

Chapter 8

Electrolyte Solutions

In the last few chapters of this book, we will deal with several specific types of chemical systems. The first one is solutions and equilibria involving electrolytes, which we will take up in this chapter. The thermodynamics of electrolyte solutions is important for a large number of chemical systems, such as acid-base chemistry, biochemical processes and electrochemical reactions.

8.1 Electrolyte Solutions and Their Nonideality

An electrolyte is a compound which produces an ionic solution when dissolved in an aqueous solution. For example, a salt like KCl would produce an electrolyte solution. Those compounds which produce a large number of ions in solution are called *strong electrolytes*. KCl, because it is highly soluble, would be a strong electrolyte. On the other hand, those compounds which produce a small number of ions in solution are *weak electrolytes*. Notice that nonionic compounds can produce electrolyte solutions too. Common examples are acids produced by dissolving molecules such as HCl in water. Soluble compounds that produce no dissolved ions are called *nonelectrolytes*.

In the last few chapters when we deal with solutions, we see that the activity is used to describe the correction to the chemical potential when a compound is not pure:

$$\mu_i = \mu_i^\circ + RT \ln a_i, \quad (8.1)$$

where μ_i° is the chemical potential of the pure standard state and a_i is the activity. When a solution is ideal, the activity of the solvent a_s are just equal to its mole fraction x_s . But for a dilute solute i , the approximation $a_i \approx x_i$ is expected to also hold, because as we have seen in Ch. 5, the Gibbs-Duhem equation demands that if the solvent has $a_s = x_s$, a dilute solute should also have $a_i = x_i$. In fact, when studying the liquid-vapor coexistence of binary mixtures, we have found that because of Henry's law, the chemical potential of the solute is indeed approximately given by

$$\mu_i \approx \mu_i^* + RT \ln x_i, \quad (8.2)$$

where μ_i^* is the chemical potential for Henry's law standard state. The approximation $a_i \approx x_i$ is good for many nonelectrolyte solutions up to rather large solute mole fractions $x_i \approx 0.05$ or even 0.1. But for most electrolyte solutions, substantial deviations from ideality begin to show at mole fractions as small as 10^{-4} or 10^{-5} . Therefore, the nonideality of nonelectrolyte solutions cannot be ignored.

8.2 Activity Coefficients of Electrolyte Solutions

To begin the discussion of nonideality in electrolyte solutions, we first define the activity coefficients. Let's say we have an electrolyte which when one mole of it is dissolved in an aqueous solution, ν_+ moles of positive ions with charge z_+ and ν_- moles of negative ions with charge z_- are produced. An example is Na_2SO_4 , for which $\nu_+ = 2$, $z_+ = +1$, $\nu_- = 1$, and $z_- = -2$. If n moles of this electrolyte is dissolved, the solute's contribution to the Gibbs free energy of the entire solution is:

$$G - G_s = n\mu = n(\nu_+\mu_+ + \nu_-\mu_-), \quad (8.3)$$

where μ_+ and μ_- are the chemical potentials of the positive and negative ions separately, and G_s is the free energy due to the solvent.

Because the effects of the positive and negative ions are difficult to separate, we often define the **mean ionic chemical potential** μ_{\pm} as:

$$\mu = \nu\mu_{\pm} = \nu_+\mu_+ + \nu_-\mu_- \quad (8.4)$$

where ν is the total number of ions produced by one mole of solute:

$$\nu = \nu_+ + \nu_- \quad (8.5)$$

In this way, the chemical potential of the solute (from both the positive and negative ions) becomes:

$$\mu = \mu^\circ + RT \ln a = \nu(\mu_{\pm}^\circ + RT \ln a_{\pm}), \quad (8.6)$$

where a_{\pm} is the **mean ionic activity** of the solute, which is related to the activity a by $a = a_{\pm}^\nu$. On the other hand, if we were able to write the chemical potential separately for the positive and the negative ions, we would have:

$$\mu = \nu_+(\mu_+^\circ + RT \ln a_+) + \nu_-(\mu_-^\circ + RT \ln a_-), \quad (8.7)$$

where a_+ and a_- are their activities separately, we see that the mean ionic activity is just the geometric mean of the two separate ionic activities:

$$a_{\pm}^\nu = a_+^{\nu_+} \cdot a_-^{\nu_-} \quad (8.8)$$

To quantify the concentration of electrolyte solutions, it is often convenient to use the **molality** instead of mole fraction. The molality m of a solute is defined as the number of moles of the solute n per kilogram of *solvent*. Because

the solvent has a certain molar mass, the molality of solute i is simply related to its mole fraction x_i by:

