10.1: Single-ion Quantities

Consider a solution of an electrolyte solute that dissociates completely into a cation species and an anion species. Subscripts $+$ and $-$ will be used to denote the cation and anion, respectively. The solute molality m_B is defined as the amount of solute formula unit divided by the mass of solvent.

We first need to investigate the relation between the chemical potential of an ion species and the electric potential of the solution phase.

The electric potential ϕ in the interior of a phase is called the *inner electric potential*, or *Galvani potential*. It is defined as the work needed to reversibly move an infinitesimal test charge into the phase from a position infinitely far from other charges, divided by the value of the test charge. The electrical potential energy of a charge in the phase is the product of ϕ and the charge.

Consider a hypothetical process in which an infinitesimal amount dn_+ of the cation is transferred into a solution phase at constant T and p. The quantity of charge transferred is $\delta Q = z_+ F \, dn_+$, where z_+ is the charge number ($+1$, $+2$, etc.) of the cation, and F is the Faraday constant. (The Faraday constant is the charge per amount of protons.) If the phase is at zero electric potential, the process causes no change in its electrical potential energy. However, if the phase has a finite electric potential ϕ, the transfer process changes its electrical potential energy by $\phi \delta Q = z_+ F \phi \, dn_+$. Consequently, the internal energy change depends on ϕ according to

$$dU(\phi) = dU(0) + z_+ F \phi \, dn_+ \tag{10.1.1}$$

where the electric potential is indicated in parentheses. The change in the Gibbs energy of the phase is given by $dG = d(U - TS + pV)$, where T, S, p, and V are unaffected by the value of ϕ. The dependence of dG on ϕ is therefore

$$dG(\phi) = dG(0) + z_+ F \phi \, dn_+ \tag{10.1.2}$$

The Gibbs fundamental equation for an open system, $dG = -S \, dT + V \, dp + \sum_i \mu_i \, dn_i$ (Eq. 9.2.34), assumes the electric potential is zero. From this equation and Eq. 10.1.2, the Gibbs energy change during the transfer process at constant T and p is found to depend on ϕ according to

$$dG(\phi) = [\mu_+(0) + z_+ F \phi] \, dn_+ \tag{10.1.3}$$

The chemical potential of the cation in a phase of electric potential ϕ, defined by the partial molar Gibbs energy $[\partial G(\phi)/\partial n_+]_{T,p}$, is therefore given by

$$\mu_+(\phi) = \mu_+(0) + z_+ F \phi \tag{10.1.4}$$

The corresponding relation for an anion is

$$\mu_-(\phi) = \mu_-(0) + z_- F \phi \tag{10.1.5}$$

where z_- is the charge number of the anion (-1, -2, etc.). For a charged species in general, we have

$$\mu_i(\phi) = \mu_i(0) + z_i F \phi \tag{10.1.6}$$

We define the *standard state of an ion* on a molality basis in the same way as for a nonelectrolyte solute, with the additional stipulation that the ion is in a phase of zero electric potential. Thus, the standard state is a hypothetical state in which the ion is at molality m° with behavior extrapolated from infinite dilution on a molality basis, in a phase of pressure $p = p^\circ$ and electric potential $\phi = 0$.

The *standard chemical potential* μ_+° or μ_-° of a cation or anion is the chemical potential of the ion in its standard state. Single-ion activities a_+ and a_- in a phase of zero electric potential are defined by relations having the form of Eq. 9.7.8:

$$\mu_+(0) = \mu_+^\circ + RT \ln a_+ \qquad \mu_-(0) = \mu_-^\circ + RT \ln a_- \tag{10.1.7}$$

As explained in Sec. 9.7, a_+ and a_- should depend on the temperature, pressure, and composition of the phase, and not on the value of ϕ.

From Eqs. 10.1.4, 10.1.5, and 10.1.7, the relations between the chemical potential of a cation or anion, its activity, and the electric potential of its phase, are found to be

$$\mu_+ = \mu_+^\circ + RT \ln a_+ + z_+ F \phi \qquad \mu_- = \mu_-^\circ + RT \ln a_- + z_i F \phi \tag{10.1.8}$$

These relations are definitions of single-ion activities in a phase of electric potential ϕ.

