CHEM-UA 652: Thermodynamics and Kinetics

Notes for Lecture 15

I. DEFINING SOLUTIONS

When two or more substances are combined to form a homogeneous mixture, the result is a multi-component solution. Solutions can be mixtures of multiple liquids, solids and liquids, or solids and solids. If there is a major component, it is called the solvent, and the minor components are called the solutes. If all components are present in equal amounts, no such distinction is possible.

II. CHARACTERIZING THE MICROSCOPIC STRUCTURE OF SOLUTIONS USING STATISTICAL MECHANICS

When a solid is dissolved in a solvent, it might dissociate or remain intact. If the former, it becomes solvated. This means that solvent molecules will form a solvent shell or solvation shell around the solute species. The number of such nearest neighbor solvent molecules is called the coordination number. Some examples, shown as snapshots from computer simulations of solvation, illustrate the concept of coordination shells and their structures.

Simulations of the aqueous solvation of the Be$^{2+}$ ion show a solvation shell that fluctuates between 6 and 4 water molecules, as the two snapshots below illustrate: The average is strongly weighted toward a coordination number of four, which is the favored state for this ion.

Several other examples arise in the chemistry of acids and bases. First, consider the case of a strong acid such as HCl, which dissociates into H$^+$ and Cl$^-$. What does the solvation of the excess proton look like? First, it is well known that excess protons in water attach to water molecules to form the hydronium ion H$_3$O$^+$, which is a highly mobile
ion in water (its diffusion constant is roughly 5 times that of the self-diffusion of water molecules). The hydronium ion forms a solvation shell in which it donates three hydrogen bonds to neighboring water molecules as shown in the snapshot below: The hydronium ion is transported via a conversion between this solvated complex and one in which the excess proton is shared between two water molecules. This process is initiated when a first solvation shell water loses one of its acceptor hydrogen bonds. This is illustrated in the snapshots shown below: Thus, it is clear that hydronium does not diffuse as an intact object but rather as a topological defect in the hydrogen bond network of the water solvent. The structural defect moves from oxygen to oxygen in the network mediated by a series of proton transfer reactions. This type of diffusion is known as structural diffusion.

Another example of structural diffusion occurs in basic solutions and describes how the hydroxide ion is transported. Hydroxide is present in aqueous solution when a strong base such as KOH or NaOH is dissolved in water. The

![Snapshot of hydronium ion in water](image1)

**FIG. 2:** Snapshot from a simulation of the hydronium ion in water.

![Snapshots of hydronium ion](image2)

**FIG. 3:** Snapshots from a simulation of the transport of H\(_3\)O\(^+\) ion in water. The left panel shows the hydronium in its normal solvation state. The right panel shows the hydronium diffusing via a structural diffusion process in which one of its protons is transferred to a neighboring water molecule.
The snapshot below shows the most probable coordination structure of a hydroxide ion in water: In this snapshot, we see the hydroxide ion accepting four hydrogen bonds at the oxygen site from neighboring water molecules. At first, this solvation pattern might seem strange if we think of the Lewis structure of the hydroxide ion. The Lewis structure shows three lone pairs of electrons around the hydroxide oxygen. If we regard each lone pair as a hydrogen bond acceptor site, then we might expect hydroxide to accept at most three hydrogen bonds. What allows it to accept four. Here, we can use our understanding of quantum mechanics to help out. The figure below shows a measure of regions of highest probability to find the lone-pair electrons: From this figure, we see that the lone pairs are completely

![FIG. 4: Snapshot from a simulation of the hydroxide ion in water.](image)

![FIG. 5: Isosurface of high probability regions for finding lone-pair electrons in the hydroxide ion.](image)
delocalized into a ring centered on the OH\(^{-}\) bond axis. Given this delocalization of the lone pairs, the number of hydrogen bonds that can be donated to the hydroxide ion depends only on the number of waters that can be packed around the ring. This explains the coordination pattern that is observed in Fig. 4. The structural diffusion process of the hydroxide ion starts with a change in the number of coordinating water molecules around the oxygen from 4 to 3 as shown in the snapshots below:

![Snapshots showing the first step of the structural diffusion process of the hydroxide ion.](image)

The unusual coordination pattern seen for the hydroxide ion is not unique to this ion or to aqueous solutions. Consider the analogous isosurface of Fig. 5 for the amide ion NH\(_2\)^{-}. This shown below: If we take NH\(_2\)^{-} in an ammonia solvent,

![Isosurface of high probability regions for finding lone-pair electrons in the amide ion.](image)

we get solvation patterns such as that shown in the figure below: As with the hydroxide ion, we see that the number of coordinating ammonia molecules is determined only by the number that can be packed around the semi-ring seen in Fig. 7.