$$m_i = \frac{1000x_i}{x_s M_s}, \quad (8.9)$$

where x_s and M_s are the mole fraction and the molar mass (in g/mol) of the *solvent* (the factor 1000 is needed because the molar mass is usually represented in units of grams per mole). The nice feature about using the molality to describe solute concentration instead of the mole fraction or the molarity is that the molality of one solute is independent of all other solutes. In contrast to the molarity, the molality is also independent of temperature or the mixing volume. In the dilute limit, all three concentration measures are proportional to each other. The activity of a solute in an electrolyte solution is often written as the **activity coefficient** γ multiplied by its molality m , so that Eqs.(8.6) and (8.7) become:

$$\mu = \mu^\circ + RT \ln \gamma m = \nu(\mu_\pm^\circ + RT \ln \gamma_\pm m_\pm) \quad (8.10)$$

$$= \nu_+(\mu_+^\circ + RT \ln \gamma_+ m_+) + \nu_-(\mu_-^\circ + RT \ln \gamma_- m_-), \quad (8.11)$$

which requires that the **mean ionic activity coefficient** γ_\pm and the **mean ionic molality** m_\pm be related to the corresponding properties of the separate ions as:

$$\gamma_\pm^\nu m_\pm^\nu = \gamma_+^{\nu_+} \gamma_-^{\nu_-} m_+^{\nu_+} m_-^{\nu_-}, \quad (8.12)$$

or separating the activity coefficient from the molality:

$$\gamma_\pm^\nu = \gamma_+^{\nu_+} \gamma_-^{\nu_-}, \quad (8.13)$$

$$m_\pm^\nu = m_+^{\nu_+} m_-^{\nu_-}. \quad (8.14)$$

Using the molality of the positive and negative ions

$$m_+ = \nu_+ m \quad m_- = \nu_- m, \quad (8.15)$$

we can obtain the necessary relationship between the mean ionic molality and the molality of the solute as

$$m_\pm = (\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu} m. \quad (8.16)$$

With this relationship, we can calculate m_\pm from the molality of the solute. The corresponding expression for the chemical potential is:

$$\mu = \mu^\circ + \nu RT \ln \gamma_\pm m_\pm. \quad (8.17)$$

8.3 Equilibria in Electrolyte Solutions

Before we discuss how to determine the mean ionic activity coefficient, we will look at how nonideality may affect equilibria in electrolyte solutions.

As we know, to first order the correction to the chemical potential for a compound i that is not pure is given by the term $RT \ln x_i$. Since the molality m_i is proportional to x_i , we can replace x_i by m_i by switching to a standard state where $m_i = 1$ instead of $x_i = 1$. The activity coefficient can then be thought of as the second order correction to the chemical potential due to concentration:

$$\mu = \mu^\circ + RT \ln m_i + RT \ln \gamma_i. \quad (8.18)$$

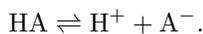
For an ideal solution $\gamma_i \rightarrow 1$.

To illustrate how the inclusion of the activity coefficient influences equilibria in electrolyte solutions, consider first the effect of the solute on the freezing point of the solution. In Ch. 7, we saw how freezing point depression is related to the solute's mole fraction. For a nonideal solution, the mole fraction should be replaced by the activity $a_i = \gamma_i m_i$, so for a dilute solution with only one solute:

$$T'_f - T_f = \left(\frac{RT_f^2 M_s}{1000 \Delta H_{\text{fus}}^\circ} \right) \gamma m, \quad (8.19)$$

where we have used the definition of the molality in Eq.(8.9) and approximated the mole fraction of the solvent by 1. The freezing point depression of an electrolyte solution therefore provides an estimate of the activity coefficient near the freezing temperature. The mean ionic activity coefficients for several electrolyte solutions are shown in Fig. 8.1 as a function of the square root of the molality. One thing is immediately clear – in this molality range (1 molal or less), the activity coefficients are all less than unity and the larger the charges of the dissolved ions, the small it becomes. A second thing that may not be as obvious is that solutions with ions of the same charge composition (e.g. +1:-1 electrolytes like HCl and KCl) seem to have the same activity coefficient in the dilute limit. Interestingly, solutions of a +1:-2 electrolyte like $\text{Ca}(\text{NO}_3)_2$ and a +2:-1 electrolyte like H_2SO_4 also seem to have the same activity coefficients in the dilute limit. Therefore, it appears that it is *not* the sign of the ionic charges that is important for determining the mean activity coefficient, but rather the absolute values of the charges of the ions and their density in the solution. Other colligative properties, such as the osmotic pressure, can also be used to determine the activity coefficients of electrolyte solutions, but the freezing point depression is by far the easiest and most accurate though it only provides activity data near the freezing temperature. Other than colligative properties, equilibrium constants in electrolyte solutions can also be used to determine their activity coefficients.