For a charged species in general, we can write

$$\mu_i = \mu_i^\circ + RT \ln a_i + z_i F\phi \tag{10.1.9}$$

Note that we can also apply this equation to an uncharged species, because the charge number z_i is then zero and Eq. 10.1.9 becomes the same as Eq. 9.7.2.

Some thermodynamicists call the quantity $(\mu_i^\circ + RT \ln a_i)$, which depends only on T, p, and composition, the *chemical potential* of ion i, and the quantity $(\mu_i^\circ + RT \ln a_i + z_i F\phi)$ the *electrochemical potential* with symbol $\tilde{\mu}_i$.

Of course there is no experimental way to evaluate either μ_+ or μ_- relative to a reference state or standard state, because it is impossible to add cations or anions by themselves to a solution. We can nevertheless write some theoretical relations involving μ_+ and μ_-.

For a given temperature and pressure, we can write the dependence of the chemical potentials of the ions on their molalities in the same form as that given by Eq. 9.5.18 for a nonelectrolyte solute:

$$\mu_+ = \mu_+^{\text{ref}} + RT \ln\left(\gamma_+ \frac{m_+}{m^\circ}\right) \qquad \mu_- = \mu_-^{\text{ref}} + RT \ln\left(\gamma_- \frac{m_-}{m^\circ}\right) \tag{10.1.10}$$

Here μ_+^{ref} and μ_-^{ref} are the chemical potentials of the cation and anion in solute reference states. Each reference state is defined as a hypothetical solution with the same temperature, pressure, and electric potential as the solution under consideration; in this solution, the molality of the ion has the standard value m°, and the ion behaves according to Henry's law based on molality. γ_+ and γ_- are single-ion activity coefficients on a molality basis.

The single-ion activity coefficients approach unity in the limit of infinite dilution:

$$\gamma_+ \to 1 \quad \text{and} \quad \gamma_- \to 1 \quad \text{as} \quad m_{\text{B}} \to 0 \tag{10.1.11}$$
$$(\text{constant } T, p, \text{ and } \phi)$$

In other words, we assume that in an extremely dilute electrolyte solution each individual ion behaves like a nonelectrolyte solute species in an ideal-dilute solution. At a finite solute molality, the values of γ_+ and γ_- are the ones that allow Eq. 10.1.10 to give the correct values of the quantities $(\mu_+ - \mu_+^{\text{ref}})$ and $(\mu_- - \mu_-^{\text{ref}})$. We have no way to actually measure these quantities experimentally, so we cannot evaluate either γ_+ or γ_-.

We can define single-ion pressure factors Γ_+ and Γ_- as follows:

$$\Gamma_+ \overset{\text{def}}{=} \exp\left(\frac{\mu_+^{\text{ref}} - \mu_+^\circ}{RT}\right) \approx \exp\left[\frac{V_+^\infty (p - p^\circ)}{RT}\right] \tag{10.1.12}$$

$$\Gamma_- \overset{\text{def}}{=} \exp\left(\frac{\mu_-^{\text{ref}} - \mu_-^\circ}{RT}\right) \approx \exp\left[\frac{V_-^\infty (p - p^\circ)}{RT}\right] \tag{10.1.13}$$

The approximations in these equations are like those in Table 9.6 for nonelectrolyte solutes; they are based on the assumption that the partial molar volumes V_+ and V_- are independent of pressure.

From Eqs. 10.1.7, 10.1.10, 10.1.12, and 10.1.13, the single-ion activities are related to the solution composition by

$$a_+ = \Gamma_+ \gamma_+ \frac{m_+}{m^\circ} \qquad a_- = \Gamma_- \gamma_- \frac{m_-}{m^\circ} \tag{10.1.14}$$

Then, from Eq. 10.1.9, we have the following relations between the chemical potentials and molalities of the ions:

$$\mu_+ = \mu_+^\circ + RT \ln(\Gamma_+ \gamma_+ m_+/m^\circ) + z_+ F\phi \tag{10.1.15}$$

$$\mu_- = \mu_-^\circ + RT \ln(\Gamma_- \gamma_- m_-/m^\circ) + z_- F\phi \tag{10.1.16}$$

Like the values of γ_+ and γ_-, values of the single-ion quantities a_+, a_-, Γ_+, and Γ_- cannot be determined by experiment.