Mixtures of liquids are typically characterized on a large length scale, as the snapshots below illustrate. These are snapshots from a 50:50 mixture of methanol and water. The figure shows just the positions of the oxygen atoms in each mixture, red spheres are water oxygens, gold spheres are methanol oxygens. The repulsive nature of the interactions between methanol and water cause the water to form small clusters with the methanols percolating between them.
Characterizing the microscopic nature of solutions amounts to finding the average distances between different components in the solution. When we have solvated ions, for example, we would like to know the average distance between the ion and the coordinating solvent molecules. For liquid-liquid mixtures, we would like to know average distances between molecules either of like type or different types in the solution. Both of these can be addressed using the techniques of neutron or X-ray scattering. How does this allow us to determine average distances? In order to answer this, let us consider a simpler question, that of determining the distance between planes of a simple crystal. The scattering technique used to do this is called Bragg scattering, as illustrated in Fig. 10 below. The wave vectors are related to the wavelength $\lambda$ of the incident and scattered waves by

$$|k_i| = |k_s| = \frac{2\pi}{\lambda}$$  \hspace{1cm} (1)

In Bragg scattering, we look for constructive interference between waves scattered from the top plane and the plane just beneath it. This can only occur if the path difference, which is $2d \sin \psi$ is an integer number of wavelengths,
FIG. 10: Illustration of Bragg scattering from neighboring planes in a crystal

which leads to the Bragg condition

\[ 2d \sin \psi = n \lambda \]  

(2)

This allows us to determine the distance \( d \) between neighboring crystal planes. Note that the angle \( \theta \) is related to \( \psi \) by

\[ \theta = \frac{\pi}{2} - \psi \]

Thus,

\[ \sin \psi = \sin \left( \frac{\pi}{2} - \theta \right) = \cos \theta \]

Thus, the Bragg condition becomes

\[ 2d \cos \theta = n \lambda \]  

(3)

Now, if we assign position vectors \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \) as shown in the figure, then we have the following relations between the vector \( \mathbf{r}_1 - \mathbf{r}_2 \) and the vectors \( \mathbf{k}_i \) and \( \mathbf{k}_s \):

\[ -\mathbf{k}_i \cdot (\mathbf{r}_1 - \mathbf{r}_2) = |\mathbf{k}_i||\mathbf{r}_1 - \mathbf{r}_2| \cos \theta \]

\[ \mathbf{k}_s \cdot (\mathbf{r}_1 - \mathbf{r}_2) = |\mathbf{k}_s||\mathbf{r}_1 - \mathbf{r}_2| \cos \theta \]  

(4)

If we add these two conditions together, we obtain

\[ (\mathbf{k}_s - \mathbf{k}_i) \cdot (\mathbf{r}_1 - \mathbf{r}_2) = (|\mathbf{k}_i| + |\mathbf{k}_s|)|\mathbf{r}_1 - \mathbf{r}_2| \cos \theta \]

\[ = \left( \frac{2\pi}{\lambda} + \frac{2\pi}{\lambda} \right) d \cos \theta \]

\[ = \frac{4\pi}{\lambda} d \cos \theta \]  

(5)

Define the difference \( \mathbf{k}_s - \mathbf{k}_i \) as the vector \( \mathbf{q} \), known as the *momentum transfer*. For constructive interference, we still have the Bragg condition \( 2d \cos \theta = n \lambda \). Thus, we can write the Bragg condition as

\[ \mathbf{q} \cdot (\mathbf{r}_1 - \mathbf{r}_2) = 2\pi n \]

(6)

which is equivalent to the condition

\[ e^{i\mathbf{q} \cdot (\mathbf{r}_1 - \mathbf{r}_2)} = 1 \]  

(7)
The reason for taking the exponential like this is that neutron and X-ray scattering measurements really measure this quantity, since the spatial dependence of a wave form is generally exp(ik·r).

