Chapter 19: Real Solutions

> Relate the observations that "oil and water don't mix," or conversely that "like dissolves like" to intermolecular forces.

The oceans, blood plasma, the cytoplasm of cells, hydrothermal fluids, and battery electrolytes are not ideal solutions. Few solutions are ideal or ideal-dilute. In ideal-dilute solution for the solute, A-B forces dominate and Henry's Law is valid. The concentration dependence of the chemical potential is adequately determined by the number of molecules alone. As the concentration of the solute increases, B-B forces become more important and the balance of intermolecular forces changes. The variation of the chemical potential in real solutions depends on the number of molecules, as measured by the concentration, and the changes in the intermolecular forces. How do we handle real solutions? The activity of a substance is used instead of the concentration. The activity of a substance takes into account the concentration dependent changes in intermolecular forces. In general, electrolyte solutions show larger deviations from ideality than non-electrolyte solutions. Simple symmetric solution theory, for non-electrolytes, and continuum dielectric models, for electrolytes, predict the activity of substances in solution.

19.1 The Activity is the "Chemically Effective" Concentration

The Activity of the Solvent is Based on Raoult's Law: The chemical potential for a real solution, using a Raoult's Law standard state and assuming the vapor is ideal, is given by Eq. 18.2.5:

$$\mu_A(x_A) = \mu_A^*(l) + RT \ln {}^{P_A}/_{P_A^*} \qquad\qquad (18.2.5)\ 19.1.1$$

In dilute solution, the solvent is well represented by Raoult's Law, Eq. 18.2.5:

$$\mu_A(x_A) = \mu_A^*(l) + RT \ln x_A \qquad\qquad \text{(ideal)} \quad (18.2.9^*)\ 19.1.2^*$$

We used this equation many times in the last chapter to find the properties of ideal and ideal-dilute solutions. Do we need to derive all those expressions again for real solutions? To find the chemical potential for a real solution, G. N. Lewis decided to use the same functional form for a real solution as for an ideal solution.[1] This choice is based on the same insight that Lewis used for the definition of the fugacity. The activity for a substance in solution, a_A, is defined using the relationship:

$$\mu_A(x_A) \equiv \mu_A^*(l) + RT \ln a_A \qquad\qquad 19.1.3$$

The activity, a_A, is the value that gives the exact chemical potential. The activity is the "chemically effective" concentration. By maintaining the same functional form, we can simply modify the expressions for ideal systems to apply to real systems. For example, the freezing point depression of a real solution is found by replacing x_A in Eq. 18.4.15[†] with the activity of the solvent, a_A:

$$\ln a_A = -\frac{\Delta_{fus}H_A}{R}\left(\frac{1}{T} - \frac{1}{T_m^*}\right) \qquad\qquad \text{(cst. P\&}\Delta_{fus}H_A) \qquad 19.1.4$$

All the other relationships for ideal solutions are similarly modified for real solutions. How can we determine the activity of a component in solution? Comparison of the arguments of the logarithmic terms in Eqs. 19.1.3 and 19.1.1 show that the activity of a substance can be quite simply and directly determined from the partial vapor pressure of the substance above the solution:

$$a_A = P_A/P_A^* \qquad\qquad 19.1.5$$

This equation rearranges to give the expression for a real solution that corresponds to Raoult's Law:

$$P_A = a_A P_A^* \qquad\qquad 19.1.6$$

Once again, to convert an expression from an ideal or ideal-dilute solution to a real solution we simply substitute a_A for x_A. We can also relate the activity to the concentration by defining an activity coefficient, γ_A:

$$a_A \equiv \gamma_A x_A \qquad\qquad 19.1.7$$

For the activity to be meaningful, we require that $\gamma_A \to 1$ as the solution becomes ideal. For an ideal or ideal-dilute solution the activity of the solvent is equal to the concentration, with $\gamma_A = 1$.

We can derive a visual depiction of the activity coefficient for the solvent. The activity is given by the ratio of the real partial vapor pressure of the solvent to the pure vapor pressure, Eq. 19.1.5. For an ideal solvent, the predicted ratio is given by Raoult's Law, Figure 19.1.1a:

$$P_A^{Raoult} = x_A P_A^* \qquad\qquad x_A = P_A^{Raoult}/P_A^* \qquad\qquad \text{(ideal)} \qquad (18.2.6^*)\ 19.1.8^*$$

We use the "Raoult" superscript to remind us that the equation holds only for an ideal solution. Solving Eq. 19.1.7 for the activity coefficient and then dividing Eq. 19.1.5 by Eq. 19.1.8* for x_A gives:

$$\gamma_A = a_A/x_A = P_A/P_A^{Raoult} \qquad\qquad 19.1.9$$
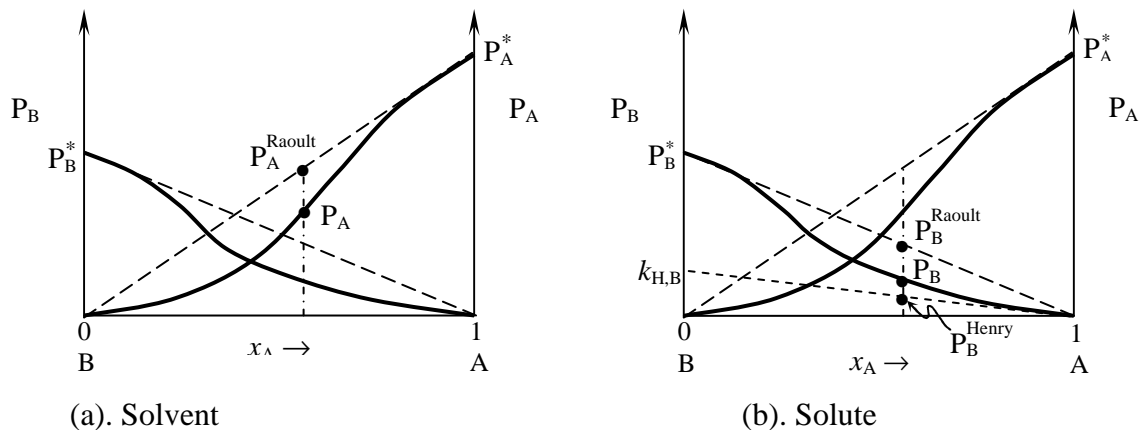

(a). Solvent   (b). Solute

Figure 19.1.1: (a) A Raoult's Law standard state is used for the solvent with $\gamma_A = a_A/x_A = P_A/P_B^{Raoult}$. (b). A Henry's Law standard state is used for the solute with $\gamma_B = a_B/x_B = P_B/P_B^{Henry}$.

In Figure 19.1.1a, we find the activity coefficient by dividing the partial vapor pressure of the substance by the Raoult's Law prediction. In this example $\gamma_A < 1$, since $P_A < P_A^{Raoult}$.

The Activity of the Solute is Based on Henry's Law: In an ideal-dilute solution, the solute obeys Henry's Law and the chemical potential is given by Eq. 18.3.10[†]:

$$\mu_B(x_B) = \mu_B^†(l) + RT \ln x_B \qquad \text{(ideal)} \qquad (18.3.10^†) \; 19.1.10^†$$

For a real solution, the concentration is replaced by the activity of the solute:

$$\mu_B(x_B) = \mu_B^†(l) + RT \ln a_B \qquad\qquad 19.1.11$$

The Henry's Law standard state chemical potential is given by Eq. 18.3.9[†]:

$$\mu_B^†(l) = \mu_B^\circ(g) + RT \ln {k_{H,B}}/{P\circ} \qquad\qquad (18.3.9^†) \; 19.1.12^†$$

The activity of the solute can be related to its partial vapor pressure above the solution by substituting Eq. $19.1.12^†$ into Eq. 19.1.11:

$$\mu_B(x_B) = \mu_B^\circ(g) + RT \ln {k_{H,B}}/{P\circ} + RT \ln a_B = \mu_B^\circ(g) + RT \ln {k_{H,B} \, a_B}/{P\circ} \qquad 19.1.13$$

Comparing this last relationship to the exact result from Eq. 19.1.1, written in terms of the solute, gives the expression for a real solution corresponding to Henry's Law:

$$\mu_B(x_B) = \mu_B^\circ(g) + RT \ln {P_B}/{P\circ} \qquad\qquad (19.1.1)$$

$$\updownarrow$$

$$\mu_B(x_B) = \mu_B^\circ(g) + RT \ln {k_{H,B} \, a_B}/{P\circ} \qquad\qquad (19.1.13)$$

$$P_B = a_B \, k_{H,B} \qquad \text{or} \qquad a_B = {P_B}/{k_{H,B}} \qquad\qquad 19.1.14$$

This last expression is a simple and direct expression for determining the activity of a volatile solute. We can also relate the activity to the concentration by using the activity coefficient, $a_B = \gamma_B \, x_B$. The choice of a Henry's Law standard state for the solute and a Raoult's Law standard state for the solvent guarantees that as the solution becomes more dilute the solvent and solute both become ideal; as $x_B \to 0$, $x_A \to 1$, then $\gamma_B \to 1$ with $\gamma_A \to 1$.

  We can derive a visual depiction of the activity coefficient for the solute. The solute activity is given by Eq. 19.1.14 as the ratio of the real partial vapor pressure of the solute to the Henry's Law constant. Henry's Law gives the ideal vapor pressure prediction, P_B^{Henry}, from the mole fraction:

$$P_B^{Henry} = x_B \, k_{H,B} \qquad x_B = {P_B^{Henry}}/{k_{H,B}} \qquad \text{(ideal)} \qquad (18.3.1^†) \; 19.1.15^†$$

Dividing Eq. 19.1.14 by Eq. 19.1. $15^†$ gives the activity coefficient of the solute as:

$$\gamma_B = {a_B}/{x_B} = {P_B}/{P_B^{Henry}} \qquad\qquad 19.1.16$$

In Figure 19.1.1b, we find the activity coefficient for the solute by dividing the real partial vapor pressure by the Henry's Law prediction. In this example, we can see immediately that $\gamma_B > 1$, since $P_B > P_B^{Henry}$. The deviation from ideality is defined with respect to the dilute solution

environment. Using Raoult's Law for the standard state is called the **solvent convention** and using Henry's Law for the standard state is called **the solute convention.**

Example 19.1.1: *Activity from Vapor Pressure*

A solution of heptane and 1-bromobutane at 50°C has a mole fraction of heptane of 0.7638, Figure 18.3.1. The partial vapor pressure for heptane is 0.1475 bar and for 1-bromobutane is 0.0504 bar. The vapor pressure of pure heptane at 50°C is 0.1832 bar and the Henry's Law constant for 1-bromobutane in heptane is 0.2445 bar, Example 18.3.2. Calculate the activity and activity coefficients for heptane as the solvent and 1-bromobutane as the solute.

Answer: For heptane as the solvent, using Eqs. 19.1.5 and 19.1.7 with $x_A = 0.7638$:

$$a_A = P_A/P_A^* = 0.1475 \text{ bar}/0.1832 \text{ bar} = 0.8051 \quad \text{and} \quad \gamma_A = {}^{a_A}/x_A = 0.8051/0.7638 = 1.054$$

As expected from Figure 18.3.1a the solvent shows positive deviations from ideality. For 1-bromobutane as the solute, using Eq. 19.1.14 and $x_B = 1 - x_A = 0.2362$ gives:

$$a_B = {}^{P_B}/k_{H,B} = 0.0504 \text{ bar}/0.2445 \text{ bar} = 0.206 \quad \text{and} \quad \gamma_B = {}^{a_B}/x_B = 0.206/0.2362 = 0.872$$

As expected from Figure 18.3.1b the solute shows negative deviations, since $P_B < P_B^{Henry}$.

Example 19.1.2: *Activity from Freezing Point Depression*

The freezing point depression is 7.34 K for a 15.00 % by weight solution of ethanol in water. Calculate the activity and activity coefficient for water in this solution. The enthalpy of fusion of water at 0°C is 6.01 kJ mol^{-1}.

Answer: Given 100.00 g of a 15.00 % by weight solution, $n_A = 85.00 \text{ g}/18.0153 \text{ g/mol} = 4.718$ mol and $n_B = 15.00 \text{ g}/46.07 \text{ g mol}^{-1} = 0.325_6$ mol for a mole fraction of $x_A = 0.9354$. Using Eq. 19.1.4 with the melting point of the solution, T = 273.15 K – 7.34 K = 265.81 K, and assuming a constant enthalpy of fusion:

$$\ln a_A = -\frac{\Delta_{fus}H_A}{R}\left(\frac{1}{T} - \frac{1}{T_m^*}\right) = -\frac{6.01 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\left(\frac{1}{265.81 \text{ K}} - \frac{1}{273.15 \text{ K}}\right) = -0.07307$$

$$a_A = 0.9295$$

The activity coefficient is $\gamma_A = a_A/x_A = 0.9295/0.9354 = 0.994$

Different Concentration Measures Can be Used for the Solute: Our definition of the activity of a component in solution is based on mole fraction concentrations. For practical problems, we often prefer to work with molarity or molality. To convert from mole fraction based standard states, we simply express Henry's Law in terms of molarity or molality, Eqs. 18.3.3†-18.3.4† and 18.3.11†-18.3.12†. For a real solution, the concentration of a solute is replaced by the activity.

The activities are related to the corresponding activity coefficients defined in terms of mole fraction, molarity, and molality, $^x\gamma$, $^c\gamma$, and $^m\gamma$ respectively:

$$\mu_B = \mu_B^{\dagger} + RT \ln a_B \qquad\qquad a_B = \gamma_B\, x_B$$
$$\mu_B = {}^c\mu_B^{\circ} + RT \ln {}^c a_B \qquad\qquad {}^c a_B = {}^c\gamma_B\, c_B/c^{\circ}$$
$$\mu_B = {}^m\mu_B^{\circ} + RT \ln {}^m a_B \qquad\qquad {}^m a_B = {}^m\gamma_B\, m_B/m^{\circ} \tag{19.1.17}$$

The mole fraction based standard state is sometimes listed with an "^{x}", with $^x\mu_B^{\dagger} = \mu_B^{\dagger}$ and $^x\gamma_B = \gamma_B$, to distinguish the concentration measure. Luckily, for solutions at concentrations less than about 0.1 M, the different activity coefficients are approximately equal, so we don't need to determine them separately:

$$^x\gamma \cong {}^c\gamma \cong {}^m\gamma \qquad\qquad\text{(solutions more dilute than 0.1 M)} \tag{19.1.18}$$

In other words, you can use any concentration measure that is convenient.

