this last equation from $T_A^*$ to T. Note that $a_A = 1$ and $\ln a_A = 0$ at the pure standard melting point $T_A^*$. The result is:

$$\ln a_A = -\left(\frac{\Delta_{fus}H_A(T_A^*) - \Delta_{fus}C_{p,A}\, T_A^*}{R}\right)\left(\frac{1}{T} - \frac{1}{T_A^*}\right) + \frac{\Delta_{fus}C_{p,A}}{R}\,\ln(T/T_A^*)$$

*Answer*: (a). To convert the ideal solution equation to a real solution, we simply replace $x_A$ with $a_A$. The difference in the chemical potentials gives: $\Delta_{fus}G_A = \mu_A^*(l) - \mu_A^*(s) = -\,RT \ln a_A$. Then the Gibbs-Helmholtz expression, Eq. 16.3.12, gives:

$$\left(\frac{\partial\left(\frac{\Delta_{fus}G_A}{T}\right)}{\partial T}\right)_P = -\frac{\Delta_{fus}H_A}{T^2}$$

Since $\ln a_A = -\Delta_{fus}G_A/RT$, dividing both sides of the last equation by $-R$ gives:

$$\left(\frac{\partial \ln a_A}{\partial T}\right)_P = \frac{\Delta_{fus}H_A}{RT^2}$$

(b). Integrating this last equation from $T_A^*$ to T and using $\Delta_{fus}H_A(T) = \Delta_{fus}H_A(T_A^*) + \Delta_{fus}C_{p,A}\,(T - T_A^*)$:

$$\int_{\ln a_A(T_A^*)}^{\ln a_A(T)} d \ln a_A = \int_{T_A^*}^{T} \frac{\Delta_{fus}H_A(T_A^*)}{RT^2}\,dT + \int_{T_A^*}^{T} \frac{\Delta_{fus}C_{p,A}}{RT}\,dT - \int_{T_A^*}^{T} \frac{\Delta_{fus}C_{p,A}\, T_A^*}{RT^2}\,dT$$

Since at the pure standard melting point, $a_A = 1$ and $\ln a_A = 0$, the integral on the left is just $\ln a_A$ at the final temperature. The first integral on the right gives the standard form of the equation, Eq. 18.4.15[†]. The remaining two terms are the corrections:

$$\ln a_A = -\frac{\Delta_{fus}H_A(T_A^*)}{R}\left(\frac{1}{T} - \frac{1}{T_A^*}\right) + \frac{\Delta_{fus}C_{p,A}}{RT}\,\ln(T/T_A^*) + \frac{\Delta_{fus}C_{p,A}\, T_A^*}{R}\left(\frac{1}{T} - \frac{1}{T_A^*}\right)$$

Combining the first and last terms on the right gives the final result:

$$\ln a_A = -\left(\frac{\Delta_{fus}H_A(T_A^*) - \Delta_{fus}C_{p,A}\, T_A^*}{R}\right)\left(\frac{1}{T} - \frac{1}{T_A^*}\right) + \frac{\Delta_{fus}C_{p,A}}{R}\,\ln(T/T_A^*)$$

For water, $\Delta_{fus}H_A(T_A^*) = 6.008 \pm 0.004$ kJ mol$^{-1}$, $T_A^* = 273.15$ K, and $\Delta_{fus}C_{p,A} = 38.1 \pm 0.2$ J K$^{-1}$ mol$^{-1}$. Substituting these values into equation 13 gives:

$$\ln a_A = 529.16\left(\frac{1}{T} - \frac{1}{273.15}\right) + 4.583\,\ln(T/273.15)$$

So the result is actually easy to use.