Now in a solution, the atoms are constantly in motion due to the finite temperature. In addition, all possible pairs are detected in the measurement. This means that we need to sum the exponentials over all particle pairs and take an ensemble average. Alternatively, we can look at the scattering off each individual atom at position rᵢ, sum over all atoms, and then square to get a real scattering intensity. This gives us a function S(q) known as the scattering function, which is then given by

\[ S(q) = \frac{1}{N} \left\langle \left| \sum_{i=1}^{N} e^{i q \cdot r_i} \right|^2 \right\rangle \] (8)

For isotropic systems, S(q) should only depend on the magnitude |q| of q, since there are no preferred directions in space. In this case, it is straightforward to show that S(q) is related to the radial distribution function by

\[ S(q) = 4\pi \rho \int_0^\infty dr \ r^2 \left( g(r) - 1 \right) \frac{\sin qr}{qr} \] (9)

where the radial distribution function is given by

\[ g(r) = \frac{(N - 1)}{4\pi \rho r^2 Z(N, V, T)} \int_{|r_1 - r_2| = r} e^{-\beta U(r_1, ..., r_N)} dr_1 \cdots dr_N \] (10)

where \( \rho = N/V \), and \( Z(N, V, T) \) is the configurational partition function. An equivalent way to write \( g(r) \) is

\[ g(r) = \frac{(N - 1)}{4\pi \rho r^2} P(r) \] (11)

where \( P(r) \) is the spatial probability distribution

\[ P(r) = \frac{4\pi r^2 V}{Z(N, V, T)} \int dr_1 \cdots dr_N e^{-\beta U(r_1, ..., r_N)} \] (12)

If a system contains several chemical species, then radial distribution functions \( g_{\alpha\beta}(r) \) among the different species can be introduced. Here, \( \alpha \) and \( \beta \) range over the different species, with \( g_{\alpha\beta}(r) = g_{\beta\alpha}(r) \). Eqn. (9) then generalizes to

\[ S_{\alpha\beta}(q) = 4\pi \rho \int_0^\infty dr \ r^2 \left( g_{\alpha\beta}(r) - 1 \right) \frac{\sin qr}{qr} \] (13)

\( S_{\alpha\beta}(r) \) are called the partial structure factors, and \( \rho \) is the full atomic number density.

III. THERMODYNAMICS OF SOLUTIONS

A useful quantity to characterize the solution composition is the so-called mole fraction defined as follows: Suppose a solution contains \( N \) components. Let there be \( n_1 \) moles of component 1, \( n_2 \) moles of component 2, ..., \( n_N \) moles of component \( N \). The mole fraction of component \( j \) is

\[ x_j = \frac{n_j}{\sum_{k=1}^{N} n_k} \] (14)

We see, immediately, that \( \sum_j x_j = 1 \). For example, in a two-component solution, there are two mole fractions given by

\[ x_1 = \frac{n_1}{n_1 + n_2}, \quad x_2 = \frac{n_2}{n_1 + n_2} \] (15)

Concepts such as molarity and molality are generally used to describe the composition of solid-liquid solutions involving dissolved species. Hence, we will hold off on discussing these quantities until we get to this topic.
Next, let us consider the free energy for a two-component solution. There are \( n_1 \) moles of component 1 and \( n_2 \) moles of component 2. Hence, the Gibbs free energy \( G \) is a function \( G(n_1, n_2, P, T) \) of the number of moles of each component as well as pressure and temperature. From Euler’s Theorem,

\[
G(n_1, n_2, P, T) = n_1 \left( \frac{\partial G}{\partial n_1} \right)_{P,T} + n_2 \left( \frac{\partial G}{\partial n_2} \right)_{P,T} = n_1 \mu_1(P, T) + n_2 \mu_2(P, T) \tag{16}
\]

Hence, a change \( dG \) in \( G \) due to changes in the number of moles of each component as well as pressure and temperature (which changes the chemical potentials) is

\[
dG = \mu_1 dn_1 + \mu_2 dn_2 + n_1 d\mu_1 + n_2 d\mu_2 \tag{17}
\]

At equilibrium, \( dG = 0 \). If the number of moles of each component remain fixed, then \( dn_1 = dn_2 = 0 \). Then we are left with

\[
n_1 d\mu_1 + n_2 d\mu_2 = 0 \tag{18}
\]

This can be expressed as a condition in terms of mole fractions by dividing through by \( n_1 + n_2 \) to yield

\[
\frac{n_1}{n_1 + n_2} d\mu_1 + \frac{n_2}{n_1 + n_2} d\mu_2 = 0
\]

\[
x_1 d\mu_1 + x_2 d\mu_2 = 0 \tag{19}
\]

which is known as the Gibbs-Duhem equation. The Gibbs-Duhem has many uses, as we will see in our discussion of solutions. As an example, suppose we are told that the chemical potential of one of the solution components, say \( \mu_2 \), depends on its mole fraction \( x_2 \) as follows:

\[
\mu_2 = \mu_2^* + RT \ln x_2
\]

where \( \mu_2^* \) is the chemical potential of pure sample of component 2. Then, using the Gibbs-Duhem relation, we can derive the corresponding dependence of \( \mu_1 \) on the solution composition. From the Gibbs-Duhem equation,

\[
\mu_1 = - \frac{x_2}{x_1} d\mu_2 = -RT \frac{x_2}{x_1} d\ln x_2 = -RT \frac{dx_2}{x_1}
\]