Activities for Non-Volatile Solutes are Obtained Using the Gibbs-Duhem Relationship: The activity of a volatile solute is easily calculated using $a_B = P_B/k_{H,B}$. However, how can we calculate the activity coefficients for non-volatile solutes? The Gibbs-Duhem relationship is used to find the activity for the solute from the activity of the solvent over a range of concentrations by integrating Eq. 18.1.19. Substituting Eq. 19.1.3 for the solvent, Eq. 19.1.11 for the solute, and dividing by the common factor of RT in Eq. 18.1.19 gives:

$$d \ln a_B = - \frac{x_A}{1 - x_A}\, d \ln a_A \qquad\qquad \text{(cst. T\&P)} \tag{19.1.19}$$

However, in dilute solution the activity of the solvent is close to one and many significant figures are necessary for accurate determinations. In addition, we often express the solute concentration in terms of molality instead of mole fractions, by using the conversion Eq. 2.2.15. A solution to the propagation of errors problem and the units conversion is to define the **practical osmotic coefficient**. For a non-electrolyte at concentration m_B, the osmotic coefficient is defined in terms of the activity of the solvent:

$$\phi \equiv - \frac{\ln a_A}{m_B\,(\mathfrak{M}_A/1000 \text{ g kg}^{-1})} \tag{19.1.20}$$

where ϕ is unitless. For aqueous solutions, $\phi = - (55.51 \text{ mol kg}^{-1} \ln a_A)/m_B$. Solving this last equation for the activity of the solvent gives the chemical potential, the freezing point depression from 19.1.4, and the osmotic pressure from Eq. $18.4.23^{\dagger}$ as:

$$\ln a_A = - \phi\, m_B/(55.51 \text{ mol kg}^{-1}) \qquad\qquad \text{(aq)} \tag{19.1.21}$$

$$\mu_A(x_A) = \mu_A^*(l) - RT\, \phi\, m_B/(55.51 \text{ mol kg}^{-1}) \qquad\qquad \text{(aq)} \tag{19.1.22}$$

$$\phi = \frac{\Delta_{fus}H_A}{R\, m_B/(55.51 \text{ mol kg}^{-1})}\left(\frac{1}{T} - \frac{1}{T_m^*}\right) \qquad\qquad \text{(cst. P\&}\Delta_{fus}H_A\text{, aq)} \tag{19.1.23}$$

$$\pi\, \bar{V}_A = RT\, \phi\, m_B/(55.51 \text{ mol kg}^{-1}) \qquad\qquad \text{(cst. T, aq)} \tag{19.1.24}$$

Clinical and laboratory osmometers are calibrated to give direct determinations of the osmotic coefficient, taking the non-idealities of the solution into account. Osmometers do not read out

concentration directly. Substitution of Eq. 19.1.19 into the Gibbs-Duhem relationship with $a_B = {}^m\gamma_B \, m_B$ gives:

$$d \ln {}^m\gamma_B = d\phi + \frac{\phi - 1}{m_B} \, d \, m_B \qquad \text{(cst. T\&P)} \qquad 19.1.25$$

$$\ln {}^m\gamma_B = \phi - 1 + \int_0^m \frac{\phi - 1}{m_B} \, d \, m_B \qquad \text{(cst. T\&P)} \qquad 19.1.26$$

Example 19.1.3: *Solute Activity from the Solvent Activity*

Determine the activity coefficient for sucrose at 1.00 m. A curve fit of the experimental data for aqueous sucrose solutions at 298.15 K gives:

$$\phi - 1 = a \, m_B^2 + b \, m_B \qquad \text{with:} \quad a = 0.00752 \text{ kg}^2 \text{ mol}^{-2} \quad \text{and} \quad b = 0.0804 \text{ kg mol}^{-1}$$

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

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

For a 1.00 m solution:

$$\ln {}^m\gamma_B = (0.00752 \text{ m}^2 + 0.0804 \text{ m}) + \frac{0.00752}{2} m^2 + 0.0804 \text{ m} = 0.1759$$

giving $\gamma_B = 1.19$ on a molal basis.

Now that we know how to determine activities experimentally, we consider theoretical models for the prediction of activity coefficients. Accurate experimental determinations of activity coefficients are challenging, so theoretical models can fill a critical need. In addition, models relate the effects of intermolecular forces. Theories of real solutions are based on the definition of **excess thermodynamic properties**. Models of excess properties for non-electrolytes and electrolytes are sufficiently different that we treat these classes of solutes separately. We discuss simple symmetric solution theory for non-electrolytes and continuum solvation treatments for electrolytes.

19.2 Excess Thermodynamic Properties Focus on Non-ideal Behavior

The **excess Gibbs energy of solution** is the difference between the measured Gibbs energy of mixing and the ideal Gibbs energy of mixing. Using Eq. 18.2.11[*]:

$$G^E = \Delta_{mix}G - \Delta_{mix}G^{ideal} = \Delta_{mix}G - n_{tot}RT \sum_{i=1}^{c} x_i \ln x_i \qquad \text{(cst. T\&P)} \qquad 19.2.1$$

The excess Gibbs energy is entirely the result of the concentration dependent changes in intermolecular forces in solution, since the contribution of the statistical mixing has been

subtracted out. We can relate the excess Gibbs energy directly to the activity coefficient for a constituent by noting that the ideal chemical potential is given by Eq. 19.1.2[*] as $\mu_i^{ideal}(x_i) = \mu_i^{\circ}(l) + RT \ln x_i$ and the **excess chemical potential** is the difference:

$$\mu_i^E = \mu_i(x_i) - \mu_i^{ideal}(x_i) = [\mu_i^{\circ}(l) + RT \ln \gamma_i x_i] - [\mu_i^{\circ}(l) + RT \ln x_i] = RT \ln \gamma_i \qquad 19.2.2$$

The chemical potential is the derivative of the Gibbs energy with respect to the amount of substance:

$$\ln \gamma_i = \frac{1}{RT} \left(\frac{\partial G^E}{\partial n_i} \right)_{T,P,n_{j \neq i}} \qquad 19.2.3$$

As the concentration of the solute increases, the B-B forces become more important, changing the excess Gibbs energy. The change in the excess Gibbs energy causes deviations from ideal behavior. The excess Gibbs energy is given by the chemical potentials:

$$G^E = n_A \mu_A^E + n_B \mu_B^E \qquad 19.2.4$$

Using Eq. 19.2.2 for the chemical potentials of A and B in this last equation and $n = n_A + n_B$ shows the relationship between the activity coefficients and the excess Gibbs energy:

$$G^E = n_A (RT \ln \gamma_A) + n_B (RT \ln \gamma_B) \qquad 19.2.5$$

$$G^E = nRT \left(\frac{n_A}{n} \ln \gamma_A + \frac{n_B}{n} \ln \gamma_B \right) = nRT (x_A \ln \gamma_A + x_B \ln \gamma_B) \qquad 19.2.6$$

Many models have been proposed to estimate the activity coefficients in solutions of non-electrolytes. One of the simplest and most useful is **simple symmetric solution theory**.

Simple Solutions Have an Imbalance in the A-A, B-B and A-B forces: At a basic level, as the mole fraction of A approaches one, the solution becomes ideal; $x_A \rightarrow 1$, $x_B \rightarrow 0$, $\gamma_A \rightarrow 1$, and $G^E \rightarrow 0$. In addition, as the mole fraction of B approaches one, the solution becomes ideal; $x_B \rightarrow 1$, $x_A \rightarrow 0$, $\gamma_B \rightarrow 1$, and $G^E \rightarrow 0$. The simplest model for the activity coefficients that is consistent with these limits, with a Raoult's Law standard state for both components, is:

$$\ln \gamma_A = \frac{a}{RT} x_B^2 \qquad\qquad \ln \gamma_B = \frac{a}{RT} x_A^2 \qquad\qquad \text{(simple)} \qquad 19.2.7$$

where a is a constant that characterizes the imbalance in intermolecular forces and that results in a non-zero enthalpy of mixing. In short, A deviates from ideality because of the presence of B, and conversely, B deviates from ideality because of the presence of A. The system is said to be **symmetric** because the same interaction constant appears in the equations for both activity coefficients. Substituting these expressions into Eq. 19.2.6 determines the excess Gibbs energy as:

$$G^E = \frac{n\,a\,RT}{RT} [x_A (x_B^2) + x_B (x_A^2)] = n\,a\,[x_B (x_A x_B) + x_A (x_A x_B)] \qquad \text{(simple)} \qquad 19.2.8$$

$$G^E = n\,a\,x_A x_B \qquad\qquad\qquad \text{(simple)} \qquad 19.2.9$$

since $x_A + x_B = 1$. Solutions that are well approximated by Eqs. 19.2.7 and 19.2.9 are called **simple symmetric solutions**. Simple solutions have ideal entropy of mixing and an enthalpy of mixing. Eq. 19.2.9 can model a wide range of behaviors, depending on the sign of the constant a,

Figure 19.2.1. For large positive a, extreme deviations from ideality result in two minima and an intermediate positive Gibbs energy of mixing. Such systems separate into two immiscible liquid phases, since mixing to give a single liquid phase is not spontaneous. Liquid immiscibility for a large positive imbalance in forces results in the observation that "oil and water don't mix," or conversely that "like dissolves like." We show in Sec. 19.6 that a is related to the forces through:

$$a = z \left(\varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} \right) \qquad \text{(random distribution) 19.2.10}$$

where z is the number of near neighbors for both A and B, ε_{AA} are the A-A forces, ε_{BB} are the B-B forces, and ε_{AB} are the A-B forces, with $\varepsilon_{AA}, \varepsilon_{BB}, \varepsilon_{AB} < 0$. The deviation from ideality results from an imbalance in the A-B forces as compared to the average of the A-A and B-B forces. Eq. 19.2.10 assumes that the solute and solvent are roughly the same size and are randomly distributed without preference for the type of neighbor; A doesn't have a preference for an A or B near neighbor, even though the interaction energy is different.
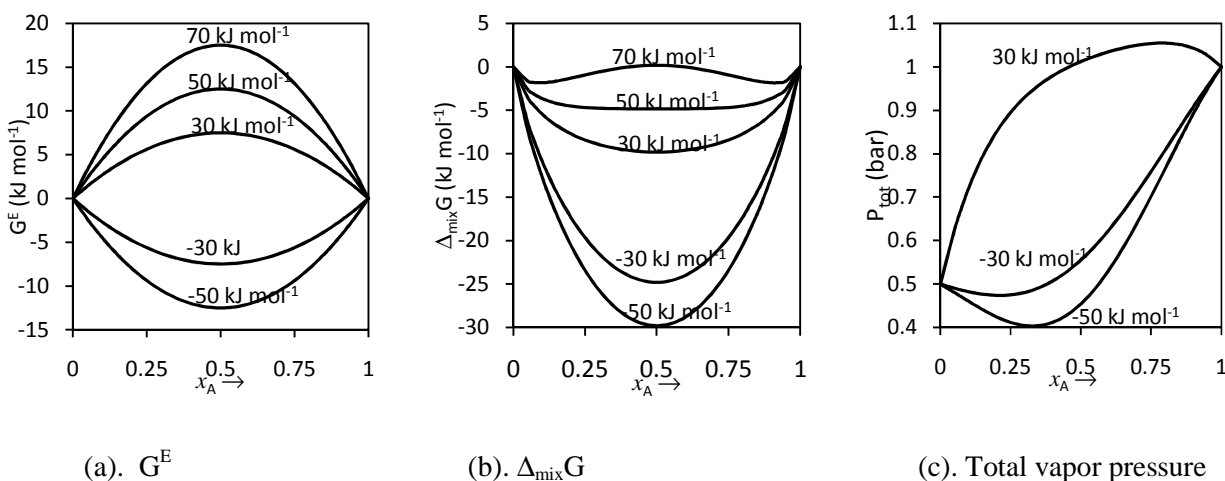

(a). G^E (b). $\Delta_{mix}G$ (c). Total vapor pressure

Figure 19.2.1: (a). Simple solution theory estimates for the excess Gibbs energy, G^E, for different values of a. (b). The corresponding Gibbs energies of mixing has two minima for very unfavorable balance of forces. (c). The corresponding total vapor pressure curves exhibit azeotropic maxima and minima for large positive and negative values for a.

More advanced theories of solvation become increasingly mathematically complex and involve fluctuations in the heat capacity of the system.[3,4] Completely satisfactory theories are as yet out of reach and are an intense area of current research. An alternative, computational approach is helpful in practical problems and in building insight into solvation at the molecular level.

Solute-Solvent Interactions Can be Studied Using Molecular Mechanics with Explicit Solvation: In Chapter 8 we discussed gas phase molecular mechanics computational methods. One approach to study solvation interactions is to include explicit solvent molecules along with the substance of interest in the molecular mechanics or molecular orbital calculation, Figure 19.2.2a. The difficulty is one of practicality. To model the solution environment, thousands of solvent

molecules are necessary, which greatly increases the time required to complete calculations. Typically around 1000 solvent molecules are used in practical, everyday calculations.

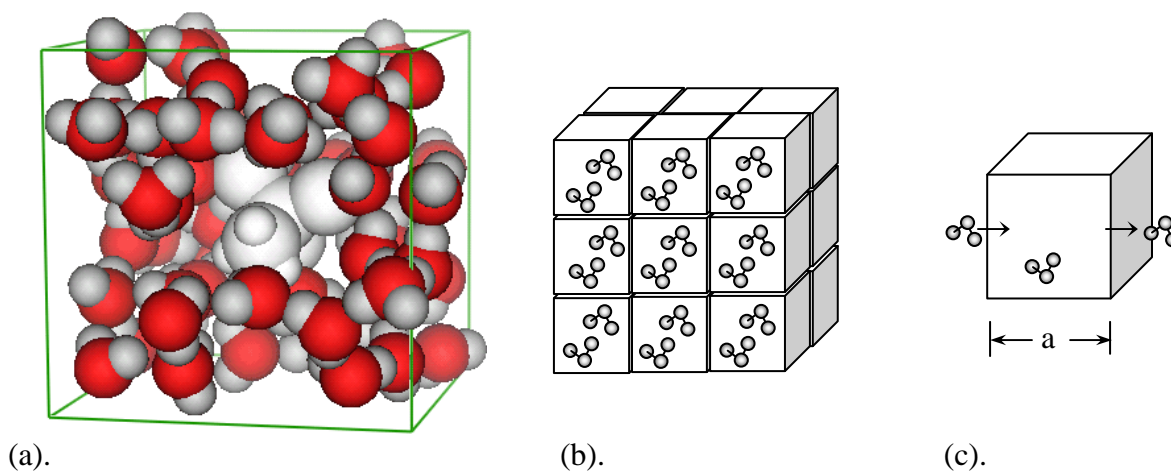(a).   (b).   (c).

Figure 19.2.2: Molecular mechanics using explicit water molecules. (a). 1,1,1-trichloroethane is shown in the light shading. (b). Copies of the original molecules are arrayed to eliminate surface effects. (c). If a solvent molecule migrates out of a box side, the coordinates are translated to force the same molecule to enter the corresponding position at the opposite side. Molecules have free motion, but they always stay in the same box.

With small numbers of solvent molecules, the surface to volume ratio of the system is large, so that surface effects dominate. Surface effects include the imbalance of forces between the bulk of the solvent and the vacuum surrounding the solution droplet. This imbalance produces surface tension. Another surface effect is evaporation. Just like real solutions, water molecules can escape into the surrounding vacuum and in essence evaporate. The best way to avoid surface effects is to use **periodic boundary conditions**. The range of coordinates that encompass all the molecules in the calculation specify a rectangular box. Exact images of the box are stacked next to each other in all directions so there are no surfaces to the solution, Figure 19.2.2b. Periodic boundary conditions eliminate any surface tension effects.

Boundary conditions are enforced in the computer algorithm by first checking if the coordinates of a molecule lie inside the box. If not, the molecule is translated so that it enters the opposite side of the box. For example for a cubic box with side length a, if the x coordinate of a molecule is found to be outside the box, $x > a$, then the coordinate is replaced by $x = x - a$, Figure 19.2.2c.

Another issue is that the common molecular mechanics force field parameters that work well for organic molecules don't work for water. A specialized force field is used to generate a structure for water that has the proper bond angle, Van der Waals constants, electrostatic distribution, and liquid phase density. One common parameter set for water is TIP3P; the partial charge on the H atoms is $+0.417$, the bond length is 0.957 Å, and the bond angle is $104.5°$. Explicit solvation treatments provide insights for the development of new solvation models.

Structure Makers Decrease the Entropy of the Secondary Solvation Sphere: Ions in solution are categorized as **structure makers** and s**tructure breakers**, or **kosmotropes** and **chaotropes**, respectively. The basis of the distinction is the effect of the ion on the surrounding solvent.

Molecular simulations have also shed light on the solvation of non-polar molecules in solution, which is called **hydrophobic hydration**. The details of these three extremes are under debate, but these categories are a good starting point for understanding solute-solvent interactions. Real molecules are a compromise of these extremes.

Water molecules can form four hydrogen-bonds. Bulk water has a tetrahedral network of hydrogen-bonds that dynamically form and break due to thermal motion. The presence of a solute perturbs this hydrogen-bond network. The solvation of an ion in solution can be divided into three concentric spheres. The boundaries between the regions are diffuse and very dynamic.
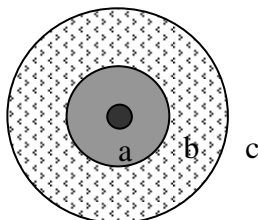

Figure 19.2.3. Solvation environment for an ion: (a). primary solvation sphere, (b). secondary solvation sphere, (c) bulk solution. The boundaries between regions are diffuse.

