Chapter 10 Electrolyte Solution

Solute in electrolyte solution exists in solvated ions (+ or - ions).

Nonelectrolyte solution (Chap 4);
\[ \Delta H^\circ_f = 0, \Delta G^\circ_f = 0 \text{ for pure substance (1bar)} \] .......(a)
→Calculate \( \Delta H^\circ_f, \Delta G^\circ_f \) for compound.

Electrolyte solution: Long range electrostatic (Coulombic) interactions exist between the ions ↔ van der Waals force between the neutral solutes (intermolecular interactions). So, in addition to (a)

→ \( \Delta G^\circ_f (H^+, aq) = 0 \) → Calculate \( \Delta H^\circ_f, \Delta G^\circ_f, S^a \) for ions.

10.1 Enthalpy, entropy, Gibbs energy of ion formation in solution

Electrolytes: Substances that dissociate into positively and negatively charged mobile solvated ions in solvent (water in our text).

Consider the following overall reaction in water:

\[ \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow H^+(aq) + Cl^-(aq) \]...... (1)

\( H^+(aq), Cl^-(aq) \) = Solvated, charged ions and their associated hydration shell. The hydration shell lowers the energy of ions, thereby making the reaction spontaneous. Although energy flow into the system is required to dissociate and ionize the hydrogen and chlorine, more energy is gained in the orientation of the dipolar water molecular around the ion in the solvation wall.

→ \( \Delta H_R = -167.2 \text{ kJ/mole } \) @ Constant pressure (for rxn 1) (Exothermic)
(What about gas phase rxn?)

The standard state enthalpy (heat of formation) for the reaction can be written in terms of formation enthalpies:
\[ \Delta H_R = \Delta H^o_1(H^+, \text{aq}) + \Delta H^o_2(\text{Cl}^-, \text{aq}) - 0 - 0 \quad (2) \]

(Note that \( \Delta H^o \) for pure element in its standard state = 0)

\( \Delta H^o_1(\text{H}^+, \text{aq}) \) and \( \Delta H^o_2(\text{Cl}^-, \text{aq}) \) are measured together (by formula unit), not by the individual ion since the solution must remain electrically neutral, and hence any dissociation reactions of neutral solute must produce both anions and cations.

How can the formation enthalpy, entropy, and Gibbs energy for individual solvated cation and anion are obtained?

This can be done by making an appropriate choice for the zero of \( \Delta H^o_f \), \( \Delta G^o_f \), and \( S^o \).

By convention
\[ \Delta G^o_f(H^+, \text{aq}) = 0 \quad \text{for all } T \quad (3) \]

Then, from \( dG = -SdT + Vdp \) and \( G = H - TS \)

\[ S^o(H^+, \text{aq}) = -\left( \frac{\partial \Delta G^o_f(H^+, \text{aq})}{\partial T} \right)_p = 0 \quad \text{and} \]

\[ \Delta H^o_f(H^+, \text{aq}) = \Delta G^o_f(H^+, \text{aq}) + T\Delta S^o(H^+, \text{aq}) = 0 \quad (4) \]

Based on this, the numerical values for \( \Delta H^o_f \), \( \Delta G^o_f \), and \( S^o \) for other ions can be assigned as shown later.

\[ \Delta H^o_R = \text{Measured using calorimeter (=C_p\Delta T). Then,} \]

\[ \Delta G^o_R = -RT \ln K \quad (b) \]

(K is determined by measuring the degree of dissociation.)

And \( \Delta S^o_R \) is determined by

\[ \Delta S^o_R = \frac{\Delta H^o_R - \Delta G^o_R}{T} \quad .......(c) \]
Then, from eq (2) and convention for $\Delta H_f^\circ$ and $\Delta G_f^\circ = 0$ for element:

$$\Delta H_R^\circ = \Delta H_f^\circ(\text{Cl}^-, \text{aq}) + 0 - 0 = \Delta H_f^\circ(\text{Cl}^-, \text{aq}),$$
$$\Delta G_R^\circ = \Delta G_f^\circ(\text{Cl}^-, \text{aq}) + 0 - 0 = \Delta G_f^\circ(\text{Cl}^-, \text{aq})$$

$$\Delta S_R^\circ = S^\circ(\text{Cl}^-, \text{aq}) + 0 - \frac{1}{2} S^\circ(\text{H}_2, g) - \frac{1}{2} S^\circ(\text{Cl}_2, g)$$

In this way the following are obtained.

$$\Delta H_f^\circ(\text{Cl}^-, \text{aq}) = -167.2 \text{ kJ/mol} \quad \text{(See also Table 10.1 @298.15K)}$$
$$S^\circ(\text{Cl}^-, \text{aq}) = 56.5 \quad \text{(See also Table 10.1 @298.15K)}$$
$$\Delta G_f^\circ(\text{Cl}^-, \text{aq}) = -131.2 \quad \text{(See also Table 10.1 @298.15K)}$$

