University of Washington
Department of Chemistry
Chemistry 452/456
Summer Quarter 2014

Lecture 20 8/14/14

A. The Electrochemical Potential

- At constant pressure and temperature ΔG is a measure of reversible work other than pressure-volume work. An important example is electrical work. At constant P and T, the free energy change ΔG related to the reversible, electrical work in the following way.
- $$dG = -SdT + VdPV + \sum_i \mu_i dn_i + \sum_i \psi_i dQ_i \tag{20.1}$$
- dQ_i is the charge of species i transferred over potential ψ_ι where dQ= $dQ_i = z\Im dn_i$ where $\Im$ is Faraday's constant=96,485C/mole
- We collect the terms in the Gibbs energy expression that depend on dn_i:
- $$dG = -SdT + VdP + \sum_i \left(\mu_i + z_i \Im \psi_i\right) dn_i = -SdT + VdP + \sum_i \tilde{\mu}_i dn_i \tag{20.2}$$

where: $\tilde{\mu}_i = \mu_i + z_i \Im \psi_i = \mu_i^0 + RT \ln a_i + z_i \Im \psi_i$ is the electrochemical potential

- In principle we might assume that the non-ideality of this system resides entirely with the charge effects so that:
$$\frac{RT}{N_A} \ln \gamma_i = k_B T \ln \gamma_i = \int \psi_i dQ_i \tag{20.3}$$
- There are two issues that complicate using equation 20.3. First, the activity coefficient for a particular charged species γ_i cannot be measured in isolation Second, electrolyte solutions are complex systems and obtaining the expression for the potential ψ_i is not simple. We will deal with each of these issues below.

B. Electrolyte Solutions: The Mean Activity Coefficient

- To btain an expression for the activity coefficient of an electrolyte solution, consider an electrolyte solution produced by dissolution of a binary salt in water:
$$M_{\nu+} X_{\nu-} \rightarrow \nu_+ M^{z+}\left(aq\right) + \nu_- X^{z-}\left(aq\right) \tag{20.4}$$
- ν_+ and ν_- are stoichiometric coefficients whereas z_+ and z_- are the cationc and anionic charges, respectively. For charge neutrality in solution we have $\left|\nu_+ z_+\right| = \left|\nu_- z_-\right|$
- If the solution is a very dilute, aqueous solution, the water solvent obeys the usual rules in the dilute limit… $\mu_1 = \mu_1^\bullet + RT \ln a_1 \approx \mu_1^\bullet + RT \ln \chi_1$
- The cationic and anionic solutes obey the equation:
$$\tilde{\mu}_2 = \nu_+ a_+ + \nu_- a_- = \nu_+\left(\mu_+^\circ + RT \ln a_+\right) + \nu_-\left(\mu_-^\circ + RT \ln a_-\right) \tag{20.5}$$

- This is not yet a useful definition of the chemical potential of an electrolyte solution because we cannot physically separate the cationic and anionic fractions. Thus the components of the chemical potential are not measureable. We must formulate instead a mean chemical potential

$$\begin{aligned}\mu_{\pm} &= \frac{\tilde{\mu}_2}{\nu_1+\nu_2} = \frac{\nu_+\mu_+ + \nu_-\mu_-}{\nu} = \frac{\nu_+}{\nu}\left(\mu_+^\circ + RT\ln a_+\right) + \frac{\nu_-}{\nu}\left(\mu_-^\circ + RT\ln a_-\right) \\ &= \frac{1}{\nu}\left(\nu_+\mu_+^\circ + \nu_-\mu_-^\circ\right) + RT\ln\left(a_+^{\nu_+}a_-^{\nu_-}\right)^{1/\nu} = \mu_\pm^\circ + RT\ln a_\pm \end{aligned} \qquad \textbf{(20.6)}$$

  where $\nu = \nu_+ + \nu_-$ and $a_\pm$ is called the mean activity.
- The mean chemical potential and mean activity are required in order to obtain a mean standard state that is realistic. A mean standard state in turn is necessary because a pure cationic and/or anionic standard state cannot be physically realized. Only a mean activity is measureable.
- We can define the activity of the cation and anion in terms of any contrations units we chose. Let's us molality m. For the cation we have

$$a_+ = \gamma_+\frac{m_+}{m^\circ} = \gamma_+\frac{m_+}{1m} \qquad \textbf{(20.7)}$$

...and a similar expression applies to the anion.