(a) The primary solvation sphere is a layer of 4-8 tightly associated waters. For alkali metals, the interactions in the primary solvation sphere are strong ion-dipole interactions. For transition metal ions the primary solvation sphere may be considered as directly bonded ligands for the metal. In the primary solvation sphere, the tetrahedral hydrogen-bonding network typical of the bulk of the solvent is completely disrupted. (b) In the secondary solvation sphere, the hydrogen-bonding network may be more or less ordered than the bulk. The structure making or breaking ability of an ion is determined by the nature and size of the secondary solvation sphere. For **structure makers** the secondary solvation sphere is more ordered than the bulk. For **structure breakers**, the secondary solvation sphere is less ordered than the bulk. (c) The third region is the bulk of the solution. The difference between structure makers and structure breakers for small ions can be rationalized using the charge to size ratio. Large charge to size ratio ions are structure makers. Good examples are ions that have strong, stabilizing interactions with water that enhance the hydrogen bonding: SO_4^{2-}, HPO_4^{2-}, Mg^{2+}, Ca^{2+}, Li^+, OH^- and HPO_4^{2-}. Small charge to size ratio ions, such as $H_2PO_4^-$, HSO_4^-, HCO_3^-, I^-, Cl^-, NO_3^-, NH_4^+, Na^+, K^+, Cs^+, and $(CH_3)_4N^+$ are structure breakers. Structure breakers don't form strong interactions with water and destabilize the hydrogen bond network in the secondary solvation sphere.[5]

Hydrophobic Hydration Results in Structure Making: Molecular dynamics simulations and neutron diffraction studies have shown that non-polar molecules are structure makers.[6] That is, the hydration sphere is more ordered than the bulk solvent. The desolvation of non-polar compounds is entropically favored, and the change in entropy is the major driving force in the hydrophobic interaction.

Ions that form weak interactions with water (weaker than water-water) are structure breakers. Hydrophobic molecules that form weak interactions with water are structure makers. It is clear that non-polar molecules need to be considered separately from small ionic solutes. The difference is that non-polar molecules don't have distinct primary and secondary solvation

spheres. The water molecules near the surface of a non-polar solute have a large imbalance in forces—Van der Waals on the solute side and hydrogen-bonding on the bulk solution side.

One centrally important insight, based on the Gibbs phase rule, is that water in aqueous solution is a single component. Since water in each solvation sphere is in equilibrium with the bulk, the water in the primary solvation sphere, secondary solvation sphere, and bulk of the solution must all have the same chemical potential.[7]

The order or disorder in a region of aqueous solution is a measure of the average number of hydrogen-bonds.[7] Each water molecule can form four hydrogen-bonds. However, thermal motions are constantly breaking and then remaking these interactions so the average number of hydrogen-bonds is less than four. In the solvation sphere of non-polar molecules and other structure makers the increased order is reflected in a larger average number of hydrogen bonds. The larger number of hydrogen bonds <u>decreases</u> the enthalpy of the solvated water, which is favorable, and <u>decreases</u> the entropy, which is unfavorable. The net result on the Gibbs energy is small, since $\Delta_{sol}G = \Delta_{sol}H - T\Delta_{sol}S$. This effect is called **enthalpy-entropy compensation**. Favorable changes in enthalpy are compensated by unfavorable changes in entropy, so that the changes in the chemical potentials are small.[8] The enthalpy and entropy for water-water interactions are completely compensated, while the solute-solvent interactions are not.[9] Enthalpy-entropy compensation does not imply that the solute has no effect on the solvent. However, the change in chemical potential of the solvent is small because of compensation and the fact that the concentration of the solvent is so much larger than the solute. In other words, small changes in the chemical potential of the solvent are important. The net result is that hydrophobic solutes are structure makers.

The early evidence concerning ionic solvation was gleaned from partial molar volume, viscosity, and ionic conductivity measurements. The different techniques can disagree and the behavior of a given ion can be a strong function of concentration and ionic strength. Clearly, experimental and theoretical advances are needed to better understand solvation.

19.3 Pressure Perturbation Calorimetry Characterizes Solute-Solvent Interactions

Pressure perturbation calorimetry, PPC, is used to study small and large molecule solvation, protein folding, denaturization, and binding.[10] PPC measures the coefficient of thermal expansion, α, for substances in solution as a function of temperature. PPC has emerged as a definitive technique for the characterization of ionic solvation.[11] Figure 19.3.1a shows α as a function of temperature for the side chains of several amino acids. Structure makers show an increase of the coefficient of thermal expansion with temperature and the structure breakers show a decrease. Hydrophobic side chains of amino acids are shown to be structure makers and ionic side chains are structure breakers. The zwitter-ionic backbone for each amino acid is a structure-breaker.

In PPC, the heat flow caused by a small change in pressure for a solution is measured. The instrument is a differential scanning calorimeter that is operated in isothermal mode, while changing the pressure above the sample and reference cells. The entropy change for a process is defined by Eq. 13.1.1, $dS = đq_{rev}/T$. Differentiating with respect to P at constant temperature gives:

$$\left(\frac{đq_{rev}}{dP}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T \qquad \text{(reversible, cst. T)} \qquad 19.3.1$$
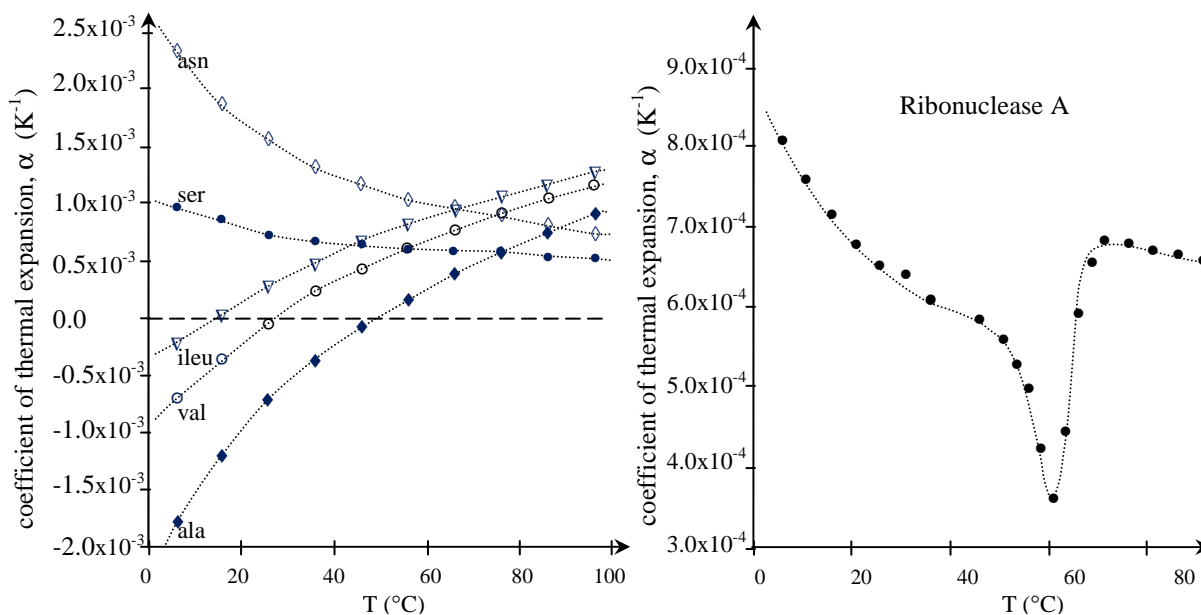
Figure 19.3.1: (a). Coefficient of thermal expansion for the side chains of several amino acids as a function of temperature.[11] Glycine was placed in the reference cell to determine the α_s of the amino acid side chains. (b). Ribonuclease A has a negative volume of unfolding, positive α_s of unfolding, and the surface of the native protein is overall structure breaking. The melting peak temperature at 60°C is a measure of protein stability.

PPC provides a direct entropy measurement for an isothermal change in pressure. Using the Maxwell relation, Eq. 16.4.11, for the entropy derivative gives:

$$\left(\frac{đq_{rev}}{dP}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{(reversible, cst. T)} \qquad 19.3.2$$

Substituting the definition of the coefficient of thermal expansion, Eq. 7.6.8, gives:

$$\left(\frac{đq_{rev}}{dP}\right)_T = -TV\alpha \qquad \text{(reversible, cst. T)} \qquad 19.3.3$$

Integration of this last equation for changes in pressure gives:

$$\int đq_{rev} = -\int TV\alpha \, dP \qquad \text{(reversible, cst. T)} \qquad 19.3.4$$

Assuming the volume and α are constant for the small pressure perturbation gives:

$$q_{rev} = -TV\alpha \, \Delta P \qquad \text{(reversible, cst. T,V\&}\alpha\text{)} \qquad 19.3.5$$

The heat flow gives the thermal expansion coefficient. The fact that an isothermal change in *pressure* results in a determination of the coefficient of *thermal* expansion is an excellent example of the power of Maxwell relationships to link concepts that are not obviously related. Eq. 19.3.5 requires that the process be reversible. The reversibility of the process is verified by measuring the heat flow with a positive pressure change and then again while returning back to

the original pressure. If the process is reversible, the heat effects are equal in magnitude and opposite in sign.

Eq. 19.3.5 applies to pure substances. For solutions the heat transfer is a function of the apparent specific volume and apparent specific coefficient of thermal expansion for the solute. The apparent specific volume, $\bar{V}_s$, is the apparent volume per gram instead of per mole; the difference being just the molar mass of the solute:

$$\bar{V}_s = {}^{\phi}V / \mathfrak{M}_B \qquad\qquad 19.3.6$$

For organic ionic compounds, such as amino acids, the apparent specific volume is often quite close to 0.7 mL g^{-1}. The specific volume of the pure solvent, V_o, is:

$$V_o = V_A^* / \mathfrak{M}_A \qquad\qquad 19.3.7$$

From Eq. 18.1.10, the total volume of the solution is:

$$V = w_o\, V_o + w_s\, \bar{V}_s \qquad\qquad 19.3.8$$

where w_o is the mass of the solvent and w_s is the mass of the solute. The α values determined by PPC are apparent specific coefficients of thermal expansion:

$$\alpha_s \equiv \frac{1}{\bar{V}_s}\left(\frac{\partial \bar{V}_s}{\partial T}\right)_P \qquad\qquad 19.3.9$$

The apparent specific coefficient of thermal expansion can be visualized by switching each V for α in Figure 18.1.2; this experiment determines the difference in α caused by the presence of the solute, on a per gram basis.

The α values determined by PPC are apparent values because of the differential nature of the measurement.[12] The differential mode of operation is required to achieve sufficient sensitivity to measure the very small heat transfers. Taking the derivative of Eq. 19.3.8 with respect to temperature at constant pressure gives:

$$\left(\frac{\partial V}{\partial T}\right)_P = w_o\left(\frac{\partial V_o}{\partial T}\right)_P + w_s\left(\frac{\partial \bar{V}_s}{\partial T}\right)_P \qquad\qquad 19.3.10$$

Substitution of Eq. 19.3.10 into Eq. 19.3.2 gives:

$$\left(\frac{đq_{rev}}{dP}\right)_T = -T\left(w_o\left(\frac{\partial V_o}{\partial T}\right)_P + w_s\left(\frac{\partial \bar{V}_s}{\partial T}\right)_P\right) \qquad \text{(reversible, cst. T)} \qquad 19.3.11$$

The relationship to the α values is facilitated by the manipulation:

$$\left(\frac{đq_{rev}}{dP}\right)_T = -T\left(w_o\frac{V_o}{V_o}\left(\frac{\partial V_o}{\partial T}\right)_P + w_s\frac{\bar{V}_s}{\bar{V}_s}\left(\frac{\partial \bar{V}_s}{\partial T}\right)_P\right) \qquad \text{(reversible, cst. T)} \qquad 19.3.12$$

and substitution of the definition of the apparent specific α results in:

$$\left(\frac{đq_{rev}}{dP}\right)_T = -T\left(w_o\, V_o\, \alpha_o + w_s\, \bar{V}_s\, \alpha_s\right) \qquad \text{(reversible, cst. T)} \qquad 19.3.13$$

where α_o is the coefficient of thermal expansion of pure solvent. Integrating this equation over the pressure perturbation, assuming that the specific properties are constant, gives:

$$q_{rev}(sample) = -T (w_o V_o \alpha_o + w_s \overline{V}_s \alpha_s) \Delta P \qquad (\text{reversible, cst. } T, V_o, \alpha_o, \overline{V}_s, \alpha_s) \quad 19.3.14$$

For the differential measurement, the solution is placed in the sample cell and the pure solvent is placed in the reference cell. The volume of the pure solvent in the reference cell can be thought of as being in two parts. The mass of solvent in the sample cell for the solution is w_o and the contribution to the total α is $w_o V_o \alpha_o$. In the reference cell, pure solvent occupies the corresponding volume and the associated contribution is also $w_o V_o \alpha_o$. The rest of the sample cell is filled with solute, which occupies the volume $w_s V_s$. In the reference cell the corresponding volume is occupied by pure solvent instead of solute and the corresponding contribution is $w_s V_s \alpha_o$. The q_{rev} for the pure solvent in the reference cell is then:

$$q_{rev}(ref) = -T (w_o V_o \alpha_o + w_s \overline{V}_s \alpha_o) \Delta P \qquad (\text{reversible, cst.} T, V_o, \alpha_o, \overline{V}_s, \alpha_s) \quad 19.3.15$$

Notice that α_o appears in both terms, since both apply to the solvent. The instrument then determines the difference in heat flow: $\Delta q_{rev} = q_{rev}(sample) - q_{rev}(ref)$:

$$\Delta q_{rev} = -T (w_s \overline{V}_s \alpha_s - w_s \overline{V}_s \alpha_o) \Delta P \qquad (\text{reversible, cst.} T, V_o, \alpha_o, \overline{V}_s, \alpha_s) \quad 19.3.16$$

Solving Eq. 19.3.16 for α_s gives:

$$\alpha_s = \alpha_o - \frac{\Delta q_{rev}}{T \Delta P\, w_s \overline{V}_s} \qquad (\text{reversible, cst.} T, V_o, \alpha_o, \overline{V}_s, \alpha_s) \quad 19.3.17$$

PPC is providing valuable insights into solvation phenomena, especially for solutions of electrolytes. Most biochemicals are electrolytes, since biochemistry primarily takes place in aqueous solution, Figure 19.3.1b. Electrolytes also play important roles in energy and biogeoenvironmental applications. The key to the study of solutions of electrolytes is the chemical potential, just as in solutions in general. How do you calculate the chemical potential of ions in solution?

19.4 The Activities of Electrolyte Solutions and Mean Ionic Activity Coefficients

For Electrolytes, the Chemical Potentials of the Ions Add and the Activities Multiply:
Calculating the chemical potential of strong electrolyte solutions is fundamentally very simple. We first assume that strong electrolytes dissociate completely. Then the chemical potentials of the constituent ions just add, Figure 19.4.1.

$$NaCl\,(aq) \rightarrow Na^+\,(aq) + Cl^-(aq) \qquad\qquad CrCl_3\,(aq) \rightarrow Cr^{3+}\,(aq) + 3\,Cl^-(aq)$$
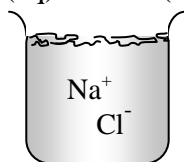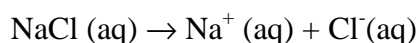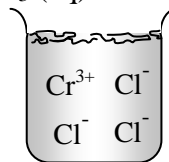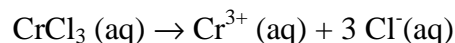
$$\mu(NaCl) = \mu_+(Na^+) + \mu_-(Cl^-) \qquad\qquad \mu(CrCl_3) = \mu_+(Cr^{3+}) + 3\,\mu_-(Cl^-)$$

Figure 19.4.1: Chemical potentials add for the constituent ions.