<u>10</u>.  Freezing point depression and boiling point elevation are used to determine the activity of the solvent at the measured phase transition temperature for the solution. We usually need to know the activity at 25°C. Find an expression for the temperature dependence of the activity of a substance by completing the following steps. (a). The chemical potential of the solvent in solution is $\mu_A(x_A) =$
$\mu_A^*(l) + RT \ln a_A$, Eq. 19.1.3. The partial molar Gibbs energy of solution for the solvent is $\Delta_{sol}\overline{G}_A = \mu_A(x_A) - \mu_A^*(l)$. Use the Gibbs-Helmholtz relationship, Eq. 16.3.12, to show:

$$\left(\frac{\partial \ln a_A}{\partial T}\right)_P = -\frac{\Delta_{sol}\overline{H}_A}{RT^2}$$

where $\Delta_{sol}\overline{H}_A$ is the partial molar enthalpy of solution. (b). Integrate this equation from $T_1$ to $T_2$. Assume the enthalpy of solution is constant over the temperature range. Show that the result is:

$$\ln\left(\frac{a_A(T_2)}{a_A(T_1)}\right) = -\left(\frac{\Delta_{sol}\overline{H}_A}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

*Answer*:  The plan is to use the same approach as the last problem, which is also based on the Gibbs-Helmholtz equation.
(a). The difference in the chemical potentials gives: $\Delta_{fus}\overline{G}_A = \mu_A(x_A) - \mu_A^*(l) = RT \ln a_A$. Then the Gibbs-Helmholtz expression, Eq. 16.3.12, gives:

$$\left(\frac{\partial\left(\frac{\Delta_{sol}\overline{G}_A}{T}\right)}{\partial T}\right)_P = -\frac{\Delta_{sol}\overline{H}_A}{T^2}$$

Since $\ln a_A = \Delta_{sol}\overline{G}_A/RT$, dividing both sides of the last equation by R gives:

$$\left(\frac{\partial \ln a_A}{\partial T}\right)_P = -\frac{\Delta_{sol}\overline{H}_A}{RT^2}$$

(b). Integrating this last equation from $T_1$ to $T_2$ and assuming $\Delta_{fus}\overline{H}_A$ is independent of temperature gives:

$$\int_{\ln a_A(T_1)}^{\ln a_A(T_2)} d \ln a_A = -\int_{T_1}^{T_2} \frac{\Delta_{sol}\overline{H}_A}{RT^2} dT$$

$$\ln\left(\frac{a_A(T_2)}{a_A(T_1)}\right) = \left(\frac{\Delta_{sol}\overline{H}_A}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

For an ideal solution $\Delta_{sol}\overline{H}_A$ is zero, and the activity is then temperature independent. For real solutions, for narrow temperature ranges, the change in activity is often small. For large changes in temperature correction terms may be added to take into account the temperature dependence of the enthalpy of solvation, analogous to the approach in the last problem.

11. The osmotic coefficient for aqueous *n*-propanol solutions is: $\phi - 1 = a\, m_B^3 + b\, m_B^2 + c\, m_B$, with: $a = -4.73$ kg$^3$ mol$^{-3}$, $b = 2.21$ kg$^2$ mol$^{-2}$, and $c = -0.365$ kg mol$^{-1}$ at 0°C, where $m_B$ is the molality of *n*-propanol. Determine the activity coefficients for *n*-propanol and water at 0.100 m.

*Answer*: Doing the integral in Eq. 19.1.26 with the cubic polynomial gives:

$$\ln{}^m\gamma_B = \phi(m) - 1 + \int_0^m \left(\frac{a\, m_B^2 + b\, m_B}{m_B}\right) d\, m_B = \phi(m) - 1 + \frac{a}{3} m^3 + \frac{b}{2} m^2 + c\, m$$

For a 0.100 m solution: $\phi(m) - 1 = -4.73\, m^3 + 2.21\, m^2 + (-0.365)\, m = -0.191_3$

$\ln{}^m\gamma_B = (-0.191_3) + (-4.73)\, m^3/3 + 2.21\, m^2/2 + (-0.365)\, m = -0.04616$

giving ${}^m\gamma_B = 0.955$ on a molal basis. For water, using Eq. 19.1.21, the activity is:

$\ln a_A = -\phi\, m_B/55.51$ mol kg$^{-1} = (1 - 0.1913)\, 0.100$ mol kg$^{-1}/55.51$ mol kg$^{-1} = 1.457 \times 10^{-3}$
$a_A = 1.001$

The mole fractions for *n*-propanol and water are given by Eq. 2.2.13:

$$x_B = \frac{0.100 \text{ mol kg}^{-1} (1 \text{ kg})}{55.51 \text{ mol} + 0.100 \text{ mol kg}^{-1} (1 \text{ kg})} = 1.798_2 \times 10^{-3} \qquad \text{and } x_A = 1 - x_B = 0.99820$$

giving the activity coefficient for water as ${}^x\gamma_A = a_A/x_A = 1.001/0.99820 = 1.003$.

12. Find the overall solution activity in terms of the mean ionic activity coefficient and the solution molality, m, for: (a). $KNO_3$, (b). $CaCl_2$, (c). $LaCl_3$, (d). $CuSO_4$.

*Answer*: (a). Using Eq. 19.4.9, $m_+ = m_- = m$ for a 1:1 electrolyte:

$$a(KNO_3) = a_+\, a_- = \left(\frac{\gamma_\pm^2\, m_+\, m_-}{m^{\circ 2}}\right) = \left(\frac{\gamma_\pm^2\, m^2}{m^{\circ 2}}\right) = \gamma_\pm^2\, (m/m^\circ)^2$$

(b). Using Eq. 19.4.16, $m_+ = m_{Ca2+} = m$ and $m_- = m_{Cl-} = 2m$ for a 1:2 electrolyte:

$$a(CaCl_2) = a_{Ca2+}\, a_{Cl-}^2 = \left(\frac{\gamma_\pm^3\, (m)\, (2m)^2}{m^{\circ 3}}\right) = 4\, \gamma_\pm^3\, (m/m^\circ)^3$$

(c). For $LaCl_3$, $m_+ = m_{La3+} = m$ and $m_- = m_{Cl-} = 3m$ for a 1:3 electrolyte:

$$a(LaCl_3) = a_{La3+}\, a_{Cl-}^3 = \left(\frac{\gamma_\pm^4\, (m)\, (3m)^3}{m^{\circ 4}}\right) = 27\, \gamma_\pm^4\, (m/m^\circ)^4$$

(d). Using Eq. 19.4.9 for $CuSO_4$, $m_+ = m_- = m$ for a 1:1 electrolyte:

$$a(CuSO_4) = a_+\, a_- = \left(\frac{\gamma_\pm^2\, m_+\, m_-}{m^{\circ 2}}\right) = \left(\frac{\gamma_\pm^2\, m^2}{m^{\circ 2}}\right) = \gamma_\pm^2\, (m/m^\circ)^2$$

13. Find the ionic strength in terms of the molality, m, for the following strong electrolytes dissolved in pure water: (a). $CaCl_2$, (b). $LaCl_3$, (c). $CuSO_4$ (neglect any hydrolysis).

*Answer*:  Using Eq. 19.4.22:

(a). For $CaCl_2$, $z_+ = 2$, $z_- = -1$, $m_{Ca2+} = m$ and $m_{Cl-} = 2$ m:

$$I = \frac{1}{2} \sum z_i^2 \frac{m_i}{m^\circ} = \frac{1}{2} [(2)^2 m + (-1)^2 (2m)]/m^\circ = 3 \ m/m^\circ$$

(b). For $LaCl_3$, $z_+ = 3$, $z_- = -1$, $m_{La3+} = m$ and $m_{Cl-} = 3$ m:

$$I = \frac{1}{2} \sum z_i^2 \frac{m_i}{m^\circ} = \frac{1}{2} [(3)^2 m + (-1)^2 (3m)]/m^\circ = 6 \ m/m^\circ$$

(b). For $CuSO_4$, $z_+ = 2$, $z_- = -2$, $m_{Cu2+} = m$ and $m_{SO42-} = m$:

$$I = \frac{1}{2} \sum z_i^2 \frac{m_i}{m^\circ} = \frac{1}{2} [(2)^2 m + (-2)^2 (m)]/m^\circ = 4 \ m/m^\circ$$

Why did we specify that hydrolysis should be neglected? The sulfate ion can hydrolyze by:

$$SO_4^{2-} + H_2O \rightleftarrows HSO_4^- + OH^- \qquad\qquad K_b = K_w/K_{a,2} = 9.71 \times 10^{-13}$$

However, this equilibrium won't have a significant effect on the ionic strength. The hydrolysis will make the solution slightly basic, however.