However, a change \( dx_2 \) in the number of moles of substance 2 must be equal and opposite to the change in \( dx_1 \) in component 1, i.e., \( dx_2 = -dx_1 \). Therefore,

\[
d\mu_1 = RT \frac{dx_1}{x_1}
\]

Integrating this, we find

\[
\mu_1 = RT \ln x_1 + C
\]

where the integration constant \( C \) can be determined from the condition \( x_1 = 1 \), corresponding to a pure sample of component 1. When \( x_1 = 1, \mu_1 = \mu_1^* = C \). Hence,

\[
\mu_1 = \mu_1^* + RT \ln x_1
\]

**IV. SOLUTION-VAPOR EQUILIBRIA**

Suppose a two-component solution is in equilibrium with its vapor. Let \( n_j^{(\text{soln})} \) and \( n_j^{(\text{vap})} \), \( j = 1, 2 \) denote the number of moles of each component in solution and in vapor, respectively. For concreteness, let component 1 be the major or solvent component. The Gibbs free energy is a function of the number of moles of each component in solution and in vapor and, of course, \( P \) and \( T \):

\[
G = G(n_1^{(\text{soln})}, n_2^{(\text{soln})}, n_1^{(\text{vap})}, n_2^{(\text{vap})}, P, T) \tag{20}
\]
Moreover,

$$G(n_{1}^{\text{soln}}, n_{2}^{\text{soln}}, n_{1}^{\text{vap}}, n_{2}^{\text{vap}}, P, T) = G^{\text{soln}}(n_{1}^{\text{soln}}, n_{2}^{\text{soln}}, P, T) + G^{\text{vap}}(n_{1}^{\text{vap}}, n_{2}^{\text{vap}}, P, T)$$

If $P$ and $T$ are held fixed, then

$$dG = \sum_{j=1}^{2} \left[ \left( \frac{\partial G^{\text{soln}}}{\partial n_{j}^{\text{soln}}} \right)_{P, T} dn_{j}^{\text{soln}} + \left( \frac{\partial G^{\text{vap}}}{\partial n_{j}^{\text{vap}}} \right)_{P, T} dn_{j}^{\text{vap}} \right]$$

However, $dn_{j}^{\text{vap}} = -dn_{j}^{\text{soln}}$. Thus, in much the same way that we analyzed phase equilibria, we have

$$dG = \sum_{j=1}^{2} \left[ \mu_{j}^{\text{soln}} dn_{j}^{\text{soln}} + \mu_{j}^{\text{vap}} dn_{j}^{\text{vap}} \right] = \sum_{j=1}^{2} \left[ (\mu_{j}^{\text{vap}} - \mu_{j}^{\text{soln}}) dn_{j}^{\text{vap}} \right]$$

In equilibrium, $dG = 0$, hence, $\mu_{j}^{\text{vap}} = \mu_{j}^{\text{soln}}$. Let the vapor phase be treated as an ideal gas with two components. From Dalton’s law of partial pressures, the total pressure $P$ in the vapor phase is the sum of partial pressures of each of the individual components coming from the solution $P = \sum_{j} P_{j}$. For simplicity, suppose we have a two-component solution, which gives rise to two components in the vapor phase. Then $P = P_{1} + P_{2}$. From the ideal gas laws for each component

$$P_{1} = \frac{n_{1}^{\text{vap}} RT}{V}, \quad P_{2} = \frac{n_{2}^{\text{vap}} RT}{V}$$

where $V$ is the volume of the vapor phase, and $T$ is the temperature. These can be written as

$$P_{1} = \frac{n_{1}^{\text{vap}} nRT}{n_{1}^{\text{vap}} V}, \quad P_{2} = \frac{n_{2}^{\text{vap}} nRT}{n_{2}^{\text{vap}} V}$$

where $nRT/V = P$ is the total pressure. Thus,

$$P_{1} = x_{1}^{\text{vap}} P, \quad P_{2} = x_{2}^{\text{vap}} P$$

Here, $x_{1}^{\text{vap}}$ and $x_{2}^{\text{vap}}$ are the vapor-phase mole fractions.