The chemical potential of an ion in solution is given by Eq. 19.1.17:

$$\mu_i = {}^m\mu_i^\circ + RT \ln a_i \tag{19.1.17}$$

Usually we choose a Henry's Law standard state on a molality basis. The ion activity is given by:

$$a_i = \frac{\gamma_i\, m_i}{m^\circ} \tag{19.4.1}$$

For a 1:1 electrolyte with general formula MX, such as NaCl, KNO_3, and $FeSO_4$, the chemical potential of the electrolyte is given as the sum of the chemical potentials of the cation and anion:

$$\mu(MX) = \mu_+ + \mu_- = \mu_+^\circ + RT \ln a_+ + \mu_-^\circ + RT \ln a_- \qquad (1:1) \quad 19.4.2$$

For NaCl, μ_+ is the chemical potential of the Na^+ ions and μ_- is the chemical potential of the Cl^- ions, and we omit the superscript "m" for notational convenience. Combining the logarithmic terms:

$$\mu(MX) = \mu_+^\circ + \mu_-^\circ + RT \ln a_+ a_- \qquad (1:1) \quad 19.4.3$$

We can relate the activities to the concentrations using Eq. 19.4.1:

$$\mu(MX) = \mu_+^\circ + \mu_-^\circ + RT \ln \left(\frac{\gamma_+ m_+ \gamma_- m_-}{m^{\circ 2}} \right) \qquad (1:1) \quad 19.4.4$$

However, it is impossible to separately determine the activity coefficients of the cations and anions. Solutions are electrically neutral; the properties of the cations alone or the anions alone cannot be determined independently. The deviations from ideality depend on the Coulomb attractions of the opposite charges and the repulsions of the like charges. Instead, experiments determine the average over all the ions in solution. The appropriate average is the geometric average; the **mean ionic activity coefficient** for a 1:1 electrolyte is defined as:

$$\gamma_\pm \equiv (\gamma_+ \gamma_-)^{\frac{1}{2}} \qquad\qquad \text{or alternately} \quad \gamma_\pm^2 \equiv \gamma_+ \gamma_- \qquad (1:1) \quad 19.4.5$$

Substituting the mean ionic activity coefficient into Eq. 19.4.4 gives:

$$\mu(MX) = \mu_+^\circ + \mu_-^\circ + RT \ln \left(\frac{\gamma_\pm^2 m_+ m_-}{m^{\circ 2}} \right) \qquad (1:1) \quad 19.4.6$$

where m_+ is the concentration of the positive ions and m_- is the concentration of the negative ions. If we define the standard state chemical potential for a 1:1 electrolyte with formula MX as $\mu^\circ(MX) \equiv \mu_+^\circ + \mu_-^\circ$, then this last equation reduces to:

$$\mu(MX) = \mu^\circ(MX) + RT \ln \left(\frac{\gamma_\pm^2 m_+ m_-}{m^{\circ 2}} \right) \qquad (1:1) \quad 19.4.7$$

We can now find the overall activity of the electrolyte, a(MX), as defined by:

$$\mu(MX) \equiv \mu^\circ(MX) + RT \ln a(MX) \qquad (1:1) \quad 19.4.8$$

Comparison of Eqs. 19.4.3 and 19.4.7 with Eq. 19.4.8 shows that the overall activity is given by:

$$a(MX) = a_+ a_- = \left(\frac{\gamma_\pm^2 m_+ m_-}{m^{\circ 2}} \right) = \left(\frac{\gamma_\pm^2 m^2}{m^{\circ 2}} \right) \qquad (1:1) \quad 19.4.9$$

The last equality results because in a 1:1 electrolyte, the concentration of the cations and anions is equal, $m = m_+ = m_-$, where m is the analytical concentration of the electrolyte. In summary, the chemical potentials of the ions <u>add</u> to give the overall chemical potential of the substance and the activities of the ions <u>multiply</u>. The results for more complicated electrolytes are analogous.

Consider a strong electrolyte with formula M_pX_q:

$$M_pX_q \rightarrow p\, M^{z+} + q\, X^{z-} \qquad\qquad 19.4.10$$

where the cations have a charge of z+ and anions have a charge of z-. The geometric average for the mean ionic activity coefficient is now:

$$\gamma_\pm \equiv (\gamma_+^p\, \gamma_-^q)^{1/v} \qquad\qquad \text{or alternately} \quad \gamma_\pm^v \equiv \gamma_+^p\, \gamma_-^q \qquad\qquad 19.4.11$$

where the total number of ions in solution is $v = p + q$. The chemical potential of the electrolyte is then the sum of the chemical potentials of the ions:

$$\mu(M_pX_q) = p\, \mu_+ + q\, \mu_- = p\, \mu_+^\circ + p\, RT \ln a_+ + q\, \mu_-^\circ + q\, RT \ln a_- \qquad\qquad 19.4.12$$

Combining the activity terms and defining the standard state as $\mu^\circ(M_pX_q) \equiv p\, \mu_+^\circ + q\, \mu_-^\circ$, gives:

$$\mu(M_pX_q) = \mu^\circ(M_pX_q) + RT \ln(a_+^p\, a_-^q) \qquad\qquad 19.4.13$$

Substitution of the concentrations using Eq. 19.4.1 gives:

$$\mu(M_pX_q) = \mu^\circ(M_pX_q) + RT \ln\left(\frac{\gamma_+^p\, m_+^p\, \gamma_-^q\, m_-^q}{m^{\circ v}}\right) \qquad\qquad 19.4.14$$

Substitution of the definition of the mean ionic activity coefficient from Eqs. 19.4.11 gives the final result:

$$\mu(M_pX_q) = \mu^\circ(M_pX_q) + RT \ln\left(\frac{\gamma_\pm^v\, m_+^p\, m_-^q}{m^{\circ v}}\right) \qquad\qquad 19.4.15$$

Comparison of the overall form, $\mu(M_pX_q) = \mu^\circ(M_pX_q) + RT \ln a(M_pX_q)$, with Eqs. 19.4.13 and 19.4.15 gives the overall electrolyte activity as:

$$a(M_pX_q) = a_+^p\, a_-^q = \left(\frac{\gamma_\pm^v\, m_+^p\, m_-^q}{m^{\circ v}}\right) \qquad\qquad 19.4.16$$

Some authors also define the mean ionic molality as:

$$m_\pm \equiv (m_+^p\, m_-^q)^{1/v} \qquad\qquad \text{or alternately} \quad m_\pm^v \equiv m_+^p\, m_-^q \qquad\qquad 19.4.17$$

Substitution of the mean ionic molality into Eq. 19.4.16 gives:

$$a(M_pX_q) = a_+^p\, a_-^q = \gamma_\pm^v \left(\frac{m_\pm}{m^\circ}\right)^v \qquad\qquad 19.4.18$$

However, for our purposes, since we are just learning about electrolyte solutions, Eq. 19.4.16 is the preferable, more direct form.

Eq. 19.4.16 is complete once the activity coefficient is determined from experiment. Extensive tables of mean ionic activity coefficients are available in standard references. Adequate estimates

of the mean ionic activity coefficient can also be determined using the continuum dielectric approximation and the Poisson equation.

Example 19.4.1:
Find the activity in terms of the mean ionic activity coefficient and the chemical potential in terms of the standard state chemical potential of an m molal solution of $CrCl_3$. Then use a concentration of 0.100 m to determine typical values for the activity.

Answer: $CrCl_3$ dissociates completely in solution to give: $CrCl_3$ (aq) $\rightarrow$ Cr^{3+} (aq) + 3 Cl^-(aq). For m molar solution, $m_+ = m$ and $m_- = 3$ m. The chemical potential is the sum of the ion contributions: $\mu(CrCl_3) = \mu_+(Cr^{3+}) + 3 \mu_-(Cl^-)$. The mean ionic activity coefficient is given with $\nu = p + q = 4$:

$$\gamma_\pm \equiv (\gamma_+ \gamma_-^3)^{1/4} \qquad \text{or alternately} \quad \gamma_\pm^4 \equiv \gamma_+ \gamma_-^3$$

The overall electrolyte activity using Eq. 19.4.16 is:

$$a(CrCl_3) = a_+ a_-^3 = \left(\frac{\gamma_\pm^4 m_+ m_-^3}{m^{\circ 4}}\right) = \left(\frac{\gamma_\pm^4 m (3\,m)^3}{m^{\circ 4}}\right) = 27\ \gamma_\pm^4 \left(\frac{m}{m^\circ}\right)^4$$

Notice that the exponent of $\gamma_\pm$ and (m/m°) are always the same and equal to the total number of ions in solution. For the example concentration of 0.100 m, $a(CrCl_3) = 2.70 \times 10^{-3}\ \gamma_\pm^4$. The chemical potential using Eq. 19.4.13 is:

$$\mu(M_pX_q) = \mu^\circ(M_pX_q) + RT \ln\left(27\ \gamma_\pm^4 \left(\frac{m}{m^\circ}\right)^4\right)$$

Example 19.4.2:
Write the solubility product equilibrium expression for Ag_2S in water in terms of the mean ionic activity coefficient. (Neglect hydrolysis of the sulfide ion.)

Answer: For the solubility of Ag_2S:

$$Ag_2S\ (s) \overset{K_{sp}}{\rightleftarrows} 2\ Ag^+ (aq) + S^{2-} (aq)$$
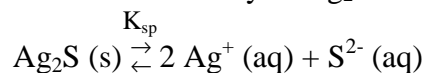
In General Chemistry you would write: $K_{sp} = [Ag^+]^2[S^{2-}]$. This expression corresponds to an ideal dilute solution. Note that in equilibrium with pure water, $m_{Ag+} = 2\ m_s$ and $m_{S2-} = m_s$, with m_s the solubility in moles of Ag_2S per kg of solvent. For a real solution, replace the concentrations with activities: $K_{sp} = (a_{Ag+})^2 (a_{S2-})$. In terms of the mean ionic activity coefficient:

$$K_{sp} = \gamma_\pm^3 \frac{(m_{Ag+})^2\ m_{S2-}}{m^{\circ 3}} = 4\ \gamma_\pm^3 \left(\frac{m_s}{m^\circ}\right)^3$$

Ionic Activity Coefficients can be Approximated Using the Debye-Hückel Approximation: To calculate the activity coefficients for small ions in solution, we assume that the deviations of

dilute electrolyte solutions from ideality are caused by electrostatic interactions between the ions and their ionic atmosphere. We assume that the solvent is modeled using a spatially constant relative permittivity and the ions are point charges with no volume. The chemical potential of an ion using Eqs. 19.1.17 and 19.4.1 can be split into a term corresponding to ideal behavior and the deviation from ideal behavior:

$$\mu_i = \mu_i^\circ + RT \ln\left(\frac{\gamma_i\, m_i}{m^\circ}\right) = \mu_i^\circ + RT \ln\left(\frac{m_i}{m^\circ}\right) + RT \ln \gamma_i = \mu_i(\text{ideal}) + RT \ln \gamma_i \qquad 19.4.19$$

The deviation from ideality is then approximated as the electrostatic work of charging the ion of interest in its ionic environment. In an ideal solution, the ion experiences an electrostatic potential established only by its own charge. In a real solution, the ion is surrounded by its "ionic halo." The electrostatic contribution to the Gibbs energy of solvation, relative to the standard state, and the activity coefficient for ion i is then given by:

$$\Delta_{sol}G_{elec} = G_{elec}(\text{real}) - G_{elec}^\circ = RT \ln \gamma_i = N_A\, w_{elec}(\text{real}) - N_A\, w_{elec}(\text{ideal}) \qquad 19.4.20$$

The activity coefficient for ion i is then $RT \ln \gamma_i = \Delta_{sol}G_{elec}$ with reference to a Henry's Law standard state. The result is called the **Debye-Hückel approximation**. We present the results in this section and derive the relationship in the next, Eq. 19.5.35:

$$\ln \gamma_\pm = -1.825 \times 10^6\, |z_+\, z_-| \left(\frac{d_o}{\varepsilon_r^3\, T^3}\right)^{\!1/2} I^{1/2} \qquad \text{(continuum dielectric, point charges, dilute)} \; 19.4.21$$

where d_o is the density and ε_r is the dielectric constant of the solvent, and I is the ionic strength. The ionic strength is defined as, Eq. 19.5.25:

$$I = \tfrac{1}{2} \sum z_i^2 \frac{m_i}{m^\circ} \qquad\qquad 19.4.22$$

The sum is over <u>all</u> ions in solution, including buffers and supporting electrolytes. The ionic strength is the appropriate measure of the total ion concentration in solution. For the special case of a unipositive-uninegative salt, the ionic strength is equal to the concentration. For example, for m molal NaCl: $I = \tfrac{1}{2}\,[z_+^2\, m_+/m^\circ + z_-^2\, m_-/m^\circ] = \tfrac{1}{2}\,[(1)^2\, m/m^\circ + (-1)^2\, m/m^\circ] = m/m^\circ$.

The T^3 term in Eq. 19.4.21 results from the disruptive influence of molecular motion on the formation of the ionic "halo" around each ion, as predicted from the Boltzmann distribution. For water at 25°C, $d_o = 0.99704$ g mL^{-3} and $\varepsilon_r = 78.54$, so that Eq. 19.4.21 simplifies to:

$$\ln \gamma_\pm = -1.171\, |z_+\, z_-|\, I^{1/2} \qquad \text{or} \qquad \log \gamma_\pm = -0.509\, |z_+\, z_-|\, I^{1/2}$$

$$\text{(continuum dielectric, point spherical ions, dilute aq., 25°C)} \quad 19.4.23$$

The Coulomb attractions of the positive and negative charges on the ions produce strong negative deviations from ideality. A plot of the experimental mean ionic activity coefficients for several electrolytes as compared to the predictions based on Eq. 19.4.23 is shown in Figure 19.4.2. The Debye-Hückel approximation gives activity coefficients higher that the experimental values at moderate concentrations. Deviations from the Debye-Hückel approximation persist even at low concentrations. The Debye-Hückel approximation is a limiting law; the approximation improves in the limit that $I \to 0$. The mean ionic activity coefficients calculated using the Debye-Hückel approximation are useful for ionic equilibrium problems.
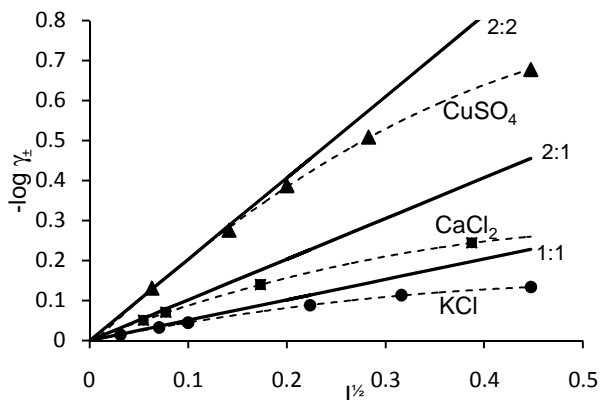
Figure 19.4.2: A plot of $-\log \gamma_\pm$ versus the square root of ionic strength. The Debye-Hückel approximation predicts linear behavior for this plot, while the experimental values (connected with a dotted line) have $\gamma_\pm$ values below that predicted by the theory. The Debye-Hückel approximation becomes exact only in very dilute solution; when $I \to 0$.

Example 19.4.3: *Debye-Hückel Approximation*
Calculate the mean ionic activity coefficient for aqueous 0.100 m $CrCl_3$ at 25°C.

Answer: Using Eq. 19.4.22 for $CrCl_3$, $z_+ = 3$, $z_- = -1$, $m_{Cr^{3+}} = m$ and $m_{Cl^-} = 3$ m:

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

For 0.100 m $CrCl_3$: $I = 0.600$. Using Eq. 19.4.23:

$$\ln \gamma_\pm = -1.171\,|z_+\,z_-|\,I^{1/2} = -1.171\,|(3)(-1)|\,(0.600)^{1/2} = -2.721_2$$

or $\log \gamma_\pm = -0.509\,|z_+\,z_-|\,I^{1/2} = -0.509\,|(3)(-1)|\,(0.600)^{1/2} = -1.182_8$

  giving $\gamma_\pm = 0.0658$, or very strong deviations from ideality.