14. Write the solubility product equilibrium expressions for the sparingly soluble salts: (a). $Ag_2CrO_4$, (b). $Cr(OH)_3$, (c). $Ca_3(PO_4)_2$.

*Answer*:  Let $m_s$ be the moles of salt dissolved per kg of solvent. Using Eq. 19.4.16:
(a). For $Ag_2CrO_4$, $m_+ = m_{Ag+} = 2m_s$ and $m_- = m_{CrO42-} = m_s$ for a 2:1 electrolyte:

$$K_{sp} = (a_{Ag+})^2 \ a_{CrO4^{2-}} = \left( \frac{\gamma_\pm^3 (2m_s)^2 (m_s)}{m^{\circ3}} \right) = 4 \ \gamma_\pm^3 \ (m_s/m^\circ)^3$$

(b). For $Cr(OH)_3$, $m_+ = m_{Cr3+} = m_s$ and $m_- = m_{OH-} = 3m_s$ for a 1:3 electrolyte:

$$K_{sp} = a_{Cr3+} \ a_{OH^-}^3 = \left( \frac{\gamma_\pm^4 (m_s) (3m_s)^3}{m^{\circ4}} \right) = 27 \ \gamma_\pm^4 \ (m_s/m^\circ)^4$$

(c). For $Ca_3(PO_4)_2$, $m_+ = m_{Ca2+} = 3m_s$ and $m_- = m_{PO43-} = 2m_s$ for a 3:2 electrolyte:

$$K_{sp} = (a_{Ca2+})^3 \ (a_{PO43-})^2 = \left( \frac{\gamma_\pm^5 (3m_s)^3 (2m_s)^2}{m^{\circ5}} \right) = 108 \ \gamma_\pm^5 \ (m_s/m^\circ)^5$$

15. Calculate the mean ionic activity coefficient for a 0.100 m aqueous solution of $CaCl_2$ at 25°C using the Debye-Hückel approximation.

*Answer*: The ionic strength for $CaCl_2$ is given in Problem 2a as $I = 3$ m/m°. For the given concentration:

$$I = 3 \text{ m/m}° = 0.300$$

For $CaCl_2$, $z_+ = 2$ and $z_- = -1$. Using Eq. 19.4.23:

$$\ln \gamma_\pm = -1.171 \, |z_+ \, z_-| \, I^{\frac{1}{2}} = -1.171 \, |(2)(-1)| \, (0.300)^{\frac{1}{2}} = -1.2828$$

or $\quad \log \gamma_\pm = -0.509 \, |z_+ \, z_-| \, I^{\frac{1}{2}} = -0.509 \, |(2)(-1)| \, (0.300)^{\frac{1}{2}} = -0.55758$

giving $\gamma_\pm = 0.277$.

16. Mercury pollution is an increasing problem in northern lakes. The source of the mercury is primarily coal combustion. Mercury compounds can be carried long distances by atmospheric aerosols. Calculate the solubility of mercury(I)chloride, $Hg_2Cl_2$, in pure water and in 0.0100 m $KNO_3$, $K_{sp} = 1.2 \times 10^{-18}$. Remember that the dissociation is given by:

$$Hg_2Cl_2 \text{ (s)} \rightleftarrows Hg_2^{2+} + 2 \, Cl^-$$
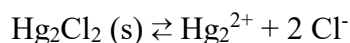
*Answer*: For $Hg_2^{2+}$, $z_+ = 2$, and for $Cl^-$ $z_- = -1$. For this 1:2 electrolyte, $m_+ = m_{Hg2^{2+}} = m$ and $m_- = m_{Cl^-} = 2m$. In pure water the ionic strength is given by:

$$I = \frac{1}{2} \sum z_i^2 \frac{m_i}{m°} = \frac{1}{2} \, [(2)^2 \, m + (-1)^2 \, (2m)]/m° = 3 \text{ m/m}°$$