As a second example of how the activity coefficient of electrolyte solutions may modify their equilibria, consider the dissociation equilibrium of a weak acid HA:



The equilibrium constant for this reaction is

$$K = \frac{a_{\text{H}^+} a_{\text{A}^-}}{a_{\text{HA}}}. \quad (8.20)$$

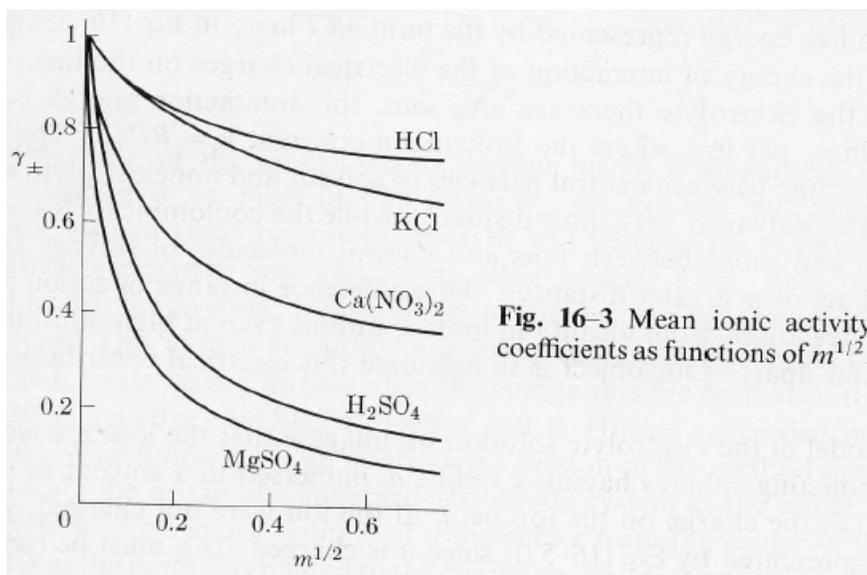


Figure 8.1: Mean ionic activity coefficients of some electrolyte solutions as a function of the molality.

Since

$$a_{\text{H}^+} = \gamma_+ m_{\text{H}^+}, \quad a_{\text{A}^-} = \gamma_- m_{\text{A}^-}, \quad a_{\text{HA}} = \gamma_{\text{HA}} m_{\text{HA}}, \quad (8.21)$$

expressing the molalities in terms of the extent of reaction ξ and the initial molality m :

$$m_{\text{H}^+} = m_{\text{A}^-} = \xi m, \quad m_{\text{HA}} = (1 - \xi)m, \quad (8.22)$$

we obtain the following equation for the equilibrium constant:

$$K = \frac{\gamma_{\pm}^2 \xi^2 m}{\gamma_{\text{HA}} (1 - \xi)}, \quad (8.23)$$

where we have used the mean activity coefficient $\gamma_{\pm} = \gamma_+ \gamma_-$. If the acid is weak ($\xi \ll 1$) and assuming that $\gamma_{\text{HA}} \approx 1$, we can estimate the extent of reaction by the approximation:

$$\xi = \left(\frac{K}{m} \right)^{1/2} \frac{1}{\gamma_{\pm}}. \quad (8.24)$$

As we have seen in Fig. 8.1, deviation from ideality produces an activity coefficient less than unity. Therefore, the extent of dissociation is larger than expected. For example for chloroacetic acid, $K = 1.4 \times 10^{-3}$. The extent of dissociation in a 1 molal solution assuming an ideal value of $\gamma_{\pm} = 1$ is 3.7%. Based on this, the effective ionic molality of this solution is approximately 0.04 m. We

can use Fig. 8.1 to estimate γ_{\pm} for a +1:-1 electrolyte, which for $m = 0.04$ is about 0.8. Using this value for γ_{\pm} , we obtain a dissociation of 4.6%, which is about 25% larger than the ideal value.

By measuring the equilibrium constants of various reactions in electrolyte solutions, their activity coefficients can be determined under a variety of conditions. The majority of activity data for electrolyte solutions comes from electrochemical reactions, which we will discuss later in this chapter. Activity coefficients for some strong electrolyte solutions are shown in the table below.

Table 16-1† Activity coefficients of strong electrolytes

m	0.001	0.005	0.01	0.05	0.1	0.5	1.0
HCl	0.966	0.928	0.904	0.830	0.796	0.758	0.809
NaOH	—	—	—	0.82	—	0.69	0.68
KOH	—	0.92	0.90	0.82	0.80	0.73	0.76
KCl	0.965	0.927	0.901	0.815	0.769	0.651	0.606
NaBr	0.966	0.934	0.914	0.844	0.800	0.695	0.686
H ₂ SO ₄	0.830	0.639	0.544	0.340	0.265	0.154	0.130
K ₂ SO ₄	0.89	0.78	0.71	0.52	0.43	—	—
Ca(NO ₃) ₂	0.88	0.77	0.71	0.54	0.48	0.38	0.35
CuSO ₄	0.74	0.53	0.41	0.21	0.16	0.068	0.047
MgSO ₄	—	—	0.40	0.22	0.18	0.088	0.064
La(NO ₃) ₃	—	—	0.57	0.39	0.33	—	—
In ₂ (SO ₄) ₃	—	—	0.142	0.054	0.035	—	—

† By permission from Wendell M. Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*. 2nd ed., Prentice-Hall, Inc., Englewood Cliffs, N.J., 1952, pp. 354–356.