Ionic Strength Changes the Solubility of Sparingly Soluble Salts: A good example problem that shows the utility of the Debye-Hückel approximation is the ionic strength dependence of the solubility of sparingly soluble salts. Barium salts are very toxic, yet aqueous slurries of $BaSO_4$ are commonly used in gastrointestinal X-ray imaging. How can such a toxic salt be in common use for radiological imaging? Consider the solubility of $BaSO_4$ in aqueous solution at 25°C:

$$BaSO_4 \text{ (s)} \underset{\leftarrow}{\rightarrow} Ba^{2+} \text{ (aq)} + SO_4^{2-} \text{ (aq)} \qquad\qquad 19.4.24$$

In pure water in equilibrium with $BaSO_4$, $m_s = m_{Ba^{2+}} = m_{SO_4^{2-}}$, where m_s is the solubility in moles $BaSO_4$ dissolved per kg of solution. In General Chemistry, in the ideal dilute solution limit, you wrote the equilibrium expression as $K_{sp} \approx [Ba^{2+}][SO_4^{2-}] = m_s^2$, with K_{sp} the solubility product equilibrium constant. The ideal solubility is:

$$m_s^{ideal} = \sqrt{K_{sp}} \qquad\qquad 19.4.25^\dagger$$

For real solutions we replace the concentration by the activity:

$$K_{sp} = a_{Ba^{2+}}\, a_{SO_4^{2-}} = \frac{\gamma_\pm^2\, m_{Ba^{2+}}\, m_{SO_4^{2-}}}{m^{\circ 2}} = \gamma_\pm^2 \left(\frac{m_s}{m^\circ}\right)^2 \qquad\qquad 19.4.26$$

Solving for the solubility gives:

$$m_s = m^\circ \sqrt{\frac{K_{sp}}{\gamma_\pm^2}} \qquad\qquad 19.4.27$$

Example 19.4.4
Calculate the K_{sp} of $BaSO_4$ given that the solubility in pure water at 25°C is 1.06×10^{-5} m. Use the Debye-Hückel approximation to approximate the mean ionic activity coefficient.

Answer: The ionic strength for an m molal solution of $BaSO_4$ (aq) is given by Eq. 19.4.22:

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

The solubility of $BaSO_4$ is 1.06×10^{-5} m, giving the ionic strength as $I = 4(1.06 \times 10^{-5}\ m/1\ m) = 4.24 \times 10^{-5}$. Eqs. 19.4.23 give the mean ionic activity coefficient as:

$$\ln \gamma_\pm = -1.171\, |z_+\, z_-|\, I^{1/2} = -1.171\, |(2)\,(-2)|\, (4.26 \times 10^{-5})^{1/2} \qquad \text{so that}\ \ \gamma_\pm = 0.970$$

Then the K_{sp} is given by Eq. 19.4.26: $K_{sp} = \dfrac{\gamma_\pm^2\, m_{Ba^{2+}}\, m_{SO_4^{2-}}}{m^{\circ 2}} = (0.970)^2(1.06 \times 10^{-5})^2 = 1.06 \times 10^{-10}$.

Had we neglected the activity coefficient, the K_{sp} would have been 6% larger: $K_{sp}^{ideal} \approx (1.06 \times 10^{-5})^2 \approx 1.12 \times 10^{-10}$. Even in such a very dilute solution, the deviation from ideality exceeds normal experimental error.

Example 19.4.5: *The Salt Effect*
Calculate the solubility of $BaSO_4$ in a solution of 0.100 m NaCl.

Answer: The ionic strength includes all ions in solution. The effect of non-ideality on the solubility is small so we can approximate the contribution of dissolved $BaSO_4$ to the overall ionic strength using the pure-water solubility. Then we add in all the other electrolytes:

$$I = \tfrac{1}{2} \sum z_i^2\, \frac{m_i}{m^\circ} = \tfrac{1}{2}\,[(2)^2\, m_{Ba^{2+}} + (-2)^2\, m_{SO_4^{2-}} + (1)^2\, m_{Na^+} + (-1)^2\, m_{Cl^-}]/m^\circ = 0.100$$

The ionic strength of the dissolved $BaSO_4$ is negligible compared to the added electrolyte. The mean ionic activity coefficient of aqueous $BaSO_4$ is decreased to:

$$\ln \gamma_{\pm} = -1.171 \; |z_+ \; z_-| \; I^{\frac{1}{2}} = -1.171 \; |(2) \; (-2)| \; (0.100)^{\frac{1}{2}} \quad \text{so that} \; \gamma_{\pm} = 0.227$$

Giving the solubility from Eq. 19.4.27:

$$m_s = m° \sqrt{\frac{K_{sp}}{\gamma_{\pm}^2}} = (1 \; m) \sqrt{\frac{1.06 \times 10^{-10}}{(0.227)^2}} = 4.54 \times 10^{-5} \; m$$

or a factor of 4.3 higher than in pure water. The solubility of $BaSO_4$ is still quite small, minimizing the toxicity for medical imaging uses.

From the point of view of the solubility product equilibrium expression, the added NaCl is a **non-participating electrolyte**. However, the solubility of $BaSO_4$ is greater in 0.100 m NaCl than pure water, because of the increase in ionic strength. This effect is called the **salt effect** for electrolyte solubility. The salt effect is important in areas such as soil geochemistry. The increased ionic strength upon salinization of agricultural land in arid climates can increase the leaching of nutrients into ground water. Salinization results from extensive irrigation.

Osmotic Pressure Depends on Total Number of Ions in Solution: Another ramification of the additivity of the chemical potentials for ions is the dependence of the colligative properties on ion number, Sec. 18.4. The osmotic pressure is a function of all species present in solution, as are all colligative property based measurements. For multicomponent solutions the osmotic coefficient is given by a sum over all solute species, s, in Eq. 19.1.20. The chemically effective concentration determined in osmometry is called the **osmolality**, $\mathcal{E}_m$:

$$\phi \equiv - \frac{\ln a_A}{\sum\limits_{i=1}^{s} m_i \; (\mathfrak{M}_A/1000 \; \text{g kg}^{-1})} \qquad\qquad \mathcal{E}_m = \sum\limits_{i=1}^{s} m_i \; \phi \qquad\qquad 19.4.28$$

For a single electrolyte with analytical concentration m that dissociates into ν ions in solution, $\Sigma \; m_i = \nu m$ and then $\mathcal{E}_m = \nu \; m \; \phi$. The osmolality is the parameter necessary to determine osmotic equilibrium in living organisms. To make further progress on understanding solution non-idealities, we need to take a molecular approach.

19.5 The Gibbs Energy of Solvation can be Approximated Using the Poisson Equation

The Gibbs Energy of Solvation and Electrical Work: In continuum dielectric models, the solvent is modeled as a continuous, uniform medium with relative permittivity, ε_r. Since there are no discrete solvent molecules, specific interactions such as extensive hydrogen bonding or directional dipole-dipole interactions cannot be studied. However, the continuum dielectric model does allow the study of the stabilization and destabilization of polar species in solution.

The electrostatic energy of two charges, q_i and q_j, separated by a distance r_{ij} in a uniform medium with relative permittivity ε_r is given by the Coulomb energy, Eq. 8.7.18:

$$\varepsilon(r_{ij}) = \frac{q_i q_j}{4\pi\varepsilon_o\varepsilon_r \; r_{ij}} \qquad\qquad 19.5.1$$

where ε_o is the permittivity of free space, which is the permittivity of vacuum. The relative permittivity for water is 78.54 and hexane is 1.815 at 25°C. The relative permittivity is also

called the dielectric constant. The Coulomb energy is the product of the electric potential, $\phi_i(r_{ij})$, multiplied by the charge of interest. For i as the central charge, the interaction with charge j in terms of the electric potential, using Eq. 19.5.1, is:

$$\varepsilon(r_{ij}) = \phi_i(r_{ij})\, q_j \qquad \text{with} \quad \phi_i(r_{ij}) = \frac{q_i}{4\pi\varepsilon_o\varepsilon_r\, r_{ij}} \qquad \text{(uniform dielectric)} \quad 19.5.2$$

Because the relative permittivity appears in the denominator of the electric potential, the effect of the relative permittivity of the solvent is to attenuate the electrostatic interaction. Interaction energies in water are less than in non-polar solvents.
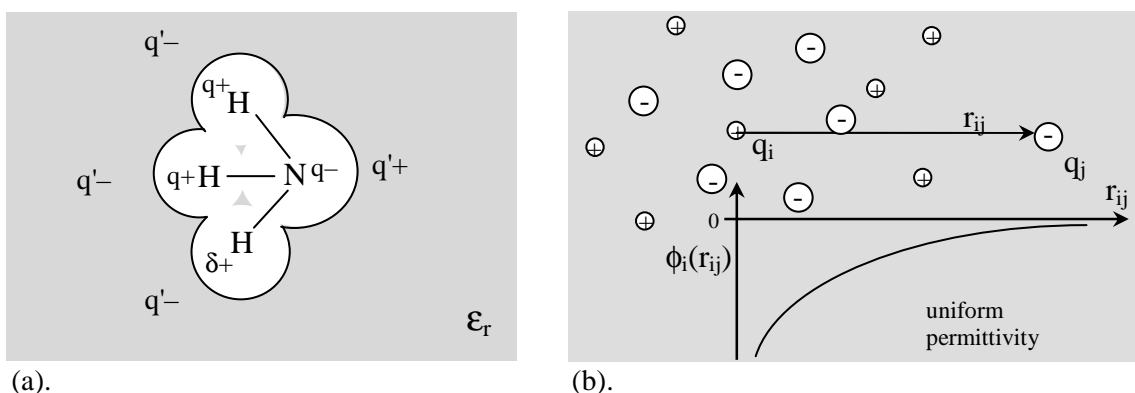
(a).   (b).

Figure 19.5.1: In the continuum dielectric model, the solvent is assumed to be a continuous medium of constant dielectric, ε_r. (a). The solute induces "image" charges in the solvent. (b). An ion is surrounded by a halo of ions of opposite charge. The relative permittivity of the solvent screens the interactions. The dielectric screening is symbolized by the gray background.

The electrostatic distribution in a molecule or ion is modeled by point charges that are placed at each nucleus. The molecule or ion is then placed in a cavity in the solvent. The size of the cavity is determined by the Van der Waals surface of the molecule. The relative permittivity inside this cavity is taken to be that of vacuum, $\varepsilon_r = 1$. We will apply the model for two specific extremes, small polar molecules and small spherical ions. We will also discuss applications to proteins. Consider first a polar molecule. The presence of partial charges in the molecule polarizes the solvent, Figure 19.5.1a. These induced charges, or image charges, effectively "mirror" the charges on the molecule. For polar molecules, the electrostatic interaction energy is the sum of the electrostatic energies of the induced image charges in the solvent with the partial charges on the atoms in the molecule or ion.

The Gibbs energy of solvation is approximated as:[13,14]

$$\Delta_{sol}G = \Delta_{sol}G_{VdW} + \Delta_{sol}G_{cav} + \Delta_{sol}G_{elec} \qquad\qquad 19.5.3$$

where $\Delta_{sol}G_{VdW}$ is the solute-solvent Van der Waals interaction, $\Delta_{sol}G_{cav}$ is the work necessary to create the cavity in solvent, and $\Delta_{sol}G_{elec}$ is the electrostatic contribution, Eq. 19.4.20. $\Delta_{sol}G_{cav}$ is approximated by:

$$\Delta_{sol}G_{cav} = (\text{surface tension})(\text{surface area}) = \gamma\,\sigma \qquad\qquad 19.5.4$$

This term includes the entropy change for rearrangement of solvent molecules around the molecule. The $\Delta_{sol}G_{VdW}$ and $\Delta_{sol}G_{cav}$ terms are often combined, since both are approximately proportional to the solvent accessible surface area. The combined Van der Waals and cavity surface tension in aqueous solution at 25°C is 7-10 J/Å^2.

Now consider a small spherical ion in solution. The neighborhood of an ion is predominately comprised of counter ions of opposite charge, Figure 19.5.1b. Near a central cation, the concentration of anions is greater than the bulk and the concentration of cations is less than the bulk. $\Delta_{sol}G_{elec}$ includes the interaction of central ion i with the ionic atmosphere of neighbor ions j. The Coulomb interaction of the central ion with this halo is stabilizing, negative in energy. The permittivity of the solvent and the counter ions attenuate, or screen, electrostatic interactions.

The screening caused by the ionic atmosphere is determined by the distribution of ions near the central ion. The distribution function, p(r) dr, is the probability of finding a counter ion at a distance r to r + dr from the central ion. This distribution is given by the Boltzmann distribution using the Coulomb energy of the interaction of the central ion i with counterion j, $\phi_i(r)q_j$. The number of ions j at a given point, a distance r from the central solute ion i, is:

$$N_j = N_{oj}\, e^{\frac{-\phi_i(r)q_j}{kT}} \qquad\qquad 19.5.5$$

where N_{oj} is the total number of ions j in solution. The probability of finding an ion for any angle at a radius of r from the central ion is the **radial probability distribution** for ion j is:

$$p_j(r)\, dr = 4\pi r^2 N_{oj}\, e^{\frac{-\phi_i(r)q_j}{kT}}\, dr \qquad\qquad 19.5.6$$

The $4\pi r^2 dr$ is the annular volume at all angles between the radius of r and r + dr. This probability distribution of the counter ion halo is shown in Figure 19.5.2.
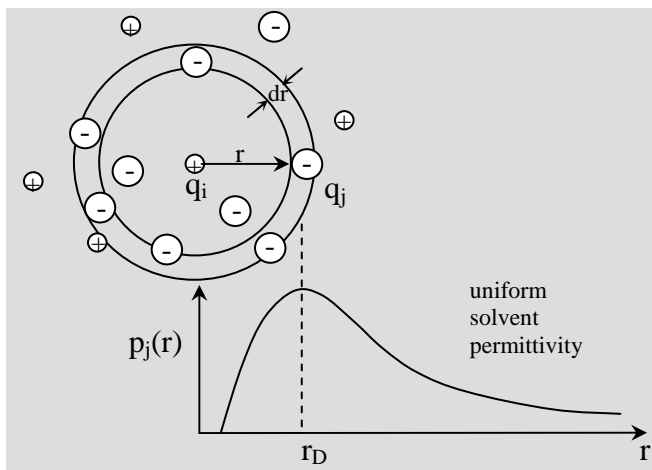

Figure 19.5.2: The distribution of counter ions around a central ion i. The ionic atmosphere has a probability maximum at the Debye length, r_D.

The Boltzmann distribution takes into account the thermal jostling of molecular collisions within the solvent that disrupt the ionic halo. The exponential decrease of the Boltzmann distribution and the r^2 increase of the annular volume multiply to give a distribution that has a maximum. The

maximum probability distance is called the **Debye length**, r_D. The Debye length is a measure of the thickness of the ionic atmosphere. The Debye length for very dilute aqueous solutions with uniform solvent dielectric and unipositive and uninegative ions (e.g. NaCl) gives:

$$r_D = \frac{305 \text{ pm}}{(m/m^\circ)^{1/2}} = \frac{1}{\kappa} \qquad \text{(dilute, aq, 25°C, unipositive-uninegative)} \qquad 19.5.7$$

The concentration term, $m^{1/2}$, in the denominator is the square root of the ionic strength for a unipositive-uninegative electrolyte. We discuss ionic strength in more detail below. The Debye length is often specified by the reciprocal parameter κ. The polarization of the solvent and the ionic halo determine the electric potential at each point in the solution. Once the electric potential is known, the probability distribution of the ions can be calculated. Unfortunately, these calculations depend on each other. A common approach is to first make a rough guess of the electric potential and then to solve for the counter ion distribution. This distribution is then used to calculate a better guess for the electric potential. This process of successive approximations is continued until the electric potential no longer changes.

   The electric potential is used to calculate $\Delta_{sol}G_{elec}$, Eq. 19.4.20. The work necessary to charge the solute ion within the solution is calculated with $q_i = z_i e$ and z_i the charge number on ion i:

$$w_{elec} = \int_0^{z_i e} \phi_i \, dq_i \qquad 19.5.8$$

where ϕ_i corresponds to a real or ideal solution. The calculations are computationally demanding so approximations are often made. We proceed by considering small spherical ions.