However, we don't know the concentration of dissolved $Hg_2Cl_2$. We can estimate the solubility by neglecting the activity coefficients:

$$K_{sp} \approx [Hg_2^{2+}][Cl^-]^2 = (m_s/m°)(2m_s/m°)^2 = 4 \, m_s^3$$

giving $m_s/m° \approx (1.2 \times 10^{-18}/4)^{1/3} \approx 6.694 \times 10^{-7}$

With this approximate concentration, the ionic strength is $I = 3$ m/m° $= 2.008 \times 10^{-6}$. Using the Debye-Hückel approximation gives the mean ionic activity coefficient:

$$\ln \gamma_\pm = -1.171 \, |z_+ \, z_-| \, I^{\frac{1}{2}} = -1.171 \, |(2)(-1)| \, (2.008 \times 10^{-6})^{\frac{1}{2}} = -3.319 \times 10^{-3}$$

or $\quad \log \gamma_\pm = -0.509 \, |z_+ \, z_-| \, I^{\frac{1}{2}} = -0.509 \, |(2)(-1)| \, (2.008 \times 10^{-6})^{\frac{1}{2}} = -1.443 \times 10^{-3}$

giving $\gamma_\pm = 0.997$. The solubility in pure water is then:

$$K_{sp} = (a_{Hg2^{2+}}) \, (a_{Cl^-})^2 = \left( \frac{\gamma_\pm^3 (m_s) \, (2m_s)^2}{m°^3} \right) = 4 \, \gamma_\pm^3 \, (m_s/m°)^3$$

giving $m_s = m° \, (1.2 \times 10^{-18}/4/(0.997)^3)^{1/3} = 6.714 \times 10^{-7}$ m

The effect of the non-ideality is well within the limits of the experimental uncertainty. However, with the non-participating electrolyte, the ionic strength will be dominated by the 0.0100 m $KNO_3$:

$$I = \tfrac{1}{2}\,[(2)^2\,m_{Hg_{2}^{2+}} + (-1)^2\,(2m_{Cl^-}) + (1)^2\,m_{K^+} + (-1)^2\,m_{NO_3^-}]/m° = 0.0100$$
$$I = \tfrac{1}{2}\,[(2)^2\,6.7\times10^{-7} + (-1)^2\,2\,(6.7\times10^{-7}) + (1)^2\,0.0100 + (-1)^2\,0.0100]/m° = 0.0100$$

[For a 1:1, uni-positive-uni-positive electrolyte the ionic strength is equal to the molality.] The mean ionic activity coefficient in 0.0100 m $KNO_3$ is then:

$$\ln \gamma_\pm = -1.171\,|z_+\,z_-|\,I^{\frac{1}{2}} = -1.171\,|(2)(-1)|\,(0.0100)^{\frac{1}{2}} = -0.2342$$
or      $$\log \gamma_\pm = -0.509\,|z_+\,z_-|\,I^{\frac{1}{2}} = -0.509\,|(2)(-1)|\,(0.0100)^{\frac{1}{2}} = -0.1018$$

giving $\gamma_\pm = 0.791$. The solubility in 0.0100 m $KNO_3$ is then:

$$m_s = m°\,(1.2\times10^{-18}/4/(0.791)^3)^{1/3} = 8.46\times10^{-7}\ m$$

<u>17</u>. Write the acid dissociation equilibrium expressions in terms of the concentration of the undissociated acid, $m_{HA}$, the $H^+$ concentration, $m_{H^+}$, and the mean ionic activity coefficient, for the weak acids: (a). $CH_3COOH$, acetic acid (HOAc),  (b). $H_2S$ (for the first dissociation only).