Figure 8.2: Activity coefficients for some strong electrolyte solutions.

8.4 Electrostatics

In the next section, we will describe how to estimate the activity coefficients of electrolyte solutions. To prepare for that, we will first review some basic ideas of electrostatics.

The key to understanding electrolyte solutions is to realize that the interactions between ions are *long range*. In contrast with other nonbonded interactions, such as dispersion interactions between gas molecules discussed in Ch. 1 which operate over a distance of just a few angstroms, the Coulombic interactions between charged particles reach over much longer distances, often

hundreds of angstroms or more. This means that a large number of ions can interact with each other at the same time, and so to understand a single ion, we must account for the influence of the rest of the ions on it.

To appreciate this, we turn to a familiar example. Everyone knows that high and low tides are caused by the gravitational field of the moon, but few people question why the moon can have such large effects on the ocean on earth's surface when it is almost 400,000 km away. Just like the Coulombic forces between charged particles, gravitational forces act over large distances though they are small in absolute magnitude. In fact, gravitational forces has exactly the same distance dependence as Coulombic forces.

The potential energy between two charged particles with charge z_1q_e and z_2q_e (q_e is the electron charge) separated by a distance r follows the Coulomb law:

$$u(r) = \frac{q_e^2}{4\pi\epsilon} \frac{z_1z_2}{r}, \quad (8.25)$$

where the **electric permittivity** $\epsilon = \epsilon_0\epsilon_r$ is the product of the vacuum permittivity ϵ_0 and the dielectric constant ϵ_r of the medium. The dielectric constant ϵ_r accounts for the fact that the medium might contains flexible dipoles which to a certain degree can reorient themselves to dilute the Coulombic interactions between the ions. In vacuum, the dielectric constant is one, and in water it is 78.

Now, imagine that we have a collection of ions at positions $\mathbf{r}_1, \mathbf{r}_2$, etc. If I place a new charge z at position \mathbf{r} , the potential energy of this charge is given by the the electric potential ϕ at this point multiplied by z :

$$U(\mathbf{r}) = zq_e\phi(\mathbf{r}) \quad (8.26)$$

and for the present case, the electric potential is produced a sum over the effects of all the ions:

$$zq_e\phi(\mathbf{r}) = \sum_i u(|\mathbf{r} - \mathbf{r}_i|). \quad (8.27)$$

We can also use the **charge density** ρ to rewrite this equation as:

$$\phi(\mathbf{r}) = \frac{1}{4\pi\epsilon} \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (8.28)$$

where $\rho(\mathbf{r}')$ is the total charge per unit volume at position \mathbf{r}' . According to electrostatics, the charge density is related to the electric potential by the **Poisson equation**:

$$-\nabla^2\phi(\mathbf{r}) = \frac{\rho(\mathbf{r})}{\epsilon}. \quad (8.29)$$

(The Poisson equation can be easily proven by substituting Eq.(8.28) into Eq.(8.29) in Fourier space.)

In general, the electric potential does not provide any additional information beyond what is given by the charge density ρ in conjunction with Coulomb's law. But if the ions are free to move about in solution, they will arrange themselves

according to the electric potential, and the resulting charge density will be a function of the electric potential. If we can express ρ as a function of ϕ , the Poisson equation can be solved self-consistently for the density ρ .

8.5 Debye-Hückel Theory

The first successful theory of electrolyte solutions was formulated by Debye and Hückel in 1923, which now bears their names.

The basic idea behind Debye-Hückel theory is that the ions, since they are free to move about in the solution, will try to arrange themselves around a certain ion in order to lower the energy. Thus, surrounding an ion of a certain charge z , you will always find a higher than average density of ions of the opposite charge. While enhancing the local density of the opposite charges, this **screening layer** will greatly reduce the Coulombic force of this ion z on charges far away. The thickness of the screening layer, which is given the symbol κ^{-1} in Debye-Hückel theory, effectively cuts off the long-ranged nature of the Coulomb interactions. Beyond the screening length κ^{-1} , ions are effectively noninteracting. Whereas inside κ^{-1} , Debye-Hückel theory provides an estimate for the charge density, and the interaction between it and the charge z can be used to determine the chemical potential of each ion.