These values can be used to determine the formation functions of other ions. Example:

$$\text{NaCl}(s) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq) \quad (5)$$

The std rxn enthalpy, $\Delta H_R^\circ = +3.90$ kJ/mole (Experimental). Enthalpy change for this reaction is,

$$\Delta H_R = \Delta H_f(\text{Cl}^-, \text{aq}) + \Delta H_f(\text{Na}^+, \text{aq}) - \Delta H_f(\text{NaCl}, s) \quad (6)$$

Tabulated data: $\Delta H_f^\circ(\text{NaCl}, s) = -411.2$ kJ/mol, $\Delta H_f^\circ(\text{Cl}^-, \text{aq}) = -167.2$ kJ/mole (calculated above) $\rightarrow [\Delta H_f^\circ(\text{Na}^+, \text{aq}) + (-167.2)] - (-411.2)] = 3.9 \rightarrow \Delta H_f^\circ(\text{Na}^+, \text{aq}) = -240.1$

See Table 10.1 for $\Delta H_f^\circ$, $\Delta G_f^\circ$, $S^\circ$ for various aqueous ion species.

Notes

1) $\Delta G_f^\circ$, $\Delta H_f^\circ$, $S^\circ$ for ions are defined relative to $\text{H}^+$ (aq).

2) $\Delta H_f^\circ < 0 \rightarrow$ More exothermic than $\text{H}^+$ (aq).

(Multiple charged or smaller ion is more negative due to the greater interactions btn ions and water in solvation shell.)
3) Entropy decreases as the hydration shell is formed since water molecules are oriented in hydration shell.

► The hydration shell of an ion in water
An ion inserted into water rotates water molecules so that their polarized charges face the oppositely charged central ion while breaking their hydrogen bonds to their nearest neighbors. By doing this salt water has a lower freezing point than pure water. The group of water molecules oriented around an ion is called a hydration shell.

![Hydration Shell Diagram]

10.2 Understanding the thermodynamics of ion formation and solvation
\( \Delta H^o, \Delta G^o, S^o \) are measured for formula unit as above.

Values for individual ions can be calculated using thermodynamic model as below (Focused on \( \Delta G_f^o \)).

Individual contributions to \( \Delta G_f^o \) for \( H^+(aq) \) and \( Cl^-(aq) \) formation

\[
\begin{align*}
1/2 H_2(g) &\rightarrow H(g) & \Delta G_R^o = 203.3 kJ/mol^{-1} \\
1/2 Cl_2(g) &\rightarrow Cl(g) & \Delta G_R^o = 105.7 kJ/mol^{-1} \\
H(g) &\rightarrow H^+(g) + e^- & \Delta G_R^o = 1312 kJ/mol^{-1} \\
Cl(g) + e^- &\rightarrow Cl^-(g) & \Delta G_R^o = -349 kJ/mol^{-1} \\
Cl^-(g) &\rightarrow Cl^-(aq) & \Delta G_R^o = \Delta G_{solvation}^{o} (Cl^-,aq) \\
H^+(g) &\rightarrow H^+(aq) & \Delta G_R^o = \Delta G_{solvation}^{o} (H^+,aq)
\end{align*}
\]

\[
1/2 H_2(g) + 1/2 Cl_2(g) \rightarrow H^+(aq) + Cl^- (aq) \quad \Delta G_R^o = -131.2 kJ/mol^{-1}
\]

The pathway is shown in Figure 10.1. Green and yellow paths gives the same \( \Delta G \) (state function).

**Figure 10.1** (High resolution)

\( \Delta G^o \) in units of kJ mol\(^{-1}\) is shown pictorially for two different paths starting with \( 1/2 H_2(g) \) and \( 1/2 Cl_2(g) \) and ending with \( H^+(aq) \) + \( Cl^- (aq) \). The units for the numbers are kJ mol\(^{-1}\).

Because \( \Delta G \) is the same for both paths, \( \Delta G_{solvation}(H^+, aq) \) can be expressed in terms of gas-phase dissociation and ionization energies.

1st two rxns = dissociation
2nd two rxns = ionization
\( \Delta G^o \) for the 4 gaseous reactions are determined experimentally.
With these values \((203.9 + 105.7 + 1312 - 349 = 1272)\), \(\Delta G^o\) for the overall process is given by:

\[
\Delta G_R^o = \Delta G_{\text{solution}}^o (\text{Cl}^-, aq) + \Delta G_{\text{solution}}^o (\text{H}^+, aq) + 1272 \text{kJ/mol} \quad (7)
\]

\(\Delta G_{\text{solution}}^o\) of each ion can not be determined experimentally, but can be estimated by Max Born model.