The Gibbs Energy of Solvation is Moderated by Dielectric and Ionic Shielding: The electric potential is calculated from the Poisson equation. The Poisson equation depends on the charge density within the solution. The charge density within the solution for a charge q_i is the charge multiplied by the probability that the charge is at position (x,y,z):

$$\rho_i(x,y,z) = q_i \, p_i(x,y,z) \qquad 19.5.9$$

The charge density is the charge per unit volume, which in general depends on the polarization of the solvent and the distribution of ions in the halo around the solute. The Poisson equation also depends on the spatial variation of the relative permittivity, $\epsilon(r) = \epsilon_o \, \epsilon_r(r)$. The Poisson equation is:

$$\nabla^2 \phi_i(x,y,z) = -\frac{\rho_i(x,y,z)}{\epsilon(x,y,z)} \qquad 19.5.10$$

The term on the left is the curvature of the electric potential. The curvature is given by:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad 19.5.11$$

The Poisson equation shows that the larger the magnitude of the charge density, the narrower the range for the electric potential; the slope changes more with distance, Figure 19.5.3. For a spherical electric potential, ϕ_i is only a function of r, the radial distance. The curvature is then only a function of r, and the Poisson equation for a spherical potential is:

$$\frac{1}{r}\frac{\partial^2(r \, \phi_i(r))}{\partial r^2} = -\frac{\rho_i(r)}{\epsilon(r)} \qquad \text{(spherical ion)} \qquad 19.5.12$$
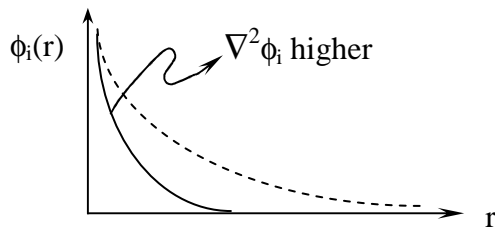
Figure 19.5.3: For a positive central ion, the more negative the charge density at small r, the higher the curvature of the electric potential. The charge density screens the electrostatic interactions.

To get a feeling for the Poisson equation we start with a very simple model. This model is for electrolyte solutions of small spherical ions. The result is the Debye-Hückel model, when applied to very dilute solutions. The ions are modeled as point charges embedded in a uniform solvent. In this model, ions do not have a "volume," and no surface tension term is used. For a uniform solvent dielectric, $\varepsilon_r(r) = \varepsilon_r$. The charge density is the sum of the charge density for the positive and negative ions in solution:

$$\rho_+(r) = q_+ \frac{N_+}{V} e^{\frac{-\phi_i(r)q_+}{kT}} \qquad \rho_-(r) = q_- \frac{N_-}{V} e^{\frac{-\phi_i(r)q_-}{kT}} \qquad \qquad 19.5.13$$

$$\rho_i(r) = \rho_+(r) + \rho_-(r) = q_+ \frac{N_+}{V} e^{\frac{-\phi_i(r)q_+}{kT}} + q_- \frac{N_-}{V} e^{\frac{-\phi_i(r)q_-}{kT}} \qquad 19.5.14$$

The concentration of ions is also assumed to be very small so that $\phi_i(r) \ll kT$ and the exponential term in the Boltzmann distribution is expanded as a Taylor series:

$$e^{\frac{-\phi_i(r)q_j}{kT}} \approx 1 - \frac{\phi_i(r)q_j}{kT} \qquad \qquad \text{(dilute)} \qquad 19.5.15$$

Then the charge density of the ions simplifies to:

$$\rho_i(r) = \rho_+(r) + \rho_-(r) = q_+\left(\frac{N_+}{V}\right)\left(1 - \frac{\phi_i(r)q_+}{kT}\right) + q_-\left(\frac{N_-}{V}\right)\left(1 - \frac{\phi_i(r)q_-}{kT}\right)$$

$$\rho_i(r) = \left(q_+\frac{N_+}{V} + q_-\frac{N_-}{V}\right) - \left(\frac{N_+}{V}\right)\frac{\phi_i(r)q_+^2}{kT} - \left(\frac{N_-}{V}\right)\frac{\phi_i(r)q_-^2}{kT} \qquad \text{(dilute)} \qquad 19.5.16$$

The first term cancels because of charge neutrality; the numbers of positive and negative charges are equal, which gives:

$$\rho_i(r) = -\frac{\phi_i(r)}{kT}\left(q_+^2\frac{N_+}{V} + q_-^2\frac{N_-}{V}\right) \qquad \qquad \text{(dilute)} \qquad 19.5.17$$

The term in parentheses is the ionic strength. If there are several sources of ions, this sum is extended to include all ions in solution; all ions contribute to the ionic atmosphere. The possible sources include background electrolytes or buffers. With $q_j = z_j e$ for ion j, Eq. 19.5.17 is:

$$\rho_i(r) = -\frac{\phi_i(r)}{kT} \sum_{j=1}^{s} q_j^2 \frac{N_j}{V} = -\frac{\phi_i(r)e^2}{kT} \sum_{j=1}^{s} z_j^2 \frac{N_j}{V} \qquad \text{(dilute)} \qquad 19.5.18$$

The sum extends over all s ions in solution. Then κ, the inverse Debye length, is defined as:

$$\kappa^2 \equiv \frac{e^2}{\epsilon_r \epsilon_o kT} \sum_{j=1}^{s} z_j^2 \left(\frac{N_j}{V}\right) \qquad 19.5.19$$

The N_j/V terms are the number concentrations with N_j equal to the number of ions of type j in solution, and V the volume of the solution in m^3. Substitution of κ^2 and Eq. 19.5.18 into the Poisson equation, Eq. 19.5.12, gives:

$$\frac{\partial^2 (r\,\phi_i(r))}{\partial r^2} = \kappa^2 \, (r\,\phi_i(r)) \qquad \text{(continuum dielectric, dilute point ions)} \quad 19.5.20$$

The solution to this equation is in the form:

$$\phi_i(r) = \frac{C}{r} e^{-\kappa r} \qquad \text{(continuum dielectric, dilute point ions)} \quad 19.5.21$$

The C constant is evaluated using the boundary conditions giving the electric potential as:

$$\phi_i(r) = \frac{q_i}{4\pi\epsilon_o\epsilon_r r} e^{-\kappa r} \qquad \text{(continuum dielectric, dilute point ions)} \quad 19.5.22$$

This result is called the **screened Coulomb potential** or **shielded Coulomb potential**, which takes into account the permittivity of the solvent and the interaction of the solute ion with its ionic atmosphere. Because $e^{-\kappa r} < 1$, the ionic halo decreases the electrostatic energy of interactions in solution. The concentrations are converted into molality using the approximation:

$$m_j = \frac{N_j/N_A}{V\,(1000\text{ L m}^{-3})\,d_o} \qquad \text{(dilute)} \qquad 19.5.23$$

where d_o is the density of the solvent in kg L^{-1}, which is equivalent to g mL^{-1}. Substituting this conversion into Eq. 19.5.19 gives κ^2 in more useful units:

$$\kappa^2 = \frac{e^2\,(1000\text{ L m}^{-3})\,d_o\,N_A\,m^\circ}{\epsilon_r\epsilon_o kT} \sum_{j=1}^{s} z_j^2 \frac{m_j}{m^\circ} \qquad \text{(point ions)} \qquad 19.5.24$$

with m° the standard state molality, $m^\circ = 1$ m. The summation is the basis of the definition of the ionic strength:

$$I \equiv \frac{1}{2} \sum_{j=1}^{s} z_j^2 \frac{m_j}{m^\circ} \qquad 19.5.25$$

which is unitless. Substitution of the fundamental constants, the density and relative permittivity of water at 25°C, $z_+ = 1$, $z_- = -1$, and $m = m_+ = m_-$ into Eq. 19.5.24 gives the Debye length specifically for a unipositive-uninegative salt, Eq. 19.5.7.

To find the deviation from ideality, the electrical work of charging the ion in real solution compared to the work in an ideal standard state solution is calculated using Eqs. 19.5.22 and 19.4.19. Combining the real and ideal integrals gives:

$$\Delta_{sol}G_{elec} = G_{elec}(real) - G^{\circ}_{elec} = RT \ln \gamma_i = N_A \, w(real) - N_A \, w(ideal)$$

$$RT \ln \gamma_i = N_A \int_0^{z_i e} [\phi_i^{real} - \phi_{ii}^{ideal}] \, dq_i \qquad \text{(continuum dielectric, dilute point ions)} \quad 19.5.26$$

The electric potentials are at the central ion, $r \to 0$. The electric potential in an ideal Henry's Law standard state corresponds to an infinitely dilute solution, which has no ionic atmosphere, $\kappa = 0$. The difference in electric potentials is then:

$$\phi_i^{real} - \phi_i^{ideal} = \left(\frac{q_i}{4\pi\varepsilon_o\varepsilon_r \, r} e^{-\kappa r}\right) - \left(\frac{q_i}{4\pi\varepsilon_o\varepsilon_r \, r}\right) = \frac{q_i}{4\pi\varepsilon_o\varepsilon_r} \left(\frac{e^{-\kappa r} - 1}{r}\right) \qquad 19.5.27$$

Taking the limit as $r \to 0$ using l'Hôpital's rule gives the electric potential at the central ion caused by the ionic atmosphere as:

$$[\phi_i^{real} - \phi_i^{ideal}]_{r=0} = -\frac{q_i \, \kappa}{4\pi\varepsilon_o\varepsilon_r} \qquad \text{(continuum dielectric, dilute point ions)} \quad 19.5.28$$

Substituting this expression into Eq. 19.5.26, with $\int q_i \, dq_i = q_i^2/2$, and $\kappa = 1/r_D$ gives:

$$\Delta_{sol}G_{elec} = RT \ln \gamma_i = -\frac{N_A \, \kappa}{4\pi\varepsilon_o\varepsilon_r} \int_0^{z_i e} q_i \, dq_i = -\frac{N_A \, z_i^2 \, e^2 \, \kappa}{8\pi\varepsilon_o\varepsilon_r} = -\frac{N_A \, z_i^2 \, e^2}{8\pi\varepsilon_o\varepsilon_r \, r_D}$$

$$\text{(continuum dielectric, dilute point ions)} \quad 19.5.29$$

This expression is equivalent to the Coulomb interaction of an induced charge, $-z_i$, with the central charge, z_i, separated by a distance $2 \, r_D$. This result is the foundation for the concept of the "image" charges that we discussed above. Solving for the activity coefficient gives:

$$\ln \gamma_i = -\left(\frac{N_A \, e^2}{8\pi\varepsilon_o\varepsilon_r \, r_D \, RT}\right) z_i^2 \qquad \text{(electrostatic only, dilute spherical point ions)} \quad 19.5.30$$

The mean ionic activity coefficient for an M_pX_q salt is given by:

$$\ln \gamma_{\pm} = \frac{p \ln \gamma_+ + q \ln \gamma_-}{p + q} \qquad 19.5.31$$

Substituting Eq. 19.5.30, separately for the positive and negative ions into Eq. 19.5.31 gives:

$$\ln \gamma_{\pm} = -\left(\frac{N_A \, e^2}{8\pi\varepsilon_o\varepsilon_r \, r_D \, RT}\right)\left(\frac{p \, z_+^2 + q \, z_-^2}{p + q}\right) \qquad 19.5.32$$

Charge neutrality for the solution gives $(pz_+ + qz_-) = 0$. Multiplying this equation by $(z_+ + z_-)$ gives:

$$(z_+ + z_-)(pz_+ + qz_-) = 0 \qquad \text{or} \quad p \, z_+^2 + q \, z_+z_- + p \, z_+z_- + q \, z_-^2 = 0 \qquad 19.5.33$$

Solving this last equation for the stoichiometric factor in Eq. 19.5.32 gives:

$$\left(\frac{p \, z_+^2 + q \, z_-^2}{p + q}\right) = -z_+z_- = |z_+ \, z_-| \qquad 19.5.34$$

$$\ln \gamma_\pm = - \left(\frac{e^6 \, (1000 \text{ L m}^{-3}) \, d_o \, N_A \, m^\circ}{32\pi^2 \, \varepsilon_o^3 \, \varepsilon_r^3 \, k^3 T^3} \right)^{1/2} |z_+ \, z_-| \, I^{1/2}$$

(continuum dielectric, electrostatic only, dilute point ions) 19.5.35

This expression is the **Debye Hückel approximation** for the mean ionic activity coefficient.

In summary, the shielded Coulomb potential accounts for the interaction of an ion with its ionic atmosphere. As a point of comparison, the shielded Coulomb potential reduces to Coulomb's Law for very dilute solutions:

$$I \to 0 \,, \quad \kappa \to 0 \,, \quad r_D \to \infty \,, \quad e^{-\kappa r} \to 1 \,, \quad \phi_i(r) \to \text{Coulomb's Law} \qquad \text{(very dilute)} \quad 19.5.36$$

The Born Approximation Takes into Account the Size of the Solute: Modeling ions as point charges with no radius is very approximate. A model that takes into account the size of the ion has been developed, which is called the **Born approximation**. The ion is modeled as a point charge in spherical cavity of radius r_i. The relative permittivity inside the sphere is that of a vacuum, $\varepsilon_r = 1$, and the solvent outside of the ion radius is assumed to be uniform with relative permittivity ε_r, Figure 19.5.4a. The model applies to very dilute electrolytes or non-electrolyte solutions. In other words, there are no counter ions nearby, as in the example above. The solution to the Poisson equation is now more involved because the relative permittivity and the charge density both change with position. We simply present the results. The electric potential at the center of a spherical ion of radius r_i in the Born approximation is:

$$\phi_i(0) = \frac{q_i}{4\pi\varepsilon_o\varepsilon_r \, r_i}$$

(very dilute spherical point ion, radius r_i) 19.5.37

The presence of the ion polarizes the solvent. The actual charge density in the bulk of the solvent remains small, because the polarization dipoles for each solvent molecule cancel each other, except at the boundaries, Figure 19.5.4b.[2] However, a surface charge is induced at the cavity surface, which is oppositely charged from the ion. This surface charge creates an electric field at the center of the sphere, which is called the **reaction field**.[2] The surface charge behaves like an "image" charge that is in the bulk of the solvent opposite the point charge on the ion.[2]
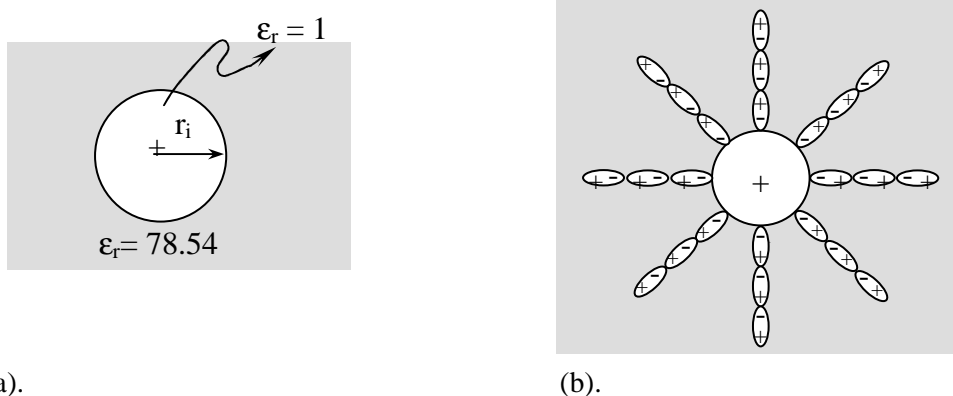

(a).   (b).

Figure 19.5.4: (a). The Born Approximation assumes a charge in a spherical cavity of radius r_i with $\varepsilon_r=1$ inside the cavity and ε_r constant for the uniform solvent for $r > r_i$. (b). The ion polarizes the solvent. The solvent dipoles don't cancel at the surface of the cavity, giving a surface charge. The surface charge generates a potential at the point charge.