*Answers*:  The plan is to write the expression as you would for General Chemistry with $[H^+]$, $[A^-]$, and $[HA]$ and then replace the concentrations by activities. The activity based acid dissociation constant is $K_a$. The acid dissociation constant written in terms of concentrations is called the effective equilibrium constant, $K_{a,eff}$, which is ionic strength dependent.

(a). For the dissociation:  $HOAc\ (aq) \rightleftarrows H^+ + OAc^-$ , $m_{H^+} = m_+ = m_-$ :

$$K_{a,eff} = \frac{[H^+]\,[OAc^-]}{[HOAc]} \qquad K_a = \frac{(a_{H^+})(a_{OAc^-})}{a_{HOAc}} = \frac{\gamma_\pm^2\,(m_+/m°)(m_-/m°)}{m_{HA}/m°} = \frac{\gamma_\pm^2\,(m_{H^+}/m°)^2}{m_{HA}/m°}$$

Note that if the analytical concentration of the weak acid is $m_{HA,o}$ then at equilibrium $m_{HA} = m_{HA,o} - m_{H^+}$. The final $pH = -\log a_{H^+} = -\log(\gamma_\pm\,m_{H^+})$.

(b) For the dissociation:  $H_2S\ (aq) \rightleftarrows H^+ + HS^-$ , again $m_{H^+} = m_+ = m_-$ (neglecting further dissociation):

$$K_{a,eff} = \frac{[H^+]\,[HS^-]}{[H_2S]} \qquad K_{a,1} = \frac{(a_{H^+})(a_{HS^-})}{a_{H_2S}} = \frac{\gamma_\pm^2\,(m_+/m°)(m_-/m°)}{m_{H_2A}/m°} = \frac{\gamma_\pm^2\,(m_{H^+}/m°)^2}{m_{H_2A}/m°}$$

If the analytical concentration of the weak acid is $m_{H_2A,o}$ then at equilibrium $m_{H_2A} = m_{H_2A,o} - m_{H^+}$.

<u>18</u>.  Using Eqs. 19.5.12, 19.5.18 and 19.5.19, derive Eq. 19.5.20.

*Answer:*  The charge density is written in terms of $\kappa$ by substituting Eq. 19.5.19 into Eq. 19.5.18:

$$\rho_i(r) = -\frac{\phi_i(r)e^2}{kT} \sum_{j=1}^{s} z_j^2 \frac{N_j}{V} = -\varepsilon_r\varepsilon_0\, \phi_i(r)\, \kappa^2$$

Dividing by $\varepsilon(r) = \varepsilon_0\varepsilon_r$ for a uniform permittivity gives:

$$\frac{\rho_i(r)}{\varepsilon(r)} = -\kappa^2\, \phi_i(r)$$

and then substitution into Eq. 19.5.12 gives:

$$\frac{1}{r}\frac{\partial^2(r\,\phi_i(r))}{\partial r^2} = \kappa^2\, \phi_i(r)$$

Multiplying both sides of this equation by r gives Eq. 19.5.20:

$$\frac{\partial^2(r\,\phi_i(r))}{\partial r^2} = \kappa^2\,(r\,\phi_i(r))$$

<u>19</u>.  Show that $\phi_i(r) = \dfrac{C}{r}\, e^{-\kappa r}$ is the solution to the Eq. 19.5.20.

*Answer:*  With $(r\,\phi_i(r)) = C\, e^{-\kappa r}$, taking the second derivative on the left-hand side of Eq. 19.5.20 gives:

$$\frac{\partial^2(r\,\phi_i(r))}{\partial r^2} = \frac{\partial^2(C\, e^{-\kappa r})}{\partial r^2} = \kappa^2\, C\, e^{-\kappa r} = \kappa^2\,(r\,\phi_i(r))$$

The result is the right-hand side of Eq. 19.5.20, proving that $\phi_i(r)$ is a solution to the equation.