Max Born model assumes:
- Solvent = Uniform fluid with a dielectric constant, \(\varepsilon\)
- Ion = A charged sphere

At constant \(T\) and \(P\), nonexpansion work = \(\Delta G \rightarrow\)

Difference of the reversible work for charging in solution and vacuum = 
\[\{(\text{A} \rightarrow \text{A}^0)_{\text{Solution}} - (\text{A} \rightarrow \text{A}^0)_{\text{Vacuum}}\} = \Delta G_{\text{Solvation}}\quad \text{(A=Neutral, A}^0\text{=Charged by Q)}\]

- Electrical potential around a sphere of radius \(r\) with charge \(Q'\) is given by 
  \[\phi = \frac{Q'}{4\pi \varepsilon r}\]

Note Coulombic law
- Coulombic force \(F = q_1 q_2 / 4\pi \varepsilon r^2\) → Electrical field strength \(E = F / q_1 = q_2 / 4\pi \varepsilon r^2\)
- \(E = \nabla \phi \rightarrow \phi = E \cdot r\) (Commonly \(E = \text{Volt/distance}\))

Electric potential at a point is the electrical potential energy divided by charge (Work for unit charge). Typically measured in Volts = Joule/Coulomb.

- Work for additional charging \(dQ = \phi dQ\).

- Then work in charging a neutral sphere in vacuum to the charge \(Q\) is 
  \[w = \int_0^Q \frac{Q' dQ'}{4\pi \varepsilon_0 r} = \frac{1}{4\pi \varepsilon_0 r} \int_0^Q Q' dQ' = \frac{Q^2}{8\pi \varepsilon_0 r}\]  \( (8)\)
\( \epsilon_0 = \) permittivity (dielectric constant) in free space

Work for the same process in solvent = \( Q^2/8\pi\epsilon_r r \) \text{(8')}\)

\( \epsilon_r = \epsilon/\epsilon_0 \) relative permittivity of solvent (See Table 10.2, Appendix).

Then for an ion of charge \( Q = ze \) is given by ( (8')-(8))

\[
W = \Delta G_{\text{solvation}} = \frac{z^2e^2N_A}{8\pi\epsilon_0r}(\frac{1}{\epsilon_r} - 1)
\]

\( N_A = \) Avogadro's number, \( e = \) Charge of a proton

Note

\( \epsilon_r = \epsilon/\epsilon_0 > 1 \rightarrow \Delta G_{\text{solvation}} < 0 \): The solvation is a spontaneous process.

See Figure 10.2 to test the validity of eq 10.9.

Figure 10.2a: Radius from crystal structure

Figure 10.2b: \( r_{\text{eff}} = \) crystal radius + 0.085 for positive ion,
\( = (\) crystal radius + 0.100 \) for negative ion (Excellent fit)

10.3 Activity and activity coefficients for electrolyte solutions
Activity and activity coefficient defined in Ch 9 is modified in electrolyte since Coulombic interaction (electrostatic) is dominant. For example:

\[ \text{NaCl}(s) + H_2O(l) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq) \] \hspace{1cm} (11)

Gibbs energy of solution can be written as:

\[ G = n_{\text{solute}} \mu_{\text{solute}} + n_{\text{solute}} \mu_{\text{solute}} \] \hspace{1cm} (12)

\[ n = \# \text{ of moles} \]

If the electrolyte completely dissociates,

\[ G = n_{\text{solute}} \mu_{\text{solute}} + n_+ \mu_+ + n_- \mu_- \]
\[ = n_{\text{solute}} \mu_{\text{solute}} + n_{\text{solute}} (\nu_+ \mu_+ + \nu_- \mu_-) \] \hspace{1cm} (13)

\[ \nu = \text{stoichiometric coefficients} \]
\[ n_+ = n_{\text{solute}} \nu_+ \text{ and } n_- = n_{\text{solute}} \nu_- \]

Ex) \( K_2SO_4 \rightarrow 2K^+ + SO_4^{2-} \)
\[ n_{\text{solute}} = 1, \nu_+ = 2, \nu_- = 1 \] (Produced from one mole of solute)

Letting
\[ (12) = (13) \]
\[ \mu_{\text{solute}} = \nu_+ \mu_+ + \nu_- \mu_- \] \hspace{1cm} (14)

Define the mean ionic chemical potential as:

\[ \mu_{\pm} = \frac{\mu_{\text{solute}}}{\nu} = \frac{\nu_+ \mu_+ + \nu_- \mu_-}{\nu} \] \hspace{1cm} (15)

where \( \nu = \nu_+ + \nu_- \)
The experimentally measured quantity is $\mu_\pm$.
($\mu_+$ and $\mu_-$ cannot be measured separately)

Chemical potential – activity coefficient relationship

$$\mu_+ = \mu_+^0 + RT \ln a_+, \quad \mu_- = \mu_-^0 + RT \ln a_- \quad (16)$$

Standard chemical potentials ($\mu_+^0$, $\mu_-^0$) are based on the Henry’s law standard state.