$$\begin{aligned} a_\pm &= \left(a_+^{\nu_+}a_-^{\nu_-}\right)^{1/\nu} = \left(\left(\frac{\gamma_+ m_+}{m^\circ}\right)^{\nu^+}\left(\frac{\gamma_- m_-}{m^\circ}\right)^{\nu^-}\right)^{1/\nu} = \left(\gamma_+^{\nu^+}\gamma_-^{\nu^-}\right)^{1/\nu}\left(\frac{m_+}{m^\circ}\right)^{\nu^+/\nu}\left(\frac{m_-}{m^\circ}\right)^{\nu^-/\nu} \\ &= \gamma_\pm\left(\frac{m_+}{m^\circ}\right)^{\nu^+/\nu}\left(\frac{m_-}{m^\circ}\right)^{\nu^-/\nu} \end{aligned} \qquad \textbf{(20.8)}$$

- $\gamma_\pm$ is the mean activity coefficient $\gamma_\pm^\nu = (\gamma_+)^{\nu+}(\gamma_-)^{\nu-}$. It is the only activity coefficient that is measureable from an electrolyte solution.
- We define the molalities m± of the ions in terms of the molality m of the original salt: $m_+ = \nu_+ m_2$, $m_- = \nu_- m_2$ and the mean molaltity $m_\pm = \left(m_+^{\nu_+}m_-^{\nu_-}\right)^{1/\nu}$. Then the mean acitivity is:

$$\begin{aligned} a_\pm &= \gamma_\pm\left(\frac{m_+}{m^\circ}\right)^{\nu^+/\nu}\left(\frac{m_-}{m^\circ}\right)^{\nu^-/\nu} = \gamma_\pm\left(\frac{\nu_+ m}{m^\circ}\right)^{\nu^+/\nu}\left(\frac{\nu_- m}{m^\circ}\right)^{\nu^-/\nu} \\ &= \gamma_\pm\left(\frac{m_\pm}{m^\circ}\right) = \gamma_\pm\nu_+^{\nu^+/\nu}\nu_-^{\nu^-/\nu}\left(\frac{m_2}{m^\circ}\right) \end{aligned} \qquad \textbf{(20.9)}$$

C. The Activity Coefficient from Debye-Huckel Theory

- Debye-Huckel theory treats the properties of very dilute electrolyte solutions by calculating the activity coefficient . This theory views a the non-ideality of an electrolyte solution as arising from Coulomb forces between ions in a continuous solution with dielectric constant ε_r of the form:

$$f\left(r\right)=\frac{Q^2}{4\pi\varepsilon_0\varepsilon_r r^2} \tag{20.10}$$

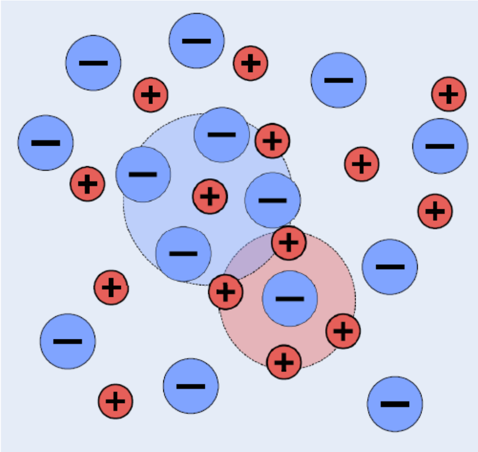
where Q=ze

and where the electrical potential is

$$\psi\left(r\right)=\frac{Q}{4\pi\varepsilon_0\varepsilon_r r} \tag{20.11}$$

- Note the relationship
- However, equation 20.11 is the electrical potential generated at the position of an ion by another ion. In a solution many, many ions contribute to the potential . This is the problem tacked by D-H theory.
- The primary assumptions of D-H theory:

a) The dissolved electrolyte is completely dissociated; it is a strong electrolyte .
b) Ions are spherical and are not polarized by the surrounding electric field .
c) The solvent plays no role other than providing a medium of constant dielectric constant
d) Individual ions surrounding a "central" ion can be represented by a statistically averaged cloud of continuous charge density, with a minimum distance of closest approach. This model is shown at right .