The electric work in charging the ion is calculated using $dw_{el} = \phi_i \, dq_i$:

$$w_{el} = \int_0^{Z_i e} \phi_i \, dq = \frac{1}{4\pi\varepsilon_o\varepsilon_r \, r_i} \int_0^{Z_i e} q_i \, dq_i \qquad \text{(very dilute spherical ion)} \qquad 19.5.38$$

You might wonder why the work is not simply just $\phi_i \, q_i$, since an ion has an integral charge, $+1e$, $+2e$, $-1e$, etc. The integral takes into account the "**self-interaction**;" the ion is interacting with its self-induced charge.[15] To do the integral, the charge is visualized as being added in small increments. Each new increment interacts with the induced charges that have built up from previous increments, Figure 19.5.5, and the integral is $\int q_i \, dq_i = q_i^2/2$. This process is also used in the integral in Eq. 19.5.29 for the Debye-Hückel approximation.
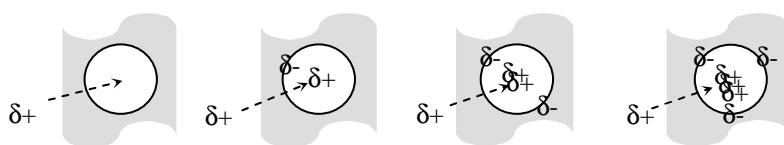

Figure 19.5.5: The work integral is done in small steps for Eqs. 19.5.30 and 19.5.38.

The electrical work in solution, from Eq. 19.5.38, is then:

$$w_{elec} = \frac{z_i^2 \, e^2}{8\pi\varepsilon_o\varepsilon_r \, r_i} \qquad\qquad 19.5.39$$

The total electrostatic contribution to the Gibbs energy of solvation is calculated using Eq. 19.4.20 for an ideal gas phase standard state by finding the difference between the electrical work necessary to charge the ion in the solvent and the work to charge the ion in vacuum:

$$\Delta_{sol}G_{elec} = N_A \, w(\text{real}) - N_A \, w(\text{vacuum}) \qquad \text{(ideal gas standard state)} \qquad 19.5.40$$

where the permittivity of vacuum is just ε_o. The electrostatic contribution to the Gibbs energy of solvation is given by Eqs. 19.5.39 and 19.5.40 as:

$$\Delta_{sol}G_{elec} = \frac{z_i^2 \, e^2 N_A}{8\pi \, r_i}\left(\frac{1}{\varepsilon_r\varepsilon_o} - \frac{1}{\varepsilon_o}\right) = \frac{-z_i^2 \, e^2 N_A}{8\pi\varepsilon_o \, r_i}\left(1 - \frac{1}{\varepsilon_r}\right) \qquad \text{(very dilute spherical ion)} \qquad 19.5.41$$

The Generalized Born Approximation is Used for More Complex Molecules and Ions:
Eq. 19.5.41 is for a simple spherical ion with a given radius in the absence of an ionic atmosphere. Eq. 19.5.29 is for a point ion with an ionic atmosphere, at a given ionic strength. The **Generalized Born** approach includes finite size and an ionic atmosphere for a molecule or ion with a complex shape by solving the Poisson equation numerically. The electrostatic energy for multi-atom ions and molecules is evaluated as the sum over all the partial charges in the solute for a molecular surface calculated from the solvent accessible surface.[13] To complete the calculation of the solvation Gibbs energy, the cavity and Van der Waals terms are added. Because these terms depend on the solvent accessible surface area of the solute, the general formulation of the Born approximation for molecules and non-spherical ions is called the Generalized Born/Solvent Accessible surface area approach, or **GB/SA** for short.[13]

The GB/SA method is rapid and does a reasonable job of modeling non-specific solvation effects. The screening effect of the relative permittivity of the solvent, the ionic atmosphere, and solvent polarization are included. The electrostatic terms primarily affect the enthalpy of solvation. The entropy changes are roughly approximated by the cavity term.

The GB/SA approach can be used for any solvent. The relative permittivity of the solvent is required. In addition, the average solvent molecule radius is necessary to calculate the solvent accessible surface area. Larger solvents cannot approach the solute as closely as water and the corresponding solvent accessible surface area is larger. The surface tension of the solvent is also needed. GB/SA treatments are used by organic chemists for studies of the solution conformation of molecules and the stabilization of polar transition states and intermediates. Solvation effects also have an important influence on molecular recognition.

The Surfaces of Enzymes Interact with Counter Ions and the Solvent to Create Shaped Electric Fields: The Generalized Born approximation and more advanced electrostatic treatments are important in modeling the surfaces of proteins and nucleic acids.[16] The combination of the partial charges on the amino acids in a protein and the corresponding polarization of the solvent create strong electric fields near the surface of proteins that may help guide substrates into the active sites of enzymes and may help orient proteins for efficient protein-protein binding.

Acetylcholine is a quaternary amine. The binding pocket of acetylcholine esterase is lined with amino acids that have negatively charged side chains, which enhance the interaction with the positive charge on acetylcholine, Figure 19.5.6a. GB/SA calculations in water with an ionic strength of 0.1 m show that the electric field near the binding pocket extends into the solvent, Figure 19.5.6b. The polar and charged amino acids on the surface of the enzyme polarize the solvent and create an ionic atmosphere that helps optimize the interaction with the substrate. The strong, specifically shaped electric field may help guide the substrate into the binding pocket.
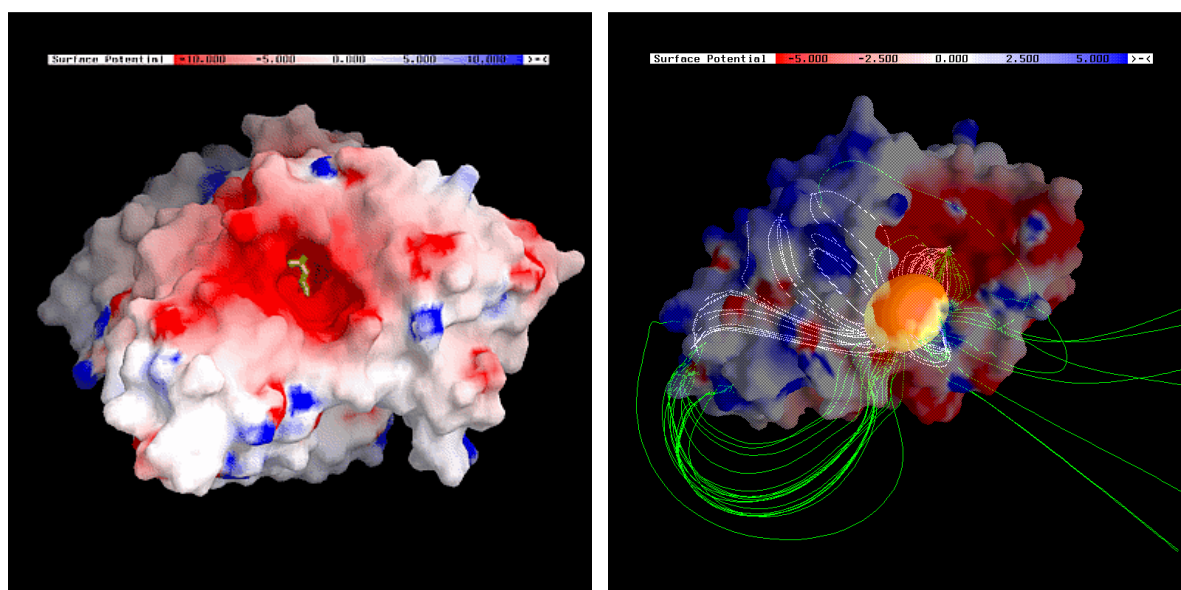

Figure 19.5.6: (a). The surface of the binding pocket of acetylcholine esterase is negatively charged to enhance binding with acetylcholine. (b). The GB/SA approach in aqueous solution with an ionic strength of 0.1 m shows electric field lines that extend into the solvent.[17]
(http://bhapp.c2b2.columbia.edu/software/GRASP/pictures.html)

19.6 A Lattice Model for Simple Symmetric Solutions[18,2]

Consider a lattice of equivalent sites that are occupied with n_A moles of A and n_B moles of B with $n = n_A + n_B$ total sites, Figure 19.6.1. Each lattice site has z near neighbors. For example, on a purely geometrical basis, for a 3D-cubic lattice, each lattice site has 6 near neighbors. Assume that the A and B molecules are approximately the same size, so that space within the lattice is efficiently filled, and the lattice site volumes are all equivalent. The energy of interaction of an A molecule with another A molecule is ε_{AA}. The number of possible interactions for n_A moles of pure A is $z\, n_A/2$. The factor of two results because two molecules of A give one interaction. The energy of pure A is $U_A^\circ = z\, n_A\, \varepsilon_{AA}/2$. The energy of interaction of a B molecule with another B molecule is ε_{BB}. The energy of pure B is $U_B^\circ = z\, n_B\, \varepsilon_{BB}/2$. Written in terms of moles fractions, with $n_A = n\, x_A$ and $n_B = n\, x_B$, the pure substance internal energies are:

$$U_A^\circ = z\, n\, x_A\, \varepsilon_{AA}/2 \qquad\qquad U_B^\circ = z\, n\, x_B\, \varepsilon_{BB}/2 \qquad\qquad \text{(pure components)} \qquad 19.6.1$$

Now consider the mixed lattice. The energy of interaction between an A and B molecule is ε_{AB}. Assume that the lattice sites are filled purely randomly. In other words, assume that A has no preference for the identity of each of its neighbors, even though the A-A, B-B, and A-B forces may differ. The probability of a given lattice site being occupied by an A molecule is given by the fraction of A molecules in the system, $p_A = n_A/n_{tot} = x_A$. The probability of occurrence of two adjacent A molecules, assuming random mixing, is $p_{AA} = x_A^2$. The probability of two adjacent B molecules is $p_{BB} = x_B^2$, and the probability of an adjacent A and B pair is $p_{AB} = x_A x_B$. The number of A-A interactions is the probability of an A-A pair multiplied by the number of possible A-A interactions, giving $z\, n_{tot}\, x_A^2/2$. The number of B-B interactions is $z\, n_{tot}\, x_B^2/2$, and the number of A-B interactions is $z\, n_{tot}\, x_A x_B$. The total energy of the system after mixing is:

$$U = z\, n\, x_A^2\, \varepsilon_{AA}/2 + z\, n\, x_B^2\, \varepsilon_{BB}/2 + z\, n\, x_A x_B\, \varepsilon_{AB} \qquad\qquad 19.6.2$$

A	B	B	B	B	A	B	B
B	A	A	A	B	A	A	A
A	B	B	B	A	A	B	A
A	A	B	B	A	B	A	A
B	B	A	A	B	A	B	A
A	A	B	A	B	A	A	B
B	B	A	B	A	B	A	A
A	A	B	A	B	B	B	B

| A | A | $N_A = 2$, interactions = 1 |

| A | B | $N_A = 1$, interactions = 1 |

(a).   (b).

Figure 19.6.1: Lattice model for solution interactions. (a). Simple solution theory assumes that molecules are similar in size and sites are distributed randomly, even though the A-A, B-B, and A-B forces may differ. (b). The possible interactions for n_A moles of pure A is $z\, n_A/2$.

The internal energy of mixing is given by the difference of Eq. 19.6.2 with Eqs. 19.6.1:

$$\Delta_{mix}U = z\, n_{tot}\, (x_A^2\, \varepsilon_{AA}/2 + x_B^2\, \varepsilon_{BB}/2 + x_A x_B\, \varepsilon_{AB} - x_A\, \varepsilon_{AA}/2 - x_B\, \varepsilon_{BB}/2) \qquad 19.6.3$$

Noting that $x_A = (1 - x_B)$ and $x_B = (1 - x_A)$ in the first two terms allows cancellations that result in:

$$\Delta_{mix}U = z\, n\, (x_A(1 - x_B)\, \varepsilon_{AA}/2 + x_B(1 - x_A)\, \varepsilon_{BB}/2 + x_A x_B\, \varepsilon_{AB} - x_A\, \varepsilon_{AA}/2 - x_B\, \varepsilon_{BB}/2)$$

$$\Delta_{mix}U = z\,n\left(\varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2}\right)x_A x_B \qquad\qquad 19.6.4$$

Assuming that the change in volume of the lattice upon mixing is zero, then $\Delta PV = 0$ and $\Delta_{mix}H = \Delta_{mix}U$. To find the Gibbs energy of mixing, we note the assumption of complete randomness for the distribution of A and B in the lattice. The entropy of mixing is then the ideal entropy of mixing. The entropy term in the excess Gibbs energy then cancels to give:

$$G^E = \Delta_{mix}G - \Delta_{mix}G^{ideal} = [\Delta_{mix}U + \Delta PV - T\Delta_{mix}S^{ideal}] - [T\Delta_{mix}S^{ideal}] = \Delta_{mix}U$$

which gives the result in Eq. 19.2.10. This model assumes that there is no change in volume upon mixing. J. Hildebrand defined a **regular solution** as a solution with an ideal entropy of mixing and a non-zero enthalpy of mixing. However, regular solutions may have a small change in volume upon mixing. Solutions that don't have specific interactions, such as hydrogen bonding, are often well approximated as regular solutions.

19.7 Summary – Looking Ahead

To modify the expressions for ideal systems to apply to real systems, we simply replace the concentration by the activity. The activity and activity coefficients for volatile species are easily determined from the partial vapor pressure of the substance. The activity of the solvent is easily determined using vapor pressure, boiling point elevation, freezing point depression, or osmotic pressure. The activity of non-volatile solutes must be determined indirectly using the Gibbs-Duhem relationship. Theories of solvation are based on the excess Gibbs energy and excess chemical potential. Approximations are necessary to model solute-solvent and solvent-solvent interactions in solution. Regular solutions have an ideal entropy of mixing and a non-zero enthalpy of mixing. The simple symmetric model of regular solutions, in addition, has no volume change on mixing. The deviation from ideality is dependent on the imbalance in forces in solution. The activity coefficients for ionic solutes are dominated by electrostatic interactions of the ion with its ionic atmosphere.

No area of Physical Chemistry has as important an impact on practical applications of chemical equilibria as the theory of solvation. The solution environment plays a central role in the stabilization or destabilization of species in chemical equilibria. The prevalence of enthalpy-entropy compensation, especially in water, requires that both enthalpy and entropy changes must be considered; neither enthalpy or entropy changes alone are sufficient. Careful evaluation of the enthalpy and entropy changes caused by solute-solvent, solute-solute, and solvent-solvent interactions are necessary for prediction of Gibbs energies of solvation and activity coefficients. For example, hydrogen bonding and some contributions to protein folding are solvent entropy driven. Small changes in the chemical potential of the solvent have a large effect on the position of equilibrium. Consequently, the theory of solvation and the development of new experimental methods to study solvation are two of the most active areas of current research. The development of accurate theories of solvation will have an immediate impact on medicinal, environmental, biochemical, separations, and geochemical applications.

Your patience in dealing with the complexities of solution theory will now pay off. The stage is set for your informed understanding of chemical equilibria, which we study in the next two chapters. Few solutions are ideal.

Summary

1. Activity is the "chemically effective" concentration, because the activity includes the effects of intermolecular forces: $\mu_A(x_A) \equiv \mu_A^*(l) + RT \ln a_A$ with a Raoult's Law standard state.

2. The activity coefficient is defined using: $a_A \equiv \gamma_A \, x_A$.

3. The activity is determined from the partial vapor pressure of the substance above the solution: $a_A = P_A/P_A^*$ for a Raoult's Law standard state and $a_B = P_B/k_{H,B}$ for a Henry's Law.

4. Raoult's Law for a real solution is $P_A = a_A \, P_A^*$. Henry's Law for a real solution is $P_B = a_B \, k_{H,B}$.

5. For a Raoult's Law standard state: $\gamma_A = {a_A}/{x_A} = P_A/P_A^{Raoult}$ and Henry's: $\gamma_B = {a_B}/{x_B} = P_B/P_B^{Henry}$.