<u>20</u>.  (a). Starting with Eq. 19.5.19, for an aqueous solution containing one pure electrolyte, show that:

$$\kappa^2 = \frac{e^2\ 1000\ \text{L m}^{-3}\ d_0\ N_A\ m^\circ}{\varepsilon_r\varepsilon_0\, kT}\left(z_+^2\frac{m_+}{m^\circ} + z_-^2\frac{m_-}{m^\circ}\right) \qquad\qquad \text{P19.20.1}$$

(b).  Given the definition of ionic strength in Eq. 19.5.25, show from Eq. P19.20.1 that:

$$\kappa = \sqrt{\frac{2\ e^2\ 1000\ \text{L m}^{-3}\ d_0\ N_A\ m^\circ}{\varepsilon_r\varepsilon_0\, kT}}\ I^{1/2} \qquad\qquad \text{P19.20.2}$$

(c).  Starting with Eq. P19.20.2 and $r_D = 1/\kappa$, prove that Eq. 19.5.7 gives the Debye length for aqueous solutions of unipositive-uninegative electrolytes, at concentration m molal, at 298.15 K. In Eq. 19.5.7 the constant is given as 305 pm; in your answer give the constant to at least four significant figures.

(d).  Find the Debye length for a 0.0100 m and 0.100 m solution of KCl.

*Answer*: (a). From Eq. 19.5.23, solving for the concentration ratio:

$$\frac{N_j}{V} = 1000 \text{ L m}^{-3} \text{ d } N_A \text{ m}_j$$

where d is the density of the solution. In dilute solution, the density of the solution is approximately the density of the pure solvent, $d \approx d_o$. The standard state concentration is introduced by multiplying and dividing each term in the concentration sum by m°. Substituting for the cationic and anionic terms for $N_+/V$ and $N_-/V$ in in terms of the molalities gives Eq. P19.20.1.

(b). From the definition of ionic strength, $(z_+^2 \text{ m}_+/m° + z_-^2 \text{ m}_-/m°) = 2I$, then taking the square root of Eq. P19.20.1 gives Eq. P19.20.2.

(c). The Debye length is $r_D = 1/\kappa$. For a unipositive-uninegative electrolyte $I = m/m°$. Using $e = 1.602177 \times 10^{-19}$ C, $d = 0.997048$ g/cm³, 1 g/cm³ = 1 kg L⁻¹, $\varepsilon_o = 8.85419 \times 10^{-12}$ J⁻¹C²m⁻¹, $\varepsilon_r = 78.54$, $k = 1.38066 \times 10^{-23}$ J K⁻¹, and $T = 298.15$K in Eq. P19.20.2 gives:

$$r_D = 1/\kappa = \frac{304.73 \text{ pm}}{(m/m°)^{1/2}}$$

(d). At $m = 0.0100$ m, $r_D = 3050$ pm = 30.5 Å while at 0.100 m, $r_D = 964$. pm = 9.64 Å.

<u>21</u>. Taking the limit as $r \to 0$ of Eq. 19.5.27 using l'Hôpital's rule, prove that the electric potential at the central ion caused by the ionic atmosphere is given by Eq. 19.5.28.

<u>22</u>. Plot the screened Coulomb potential for a 0.0100 m and 0.100 m NaCl solution.

<u>23</u>. (a). Show that the charge density for the screened Coulomb potential can be written in terms of $\kappa$ as:

$$\rho_i(r) = -\frac{q_i \kappa^2}{4\pi r} e^{-\kappa r}$$

(b). Find the maximum of the radial probability distribution for the charge density, $4\pi r^2 \rho_i$, in terms of $\kappa$.