Subing (16) into (15),

$$\mu_\pm = \frac{\mu_{\text{solute}}}{\nu} = \frac{\nu_+ \mu_+ + \nu_- \mu_-}{\nu} \quad (15)$$

$$\mu_\pm = \frac{(\nu_+ \mu_+^0 + \nu_- \mu_-^0) + RT (\nu_+ \ln a_+ + \nu_- \ln a_-)}{\nu}$$

$$= \mu_\pm^0 + RT \ln a_\pm \quad (17)$$

where the mean ionic activity $a_\pm$ is related to the individual ionic activity as,

$$\ln a_\pm = \frac{\nu_+ \ln a_+ + \nu_- \ln a_-}{\nu}$$

$$\rightarrow \ln a_\nu = \ln a_\nu^\nu \quad (18)$$

$$a_\nu = a_\nu^\nu a_\nu^- \quad \text{or}$$

$$a_\pm = (a_\nu^\nu a_\nu^-)^\nu$$

EXAMPLE PROBLEM 10.1
Write the mean ionic activities of NaCl, K$_2$SO$_4$, and H$_3$PO$_4$ in terms of ionic activities of the individuals anions and cations. Assume complete dissociation.

Solution
NaCl → Na⁺ + Cl⁻
K₂SO₄ → 2K⁺ + SO₄²⁻
H₃PO₄ → 3H⁺ + PO₄³⁻

From (18)
\[
\begin{align*}
a_{NaCl}^2 &= a_{Na^+} a_{Cl^-} \\
a_{K_2SO_4}^3 &= a_{K^+}^2 a_{SO_4^{2-}} \\
a_{H_3PO_4}^4 &= a_{H^+}^3 a_{PO_4^{3-}}
\end{align*}
\]

Since activity is dimensionless, the ionic activity must be normalized by a standard state molality (m₀ = 1 mole/kg) as,
\[
a_+ = \frac{m_+}{m_0} \gamma_+ \quad \text{and} \quad a_- = \frac{m_-}{m_0} \gamma_-
\]

(19) → (18)
\[
a_\pm = \left( \frac{m_\pm}{m_0} \right)^{\nu_\pm} \left( \frac{m_-}{m_0} \gamma_+ \gamma_-ight)^{\nu_+ \nu_-}
\]

Define mean ionic molality (m_±) and mean ionic activity coefficient (γ_±) as
\[
\begin{align*}
m_\pm &= m_+ m_- \\
m_\pm &= \left( m_+^{\nu_+} m_-^{\nu_-} \right)^{\frac{1}{\nu}} \\
\gamma_\pm &= \left( \gamma_+ \gamma_- \right)^{\frac{1}{\nu}}
\end{align*}
\]
Then
\[ a_\pm = \left( \frac{m_+}{m^o} \right)^{\nu_+} \left( \frac{m_-}{m^o} \right)^{\nu_-} \gamma_+ \gamma_- \quad \text{(a)} \]
\[ = \left( m_+ m_- \right)^{-\nu_+ \nu_-} \left( \frac{1}{m^o} \right)^{\nu_+ \nu_-} \gamma_+ \gamma_- \]
\[ = \left( \frac{m_+}{m^o} \right)^{\nu_+^{\nu_-}} \gamma_+^{\nu_-} \]
or \[ a_\pm = \frac{m_\pm}{m^o} \gamma_\pm \quad \text{(22)} \]

(19)~(22) relate the activity, activity coefficient, and molality of the individual ionic species to mean ionic quantities and measurable properties of the system such as molality and activity of the solute.

EX Calculate the mean ionic molality and mean ionic activity of a 0.150 m \( \text{Ca(NO}_3\text{)}_2 \) solution for which the mean ionic activity coefficient is 0.165.

\[ m_\pm = \left( \nu_+^{\nu_-} \right)^{\nu_-} \left( \frac{2^2}{2} \right)^{\nu_-} \text{0.150 mol kg}^{-1} = 0.238 \text{ mol kg}^{-1} \]

\[ a_\pm = \left( \frac{m_\pm}{m^o} \right)^{\nu_-} \gamma_\pm = 0.238 \times 0.165 = 0.0393 \]

EX) Calculate the mean ionic activity of a 0.0150 m \( \text{K}_2\text{SO}_4 \) solution for which the mean activity coefficient is 0.465.

Solution
Use (a) and (19)~2nd line
\[ a_\pm = \left( \frac{\nu_+^{\nu_-} \nu_-}{m^o} \right)^{\nu_-} \left( \frac{2^2}{2} \right)^{\nu_-} \text{0.0150 mols kg}^{-1} \times 0.465 = 0.0111 \]