Let's say we have a solution with positive ions having charge z_+q_e and negative ions having charge z_-q_e . Imagine there is also an ion of charge z at the origin. (This ion must have an excluded volume, so the other charges don't collapse onto the center of it.) This ion polarizes the ionic density around it creating a screening layer. We expect spherical symmetry around this ion so the density of the ions in the vicinity of the origin is a function only of r , the distance from the origin, and it is controlled by the electric potential ϕ , which is also a function of r . This is shown schematically in Fig. 8.3 for a positive z . We can separate the charge density $\rho(r)$ into the density of the positive ions $\rho_+(r)$ and the density of the negative ions $\rho_-(r)$, such that $\rho(r) = q_e(z_+\rho_+(r) + z_-\rho_-(r))$.

Now we let the charge at the origin be the same as one of the positive ions $z = z_+$. We expect $\phi(r) > 0$ close to the origin. In Ch. 4, we saw that the probability of a microstate follows the Boltzmann distribution, so we expect the density of the positive and negative ions around z to be:

$$z_+\rho_+(r) = z_+\rho_+e^{-z_+q_e\phi(r)/k_B T} \approx z_+\rho_+ \left(1 - \frac{z_+q_e\phi(r)}{k_B T}\right), \quad (8.30)$$

$$z_-\rho_-(r) = z_-\rho_-e^{-z_-q_e\phi(r)/k_B T} \approx z_-\rho_- \left(1 - \frac{z_-q_e\phi(r)}{k_B T}\right), \quad (8.31)$$

where ρ_+ and ρ_- are the average density of the positive and negative ions, which must make the entire solution neutral according to the condition:

$$0 = z_+\rho_+ + z_-\rho_-. \quad (8.32)$$

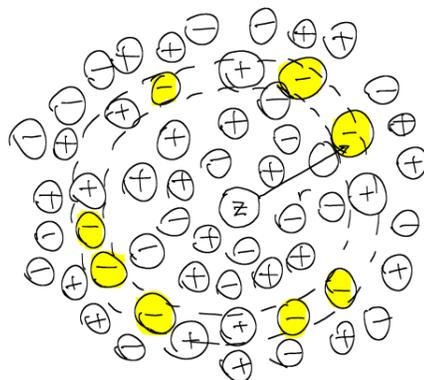


Figure 8.3: A charge with positive z at the origin and the screening layer around it.

The total charge density is the sum of $z_+\rho_+(r)$ and $z_-\rho_-(r)$:

$$\rho(r) = -\frac{(z_+^2\rho_+ + z_-^2\rho_-)q_e^2}{k_B T}\phi(r), \quad (8.33)$$

and it must obey the Poisson equation $-\nabla^2\phi = \rho/\epsilon$. It is easy to show that the charge density must be:

$$\rho(r) = -Cz\frac{e^{-\kappa r}}{r}, \quad (8.34)$$

where

$$\kappa^2 = \frac{(z_+^2\rho_+ + z_-^2\rho_-)q_e^2}{k_B T\epsilon}. \quad (8.35)$$

and the multiplicative constant is $C = q_e\kappa^2/4\pi$.

Eq.(8.34) is the key result of Debye-Hückel theory. As expected, whereas the average charge density in the solution is zero, the charge density in the neighborhood of a positive ion is negative, indicating that there is a screening layer of excess negative ions around the positive ion. The thickness of the screening layer is approximately κ^{-1} . At distances large compared to κ^{-1} , the charge density is little affected by the ion at the origin because of the exponential function. We can estimate the typical size of the screening length. In a 0.1 M solution of NaCl in water ($\epsilon_r = 78$), the screening length is 9.6 Å. Because κ^2 is proportional to the concentration, the screening length increases as the square root of decreasing concentration. In a 0.001 M NaCl solution, the screening length becomes 96 Å. (It is important to point out that these ionic concentrations are actually too large to be inside the range of applicability of Debye-Hückel theory, as we will see later.)

Finally, we can compute the contribution of the electrostatic interactions between the ion and the screening layer to the chemical potential of the solution. Since μdn is the work associated with particle insertion, we can simply compute

μ by calculating the differential work δw of adding one ion to the solution. To do this, we slowly turn on the charge z of the ion at the origin, from 0 to z_+ :

$$\delta w = \int_0^{z_+} dz \frac{q_e}{4\pi\epsilon} \int dr 4\pi r^2 \frac{\rho(r)}{r}, \quad (8.36)$$

where we have used Eqs.(8.27) and (8.28). We substitute in $\rho(r)$ from Eq.(8.34) and find that the differential work of adding a single positive ion of charge z_+ to the solution will result in an amount of work

$$-\frac{q_e^2 \kappa}{4\pi\epsilon} \frac{z_+^2}{2}. \quad (8.37)$$

(The same result may be obtained by calculated the extra electrostatic energy produced by placing a charge z_+ at the origin.) The work per mole is this multiplied by Avogadro's number, which must then be the correction to the chemical potential due to the electrostatic interactions per mole of positive ions:

$$RT \ln \gamma_+ = -\mathcal{N}_a \frac{1}{4\pi} \frac{z_+^2 q_e^2 \kappa}{2\epsilon}. \quad (8.38)$$