6. Using Raoult's Law for the standard state is called the **solvent convention** and using Henry's Law for the standard state is called **the solute convention.**

7. Different concentration measures can be used for the solute:

$$\mu_B = {}^x\mu_B^\dagger + RT \ln {}^x a_B \qquad {}^x a_B = {}^x\gamma_B \, x_B \qquad \text{with} \quad {}^x\mu_B^\dagger = \mu_B^\dagger \text{ and } {}^x\gamma_B = \gamma_B$$
$$\mu_B = {}^c\mu_B^\circ + RT \ln {}^c a_B \qquad {}^c a_B = {}^c\gamma_B \, c_B/c^\circ$$
$$\mu_B = {}^m\mu_B^\circ + RT \ln {}^m a_B \qquad {}^m a_B = {}^m\gamma_B \, m_B/m^\circ$$

8. For solutions at concentrations less than about 0.1 m: $\quad {}^x\gamma \cong {}^c\gamma \cong {}^m\gamma$.

9. For non-volatile solutes, the Gibbs-Duhem relationship relates the activity of the solute to the activity of the solvent: $\quad d \ln a_B = -(x_A/1 - x_A) \, d \ln a_A$

10. Because the activity coefficient for the solvent is usually very close to one, the practical osmotic coefficient is defined to avoid propagation of errors inaccuracies in the Gibbs-Duhem relationship and to convert to molal concentrations. The osmotic pressure and the osmotic coefficient for a single electrolyte with ion number $\nu = p + q$ are given as:

$$\pi \, \bar{V}_A = RT \, \nu \, m\phi/(1000 \text{ g kg}^{-1}/\mathfrak{M}_A) \qquad \phi \equiv -\frac{\ln a_A}{\nu \, m \, (\mathfrak{M}_A/1000 \text{ g kg}^{-1})}$$

11. The Gibbs-Duhem relationship on a molality basis, at constant temperature and pressure, gives the activity coefficient for the solute from the integral over the full concentration range:

$$\ln {}^m\gamma_B = \phi(m) - 1 + \int_0^m \frac{\phi - 1}{m_B} \, d \, m_B$$

12. The excess Gibbs energy of solution is the difference between the real Gibbs energy of mixing and the ideal Gibbs energy of mixing: $G^E = \Delta_{mix}G - \Delta_{mix}G^{ideal} = \Delta_{mix}G - nRT \, \Sigma \, x_i \ln x_i$.

13. The excess chemical potential is the difference, $\mu_i^E = \mu_i(x_i) - \mu_i^{ideal}(x_i) = RT \ln \gamma_i$, with:

$$\ln \gamma_i = \frac{1}{RT} \left(\frac{\partial G^E}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

14. The excess Gibbs energy in terms of the activity coefficients is:
$$G^E = n_A \, \mu_A^E + n_B \, \mu_B^E = nRT \, (x_A \ln \gamma_A + x_B \ln \gamma_B)$$

15. The simple symmetric solution model for the activity coefficients with a Raoult's Law standard state for both components is defined by $G^E = n \, a \, x_A x_B$ with:

$$\ln \gamma_A = \frac{a}{RT} \, x_B^2 \qquad\qquad \ln \gamma_B = \frac{a}{RT} \, x_A^2$$

16. Assuming a random distribution of near neighbors, for a simple symmetric solution the deviation from ideality results from an imbalance in the A-B forces as compared to the

average of the A-A and B-B forces: $a = z$ $[\varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB}/2)]$, where z is the number of near neighbors for both A and B.

17. (a) The primary solvation sphere is a layer of 4-8 tightly associated waters; the tetrahedral hydrogen-bonding network typical of the bulk of the solvent is completely disrupted. (b) For structure makers the secondary solvation sphere is more ordered than the bulk. For structure breakers, the secondary solvation sphere is less ordered than the bulk.

18. Hydrophobic hydration is structure making.

19. Water in the primary solvation sphere, secondary solvation sphere, and bulk of the solution must have the same chemical potential, which results in enthalpy-entropy compensation.

20. Structure makers show an increase of the coefficient of thermal expansion with temperature and the structure breakers show a decrease.

21. A pressure perturbation results in a heat transfer, which for a pure substance at constant temperature is $q_{rev} = - TV\alpha \, \Delta P$.

22. The apparent specific coefficient of thermal expansion for the solute is: $\alpha_s \equiv \dfrac{1}{\overline{V}_s}\left(\dfrac{\partial \overline{V}_s}{\partial T}\right)_P$

23. For pressure perturbation calorimetry, PPC, at constant T with a reference of pure solvent, the differential heat transfer is: $\Delta q_{rev} = - T \, (w_s \, \overline{V}_s \, \alpha_s - w_s \, \overline{V}_s \, \alpha_o) \, \Delta P$, where $\overline{V}_s$ is the apparent specific volume of the solute, w_s is the mass of the solute, and α_o is the coefficient of thermal expansion of pure solvent.

24. The chemical potentials of ions add to give the overall chemical potential of the substance and the activities of the ions multiply: $\mu(M_pX_q) = p\,\mu_+ + q\,\mu_- = \mu^\circ(M_pX_q) + RT \ln(a_+^p \, a_-^q)$.

25. The mean ionic activity coefficient is: $\gamma_\pm \equiv (\gamma_+^p \, \gamma_-^q)^{1/\nu}$ or alternately $\gamma_\pm^\nu \equiv \gamma_+^p \, \gamma_-^q$ giving the overall electrolyte chemical potential and activity as:

$$\mu(M_pX_q) = \mu^\circ(M_pX_q) + RT \ln\left(\frac{\gamma_\pm^n \, m_+^p \, m_-^q}{m^{\circ\nu}}\right) \quad \text{and} \quad a(M_pX_q) = a_+^p \, a_-^q = \left(\frac{\gamma_\pm^n \, m_+^p \, m_-^q}{m^{\circ\nu}}\right)$$

26. Assuming the deviation from ideality is only a function of the electrostatic work of charging the ion of interest in its ionic environment: $RT \ln \gamma_i = N_A \, w_{elec}(\text{real}) - N_A \, w_{elec}(\text{ideal})$.

27. The Debye-Hückel approximation assumes dilute point charges in a solvent with a continuum dielectric of relative permittivity ε_r and density d_o:

$$\ln \gamma_\pm = -1.825 \times 10^6 \, |z_+ \, z_-| \left(\frac{d_o}{\varepsilon_r^3 \, T^3}\right)^{1/2} I^{1/2}$$

28. The ionic strength, I, is the appropriate measure of the total ion concentration in solution: $I = \tfrac{1}{2} \sum z_i^2 \, (m_i/m^\circ)$. The sum is over <u>all</u> ions in solution, including buffers and supporting electrolytes. For a pure unipositive-uninegative salt, $I = m/m^\circ$.

29. For an aqueous solution at 25°C, $d_o = 0.99704$ g mL^{-3}, $\varepsilon_r = 78.54$, and:
    $\ln \gamma_\pm = -1.171 \, |z_+ \, z_-| \, I^{1/2}$ or $\log \gamma_\pm = -0.509 \, |z_+ \, z_-| \, I^{1/2}$

30. The salt effect results because a non-participating electrolyte increases the ionic strength, thereby decreasing the activity coefficients and increasing the solubility of insoluble salts.

31. For multicomponent solutions the osmotic coefficient and osmolality, $\mathcal{E}_m$, is given by a sum of all species, s (see also Summary 10, above):

$$\phi \equiv -\frac{\ln a_A}{\sum\limits_{i=1}^{s} m_i\,(\mathfrak{M}_A/1000\ \text{g kg}^{-1})} \qquad\qquad \mathcal{E}_m = \sum\limits_{i=1}^{s} m_i\,\phi$$

32. The electric potential and electrostatic energy for two charges, q_i and q_j, separated by a distance r_{ij} in a uniform dielectric with relative permittivity ε_r are : $\phi_i(r_{ij}) = q_i/(4\pi\varepsilon_o\varepsilon_r\,r_{ij})$ and $\mathcal{E}(r_{ij}) = \phi_i(r_{ij})\,q_j$.

33. The Gibbs energy of solvation is approximated as: $\Delta_{sol}G = \Delta_{sol}G_{VdW} + \Delta_{sol}G_{cav} + \Delta_{sol}G_{elec}$, where $\Delta_{sol}G_{VdW}$ is the solute-solvent Van der Waals interaction, $\Delta_{sol}G_{cav}$ is the work necessary to create the cavity in solvent, and $\Delta_{sol}G_{elec}$ is the electric work necessary to transfer the ion from ideal solution into the real solution.

34. $\Delta_{sol}G_{cav}$ is approximated: $\Delta_{sol}G_{cav} = (\text{surface tension})(\text{surface area}) = \gamma\,\sigma$. The $\Delta_{sol}G_{VdW}$ and $\Delta_{sol}G_{cav}$ terms are often combined giving the total γ in aqueous solution at 25°C as 7-10 J/Å^2.

35. The Boltzmann distribution of ions j at a given point at a distance r from the central ion i and the corresponding radial probability distribution for the ions are:

$$N_j = N_{oj}\,e^{\frac{-\phi_i(r)q_j}{kT}} \qquad\qquad p_j(r)\,dr = 4\pi r^2 N_{oj}\,e^{\frac{-\phi_i(r)q_j}{kT}}\,dr$$

36. The Debye length is the thickness of the ionic atmosphere. The Debye length for dilute aqueous solutions with uniform solvent dielectric and unipositive and uninegative ions at 25°C is: $r_D = 305\ \text{pm}/(m/m°)^{1/2}$ and $r_D = 1/\kappa$.

37. The charge density within the solution for a charge q_i is the charge multiplied by the probability that the charge is at position (x,y,z): $\rho_i(x,y,z) = q_i\,p(x,y,z)$

38. The Poisson equation for a spherical potential is: $\dfrac{1}{r}\dfrac{\partial^2(r\,\phi_i(r))}{\partial r^2} = -\dfrac{\rho_i(r)}{\varepsilon(r)}$ with $\varepsilon(r) = \varepsilon_o\,\varepsilon_r(r)$.

39. The charge density is the sum of the charge density for the positive and negative ions:

$$\rho_i(r) = \rho_+(r) + \rho_-(r) = q_+\frac{N_+}{V}\,e^{\frac{-\phi_i(r)q_+}{kT}} + q_-\frac{N_-}{V}\,e^{\frac{-\phi_i(r)q_-}{kT}}$$

40. For a continuum dielectric with dilute point ions the electric potential is: $\phi_i(r) = \dfrac{q_i}{4\pi\varepsilon_o\varepsilon_r\,r}\,e^{-\kappa r}$

41. The inverse squared Debye length is: $\kappa^2 = \dfrac{2\,e^2\,(1000\ \text{L m}^{-3})\,d_o\,N_A\,m°}{\varepsilon_r\varepsilon_o\,kT}\,I$

42. The ionic strength is the appropriate measure of the total ion concentration: $I \equiv \tfrac{1}{2}\sum\limits_{j=1}^{s} z_j^2\,\dfrac{m_i}{m°}$

43. For a continuum dielectric with dilute point ions, electrostatic work only, and a Henry's Law standard state, the Gibbs energy of solvation is approximated by:

$$\Delta_{sol}G_{elec} = G_{elec}(\text{real}) - G°_{elec} = RT \ln \gamma_i = -\frac{N_A\,z_i^2\,e^2\,\kappa}{8\pi\varepsilon_o\varepsilon_r} = -\frac{N_A\,z_i^2\,e^2}{8\pi\varepsilon_o\varepsilon_r\,r_D}$$

44. For a continuum dielectric with dilute point ions and electrostatic work only with a Henry's Law standard state, the Debye-Hückel approximation is:

$$\ln \gamma_\pm = -\left(\frac{e^6\,(1000\ \text{L m}^{-3})\,d_o\,N_A\,m°}{32\pi^2\,\varepsilon_o^3\,\varepsilon_r^3\,k^3T^3}\right)^{1/2} |z_+\,z_-|\,I^{1/2}$$

45. The electrostatic contribution to the Gibbs energy of solvation, with respect to an ideal gas phase standard state, is: $\Delta_{sol}G_{elec} = N_A\, w(real) - N_A\, w(vacuum)$

46. For a continuum dielectric with an infinitely dilute spherical ion of radius r_i, the electric potential at $r = 0$ and the corresponding solvation Gibbs energy in the Born approximation is:

$$\phi_i(0) = \frac{q_i}{4\pi\varepsilon_o\varepsilon_r\, r_i} \qquad \Delta_{sol}G_{elec} = \frac{-z_i^2\, e^2 N_A}{8\pi\varepsilon_o\, r_i}\left(1 - \frac{1}{\varepsilon_r}\right)$$

47. The total energy of a random lattice of $n = n_A + n_B$ molecules, assuming a simple symmetric solution, is: $U = z\, n\, x_A^2\, \varepsilon_{AA}/2 + z\, n\, x_B^2\, \varepsilon_{BB}/2 + z\, n\, x_A x_B\, \varepsilon_{AB}$, where z is the number of adjacent lattice sites for both A and B and the probability of an adjacent A and B pair is $x_A x_B$. The lattice sites have equal volume for A and B occupation.

48. A regular solution is a solution with an ideal entropy of mixing and a non-zero enthalpy of mixing. Regular solutions may have a small change in volume upon mixing.

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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?

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.

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.

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)?

5. (a). Using the following vapor pressure curves, calculate the activity coefficient for B at x_B =0.667 with a Raoult's Law and a Henry's Law standard state. (b). Characterize the relative forces, ε_{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.
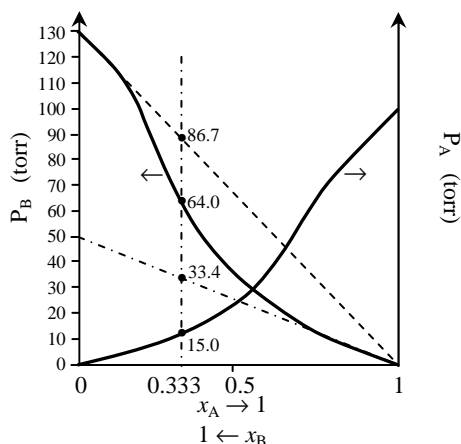
6. The partial vapor pressure of heptane above a solution of heptane and 1-bromobutane was 0.0885 bar for a heptane mole fraction of 0.4164. The vapor pressure of pure heptane is 0.187 bar. The Henry's Law constant for heptane was determined in Problem 18.13 to be $k_{H,\text{heptane}} = 0.265$ bar. Calculate the activity coefficients on both a Raoult's Law and Henry's Law basis.

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}.

8. 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}.

9. 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: $\Delta_{\text{fus}}H_A(T) = \Delta_{\text{fus}}H_A(T_A^*) + \Delta_{\text{fus}}C_{p,A} (T - T_A^*)$. 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 $\Delta_{\text{fus}}G_A = \mu_A^*(l) - \mu_A^*(s)$. Use the Gibbs-Helmholtz relationship, Eq. 16.3.12, to show:

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

(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:

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

10. 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 $\Delta_{sol}\bar{G}_A = \mu_A(x_A) - \mu_A^*(l)$. Use the Gibbs-Helmholtz relationship, Eq. 16.3.12, to show:

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

where $\Delta_{sol}\bar{H}_A$ 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:

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

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.

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). $CuSO_4$.

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).

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

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.

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, $K_{sp} = 1.2\times10^{-18}$. Remember that the dissociation is given by:

$$Hg_2Cl_2\;(s) \rightleftarrows Hg_2^{2+} + 2\;Cl^-$$
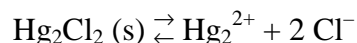
17. Write the acid dissociation equilibrium expressions in terms of the concentration of the undissociated acid, m_{HA}, the H^+ concentration, m_{H^+}, and the mean ionic activity coefficient, for the weak acids: (a). CH_3COOH, acetic acid (HOAc), (b). H_2S (for the first dissociation only).

18. Using Eqs. 19.5.12, 19.5.18, and 19.5.19, derive Eq. 19.5.20.

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

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

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

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

$$\kappa = \sqrt{\frac{2\ e^2\ 1000\ L\ m^{-3}\ d_o\ N_A\ m^\circ}{\varepsilon_r\varepsilon_o kT}}\ I^{1/2}$$
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.

21. 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.

22. Plot the screened Coulomb potential for a 0.0100 m and 0.100 m NaCl solution.

23. (a). Show that the charge density for the screened Coulomb potential can be written in terms of κ 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 κ.

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 deviations 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 tightly held.