- The average effect of surrounding ions on a given ion is represented by a continuous charge distribution or “ion atmosphere”.
- If the electrical potential at point is ψ the energy W of a charge Q=ze at that point is $W=Q\psi$. The charge density ρ around an ion is assumed to be

$$\rho=\sum_i C_iQ_ie^{-E/k_BT}=\sum_i C_iQ_ie^{-Q_i\psi/k_BT}=\sum_i C_iQ_ie^{-z_ie\psi/k_BT}\approx-\frac{e^2\psi}{k_BT}\sum_i C_iz_i^2 \tag{20.12}$$

- Note: the last step is only possible if $z_ie\psi \ll k_BT$. This is a major limitation of D-H theory because it states the inter-ionic energy is small compared to the thermal energy, which limits D-H theory to very dilute solutions.
- With this expression for the charge density the electrical potential can be obtained by solving the Poisson-Boltzmann equation:

$$\frac{d^2\psi}{dr^2}=-\frac{\rho\left(r\right)}{\varepsilon_0\varepsilon_r}\approx\frac{e^2\psi}{\varepsilon_0\varepsilon_r k_BT}\sum_i C_iz_i^2=\kappa^2\psi$$

- The parameter $\kappa^2 = \frac{e^2}{\varepsilon_0 \varepsilon_r k_B T} \sum_i C_i z_i^2$. The quantity κ^{-1} is called the Debye length and measures the thickness of the ion atmosphere or the range over which the electric field of an ion extends.
- It is possible to solve the Poisson-Boltzmann equation and obtain an expression for the average electrical potential ψ_{DH} in the dilute limit

$$\psi_{DH} \approx -\frac{ze}{4\pi\varepsilon_0\varepsilon_r}\kappa = -\frac{Q}{4\pi\varepsilon_0\varepsilon_r}\kappa \qquad \textbf{(20.13)}$$

- The contribution to the free energy from the charge of a single ion is

$$\Delta G_i^{elec} = \int_0^{z_i e} \psi_{DH}\, dQ_i = -\frac{\kappa z_i^2 e^2}{8\pi\varepsilon_0\varepsilon_r} \qquad \textbf{(20.14)}$$

- Because this contribution to the free energy is strictly non-ideal and arises from Coulombic forces, it can be treated as an activity coefficient. For the ith ion with charge $Q_i = z_i e$ we express the electrical contribution to ΔG as an activity coefficient which on a per mole basis is :

$$\Delta G_i^{elec} = k_B T \ln \gamma_i = -\frac{\kappa z_i^2 e^2}{8\pi\varepsilon_0\varepsilon_r} \qquad \textbf{(20.15)}$$

$$\text{or } \ln \gamma_i = -\frac{\kappa z_i^2 e^2}{8\pi\varepsilon_0\varepsilon_r k_B T}$$

- For a binary salt the mean activity coefficient is

$$\ln \gamma_\pm = \ln\left(\gamma_+^{\nu_+}\gamma_-^{\nu_-}\right)^{1/\nu} = -\left|z_+ z_-\right|\left(\frac{e^2\kappa}{8\pi\varepsilon_0\varepsilon_r k_B T}\right) \qquad \textbf{(20.16)}$$

- For aqueous solutions at T=298K 20 .16 simplifies to

$$\ln \gamma_\pm = -1.173\left|z_+ z_-\right|\sqrt{I} \qquad \textbf{(20.17)}$$

which is called the Debye-Huckel limiting law

  - The ionic strength is I is defined as

$$I = \frac{1}{2}\sum_i \left(C_{i+} z_{i+}^2 + C_{i-} z_{i-}^2\right)$$

  - $C_{\pm i}$ is the concentration of the ith cationic (+) or anionic (-) species with corresponding charge $z_{\pm i}$.
  - The D-H limiting law is only valid for concentrations less than 0.1M or so. Various empirically revised D-H theories have been proposed to extend treatment to higher concentrations. One such equation is the Davies Equation ...

$$\ln \gamma_\pm = -1.173\left|z_+ z_-\right|\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right) \qquad \textbf{(20.18)}$$

Example: Determine the concentration of H^+ in sea water :

The pH of seawater is typically 8.2. For concentrated electrolyte solutions $pH = -\log a_{H^+} = -\log\left(\frac{\gamma_\pm C_{H^+}}{1M}\right)$. Determine the concentration of H+ using the Davies equation.

Solution: The ionic strength of sea water is about I=0.7.

$$\ln\gamma_\pm = -1.173\left|z_+ z_-\right|\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right) = (-1.173)\left(\frac{\sqrt{0.7}}{1+\sqrt{0.7}} - 0.3(0.7)\right) = -0.288$$

$$\therefore \gamma_\pm = 0.750$$

Then

$$a_{H^+} = \frac{\gamma_\pm C_{H^+}}{1M} = 10^{-8.2} = 6.31\times10^{-9}$$

$$\therefore C_{H^+} = \frac{a_{H^+}(1M)}{\gamma_\pm} = \frac{6.31\times10^{-9}(1M)}{0.75} = 8.41\times10^{-9}M$$