There is a similar formula for the negative ions:

$$RT \ln \gamma_- = -\mathcal{N}_a \frac{1}{4\pi} \frac{z_-^2 q_e^2 \kappa}{2\epsilon}. \quad (8.39)$$

According to Eq.(8.17),

$$\nu RT \ln \gamma_{\pm} = \nu_+ RT \ln \gamma_+ + \nu_- RT \ln \gamma_-, \quad (8.40)$$

so

$$\nu \ln \gamma_{\pm} = -\frac{1}{4\pi} \frac{q_e^2 \kappa}{2\epsilon k_B T} (\nu_+ z_+^2 + \nu_- z_-^2). \quad (8.41)$$

We define the **ionic strength** of an electrolyte solution as:

$$I = \frac{1}{2} \sum_i z_i^2 m_i, \quad (8.42)$$

where z_i is the valence of the ion i and m_i is its molality, and rewrite Eq.(8.41) as

$$\nu \ln \gamma_{\pm} = -A' \sqrt{I} (\nu_+ z_+^2 + \nu_- z_-^2), \quad (8.43)$$

where the coefficient A' is

$$A' = (2\pi \mathcal{N}_a \rho_s)^{\frac{1}{2}} \left(\frac{q_e^2}{4\pi\epsilon k_B T} \right)^{\frac{3}{2}}, \quad (8.44)$$

and ρ_s is the density of the solvent in mass per unit volume. For water at 25°C, A' is approximately $1.17 \text{ (mol/ky)}^{-\frac{1}{2}}$, when the molality of the ions are expressed in mole per kilogram of solvent. Using the neutrality condition

$$\nu_+ z_+ + \nu_- z_- = 0, \quad (8.45)$$

we can get a much more compact expression from Eq.(8.43):

$$\ln \gamma_{\pm} = 2.303 \log \gamma_{\pm} = A' \sqrt{I} z_+ z_-. \quad (8.46)$$

Fig. 8.4 illustrates the validity of Debye-Hückel theory for several electrolyte solutions, plotting $\log \gamma_{\pm} = \ln \gamma_{\pm}/2.303$ as a function of \sqrt{I} . The dashed lines are the limiting behaviors predicted by Debye-Hückel theory. The figure shows that while Debye-Hückel theory provides the correct limiting behavior for the activity coefficient at infinite dilution, it quickly breaks down for ionic strength as small as 0.0005 or 0.001.

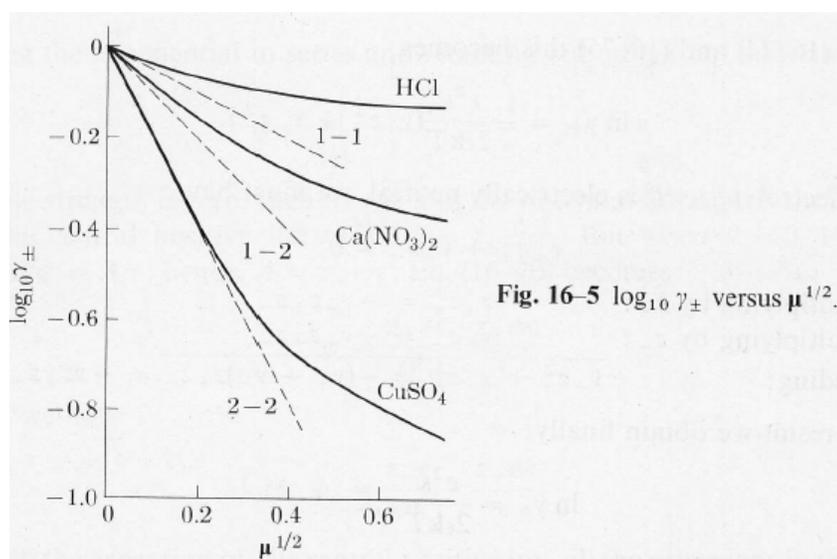


Fig. 16-5 $\log_{10} \gamma_{\pm}$ versus $\mu^{1/2}$.

Figure 8.4: The log of the mean ionic activity for several electrolyte solutions plotted as a function of the square root of the ionic strength.

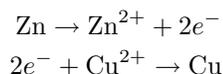
8.6 Electrochemistry

An electrochemical cell is where a chemical reaction occurs in connection with an electric current. An electric current is produced by the flow of electrons (or another mobile charge carrier). In metals, the dominant charge carriers are electrons. If a wire is made out of metals, electrons can flow through it with minimal resistance. Electrons will flow spontaneously from a position of high potential energy to low potential energy. The potential energy of a charge at a certain position \mathbf{r} is given by Eq.(8.26),

$$U(\mathbf{r}) = zq_e \phi(\mathbf{r}).$$

For example, if two ends of a metallic wire are hooked up to the terminals of a battery, a current will flow due to the electric potential difference between the two terminals, and the current flow can be used to do work.