The definition of an ideal solution is one in which

$$x_{1}^{\text{vap}} = x_{1}^{\text{soln}} \equiv x_{1}$$

meaning that the mole fractions in solution and vapor phases are the same, and we can simply denote the mole fraction of component 1 as $x_{1}$. Thus, the partial pressure of component 1 becomes

$$P_{1} = x_{1} P$$

When $x_{1} = 1$, we have a pure system consisting of component 1, and $P_{1} = P \equiv P_{1}^{*}$, which denotes the vapor pressure of the pure component 1. Thus, the partial pressure $P_{1}$ for the solution becomes

$$P_{1} = x_{1} P_{1}^{*}$$

which is known as Raoult’s Law, and it defines an ideal solution.

When $x_{1} = 1$, clearly, $P_{1} = P_{1}^{*}$ (shown as $P_{1}^{0}$ in the figure below). The plot below shows how $P_{1}$ depends on $x_{1}$, which, of course, is a linear plot with slope $P_{1}^{*}$ and zero intercept. Any solution that obeys Raoult’s law is called an ideal solution.

Fig. 11 also shows how deviations from ideal solution behavior appears. Negative deviations, $P_{1} < x_{1} P_{1}^{*}$, occur when there are strong attractive forces between the components. An example of a solution that would show negative deviations from Raoult’s law would be a mixture of trichloromethane (CHCL₃) and ethoxyethane (C₂H₂OC₂H₅).
Trichloromethane has a polar hydrogen but no H-bond acceptor sites (the chlorines are not sufficiently electronegative). Hence, a pure liquid of trichloromethane cannot form hydrogen bonds. However, ethoxyethane has an oxygen with lone pairs. However, when it is mixed with trichloromethane, hydrogen bonds can form. These are strong attractive interactions that cause negative deviations from Raoult’s law.

Positive deviations from Raoult’s law ($P_1 > x_1 P_1^*$) arise when there are strong repulsive forces between the components. Alcohol-water mixtures (e.g. ethanol-water or methanol-water) are examples of solutions that show positive deviations from Raoult’s law. In order to see why a methanol-water solution exhibits a positive deviation, consider the computer simulation snapshots of such a solution with $x_1 = x_2 = 0.5$, shown in the figure below: A solution of this type will show positive deviations from Raoult’s law.

Most solutions show deviations from ideal solution behavior. However, Raoult’s law nevertheless still provides a number of important insights. In the first place, as $x_1 \to 1$, $P_1 \to P_1^*$ because this corresponds to the case of just one component. Near $x_1 = 1$, all solutions behave ideally, just as all gases tend to ideal gas behavior as the density approaches zero. This is exactly what Fig. 11 shows. For $x_1 \lesssim 1$, $P_1 = x_1 P_1^*$, and Raoult’s law holds.
Away from $x_1 \lesssim 1$, deviations are expected, and $P_1$ does not vary linearly with $x_1$. However, looking at Fig. 11, we see that as $x_1 \to 0$, $P_1$ varies linearly with $x_1$, however, the slope is not $P_1^*$ any more. We express this linear relation as

$$P_1 = k_{H,1} x_1$$

which is called Henry’s Law. The constant $k_{H,1}$ is called the Henry’s law constant, and it clearly has units of pressure. If $k_{H,1} = P_1^*$, then the solution is an ideal solution. The degree to which $k_{H,1}$ differs from $P_1^*$ is a measure of non-ideality of the solution.

Interestingly, the shape of the $P_1$ vs $x_1$ curve can be fit accurately to a function of the following form

$$P_1(x_1) = P_1^* x_1 e^{b (1-x_1)^2 + c (1-x_1)^3}$$

(31)

Positive deviations from Raoult’s law can be described by $b > 0$ and $c > 0$, while negative deviations can be described by $b < 0$ and $c < 0$. The figure below shows a plot of Eq. (31) for several choices of $b$ and $c$.

![FIG. 13: Plot of Eq. (31) for several choices of parameters showing positive and negative deviations.](image)

**Example:** Suppose we are told that $P_1^* = 180$ torr, $b = 1$ and $c = 0.5$. What is the Henry’s law constant for this model?

**Solution:** For $x_1$ very small, we can work to linear order in Eq. (31). To linear order, we find

$$P_1(x_1) \approx P_1^* x_1 e^{1+0.5} = P_1^* x_1^{1.5}$$
from which we can read off the Henry’s law constant as

\[ k_{H,1} = P_1 x_1 = (180 \text{ torr})^{1.5} = 807 \text{ torr} \]