*Answer*: The charge density is written in terms of $\kappa$ by substituting Eq. 19.5.19 into Eq. 19.5.18:

$$\rho_i(r) = -\frac{\phi_i(r)e^2}{kT} \sum_{j=1}^{s} z_j^2 \frac{N_j}{V} = -\varepsilon_r \varepsilon_o \, \phi_i(r) \, \kappa^2$$

The screened Coulomb potential is given by Eq. 19.5.22; substitution gives:

$$\rho_i(r) = -\varepsilon_r \varepsilon_o \; \kappa^2 \; \frac{q_i}{4\pi\varepsilon_o\varepsilon_r \; r} \; e^{-\kappa r} = -\frac{q_i \; \kappa^2}{4\pi \; r} \; e^{-\kappa r}$$

This result shows that the charge density has a sign opposite to the central charge. In other words, the charge density surrounding a cation is net negative. The radial probability distribution for the charge density is given by multiplying this last equation by $4\pi r^2$:

$$4\pi r^2 \rho_i(r) = - \; q_i \; \kappa^2 \; r \; e^{-\kappa r}$$

The maximum in the radial probability function is given by taking the derivative using the product rule:

$$\frac{d \; 4\pi r^2 \rho_i(r)}{dr} = - \; q_i \; \kappa^2 \; [r \; (-\kappa)e^{-\kappa r} + e^{-\kappa r}] = 0$$

which gives the radius of maximum probability, $r_D$, the Debye length. Dividing by all the common factors gives:

$$[-\kappa \; r_D + 1] = 0 \qquad\qquad \text{or} \qquad \kappa = 1/r_D$$

as given in Eq. 19.5.7.

24. Determine if the following statements are true or false. If the statement is false, describe the changes that are necessary to make the statement true, if possible. If the statement is true but too restrictive, give the more general statement.

(a). The ionic halo of an ion contains only ions of opposite charge.

(b). For a simple symmetric solution, the activity coefficient of the solute depends only on the mole fraction of the solvent. The deviatons from ideality are dominated by changes in solvent-solvent forces.

(c). For a fixed ionic strength, as the relative permittivity of the solvent increases, the Debye length increases, because the counter ions in the ionic halo are less tigthly held.

*Answers*: (a). False: the ionic atmopshere of a ion is determined by ions of both charges, from all sources, including supporting electrolytes and buffers. Near a central cation, the concentration of anions is greater than the bulk and the concentration of cations is less than the bulk, but both are present, Eq. 19.5.17. The correct statement is: The neighborhood near an ion is dominated by ions of opposite charge.

(b). False: While Eq. 19.2.7 is written only as a function of the mole fraction of the solvent, $x_A + x_B = 1$, so the mole fractions of the solvent and solute are directly related. Using $x_A = 1 - x_B$ gives:
$x_A^2 = (1 - x_B)^2 = 1 - 2 \; x_B + x_B^2$ and the activity coefficient:

$$\ln \gamma_B = \frac{a}{RT} \; x_A^2 = \frac{a}{RT} \; (1 - 2 \; x_B + x_B^2)$$

The dependence of $\ln \gamma_B$ on the concentration of B is quite strong. For example, starting with a solution with $x_B = 0.001$ and $x_A = 0.999$, doubling the concentration of B only changes the solvent concentration to $x_A = 0.998$, or a 0.2% change. The probability of a B-B contact, $x_B^2$, is

quite small for dilute solution, but increases rapidly with increasing solute concentration. The correct statement is: For the solute in dilute solution, A-B forces dominate. As the solute concentration increases, for moderate concentrations, B-B forces dominate the change in activity coefficient for the solute.

(c). True:  Solvents, or solvent mixtures, with high relative permittivity provide enhanced dielectric screening, weakening the ionic interactions. The counter ions around a central ion are less tightly held, expanding the ionic atmosphere. Electrostatic interactions are weaker in water than in hexane. One common binding motif in protein-substrate binding is the formation of salt bridges. Salt bridges are ion pairs commonly formed from positive and negative charged amino acid sidechains. Salt bridges are not stabilizing in aqueous solution. However, salt bridges that form in the interior of a protein are in a low permittivity environment that strengthens the electrostatic interaction. The relative permittivity inside a globular protein is often estimated as ~4.