A **galvanic cell** is an electrochemical cell where a current flow is produced spontaneously by an oxidation-reduction couple. An example is the reaction between Zn and Cu^{2+} . When metallic Zn is put into a solution containing Cu^{2+} , an oxidation-reduction reaction occurs at the interface between the Zn metal and the solution, transferring electrons from Zn to the Cu^{2+} ions and producing Zn^{2+} and Cu. This direct reaction between Zn and Cu^{2+} does not produce a detectable current, because the electrons transfer directly between the Zn atoms and the Cu^{2+} ions. In order to produce an electric current, these two reactants must be separated from each other, and the electrons that need to be transferred between them can then be forced to go through a wire. This requires separating the redox couple into the two **half-reactions**:



as in Fig. 8.5. This device is called a galvanic cell. Notice that the electrons leaving the Zn electrode must travel through the circuit to reach the Cu electrode. (The salt bridge allows the ions to flow to maintain electric neutrality in the two half-cells without substantial mixing between the two solutions.) Because the electron transfer occurs spontaneously between Zn and Cu^{2+} when they were together, the electron flow when they are separated should also occur spontaneously. This means that there must be an electric potential difference between the two electrodes – the Zn electrode must have a more negative potential ϕ_{Zn} (higher energy for the electrons) and the Cu electrode a more positive potential ϕ_{Cu} (lower energy for the electrons). A galvanic cell produces the same effect as a battery and can be used as such.

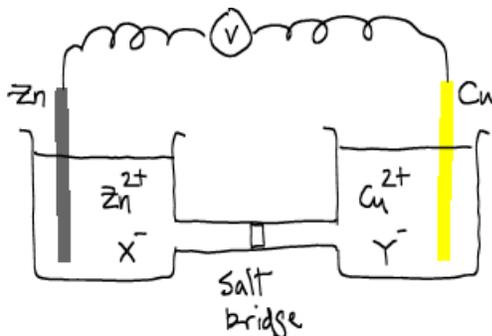


Figure 8.5: A galvanic cell utilizing the reaction $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$. (X^- and Y^- are counterions.)

We can now use thermodynamics to analyze a galvanic cell. First, we will

disconnect the wire and consider each half of Fig. 8.5. In the Zn half-cell, the chemical potentials of the Zn metal and the Zn^{2+} ions are:

$$\mu_{\text{Zn}} = \mu_{\text{Zn}}^{\circ}, \quad (8.47)$$

$$\mu_{\text{Zn}^{2+}} = \mu_{\text{Zn}^{2+}}^{\circ} + RT \ln a_{\text{Zn}^{2+}}. \quad (8.48)$$

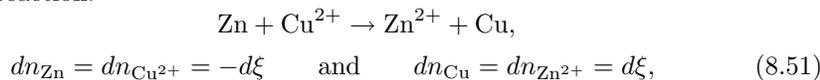
In the Cu half-cell, we have

$$\mu_{\text{Cu}} = \mu_{\text{Cu}}^{\circ}, \quad (8.49)$$

$$\mu_{\text{Cu}^{2+}} = \mu_{\text{Cu}^{2+}}^{\circ} + RT \ln a_{\text{Cu}^{2+}}. \quad (8.50)$$

With the wire disconnected and the circuit open, there is of course no reaction.

When the circuit is closed, electrons will flow producing a change in the Gibbs free energy of the cell. Let's consider an extent of reaction $d\xi$ for the overall reaction:



where n denotes the number of moles. Corresponding to $d\xi$, the change in G due to all the dn is

$$dG_1 = (\mu_{\text{Zn}^{2+}} + \mu_{\text{Cu}} - \mu_{\text{Zn}} - \mu_{\text{Cu}^{2+}}) d\xi \quad (8.52)$$

$$= \left(\Delta G_r^{\circ} + RT \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \right) d\xi, \quad (8.53)$$

where following the notation of Ch. 6, ΔG_r° is the standard Gibbs free energy change of the reaction. Since every time one mole of the reaction occurs, two moles of electrons must be transferred through the wire, the work done by the electrons when they travel from the Zn to the Cu electrode (from low electric potential ϕ_{Zn} to high electric potential ϕ_{Cu}) must also be included in the change in G :

$$dG_2 = 2\mathcal{N}_a q_e (\phi_{\text{Cu}} - \phi_{\text{Zn}}) d\xi, \quad (8.54)$$

where \mathcal{N}_a is Avogadro's number and q_e is the charge of one electron. The potential difference $\phi_{\text{Cu}} - \phi_{\text{Zn}}$ is known as the **cell potential** or the **electromotive force**, \mathcal{E} , and the total charge of one mole of electrons is $\mathcal{N}_a q_e$, which is also called the *Faraday's constant* \mathcal{F} . With these,

$$dG_2 = \nu_e \mathcal{F} \mathcal{E} d\xi, \quad (8.55)$$

where $\nu_e = 2$ is the number of electrons transferred per mole of this reaction. Adding dG_1 and dG_2 , the total change is:

$$dG = \left(\Delta G^{\circ} + RT \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} + \nu_e \mathcal{F} \mathcal{E} \right) d\xi. \quad (8.56)$$

If the reaction is carried out very slowly, e.g. by slowing down the electron flow, the system would be in equilibrium every step along the way and $dG = 0$. This requires:

$$\mathcal{E} = -\frac{1}{\nu_e \mathcal{F}} \left(\Delta G^{\circ} + RT \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \right), \quad (8.57)$$

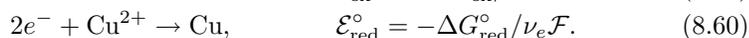
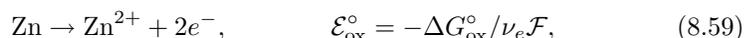
which relates the cell potential to the ΔG of reaction and the activities of the ions. One way to slow down the electrons is by putting a very large, almost infinite, resistive load on the circuit. An infinite resistance would correspond to an open circuit, so the cell potential given by Eq.(8.57) is sometimes call the **open-circuit voltage**. If the electron flow is not slow, the observed cell potential will be smaller in magnitude because $dG < 0$.

Eq.(8.57) is usually rewritten in the following way:

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{\nu_e \mathcal{F}} \ln \mathcal{Q}, \quad (8.58)$$

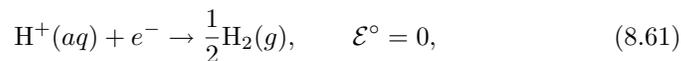
where $\mathcal{E}^\circ = -\Delta G^\circ / \nu_e \mathcal{F}$ is called the **standard cell potential** and \mathcal{Q} is the reaction quotient defined in Ch. 6, which for this reaction is $a_{\text{Zn}^{2+}} / a_{\text{Cu}^{2+}}$. The cell potential has units of energy over charge, or volts (V) in SI.

For the standard cell potential \mathcal{E}° , we can define a **standard half-cell potential** for the reduction and oxidation half-reactions as:



What to use for the standard state of the electrons is unimportant since the chemical potential for the electrons will always cancel out, and for convenience we will assume it is zero. The standard cell potential is then $\mathcal{E}^\circ = \mathcal{E}_{\text{ox}}^\circ + \mathcal{E}_{\text{red}}^\circ$. Notice that since ν_e is already divided out, you do not need to multiply \mathcal{E}° by any stoichiometric coefficient as you would with ΔG . Standard half-cell potentials are listed for reduction half-reactions in standard tables. To get the oxidation half-cell potential, simply reverse the direction of the half-reaction and flip the sign of \mathcal{E}° .

Notice that since the overall cell potential is always the difference between two half-cell potentials, where the zero is set for each half-cell potential is unimportant, as long as the same reference is used for both half-reactions. The reference that is commonly employed in chemistry is the **standard hydrogen reduction half-potential**:

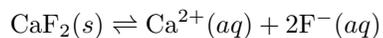


which is *defined* to be zero when $\text{H}^+(aq)$ and $\text{H}_2(g)$ are in their standard states: 1 molal for H^+ and 1 bar for H_2 .

8.7 Effects of Activities on Aqueous Equilibria

When we discussed the nonideality of electrolyte solution earlier, we have already looked at how the activities may affect acid-base equilibria and colligative properties. In general, since the activity coefficient of an electrolyte solution can be significantly different from one, its effect on any equilibrium involving ions can be very pronounced.

For example, the equilibrium constant for the dissolution of CaF_2



at 25°C is 4.0×10^{-11} .

$$K_{\text{sp}} = a_{\text{Ca}^{2+}} a_{\text{F}^{-}}^2 = (m_{\text{Ca}^{2+}} m_{\text{F}^{-}}^2)(\gamma_+ \gamma_-^2) = (m_{\text{Ca}^{2+}} m_{\text{F}^{-}}^2) \gamma_{\pm}^3 \quad (8.62)$$

In pure water, the solubility is roughly 2.2×10^{-4} mole per kg of water. Using Fig. 8.4, we can estimate the mean ionic activity of CaF_2 for different ionic strengths using the curve for another +2:-1 electrolyte $\text{Ca}(\text{NO}_3)_2$. At an ionic strength of 0.1, $\gamma_{\pm} \approx 0.6$. The solubility becomes 3.6×10^{-4} which is 60% larger than in pure water.