Chapter 10

Effect of Electrolytes on Chemical Equilibria

Effect of Electrolyte Concentration on the solubility of some salts

- Neutral species has essentially no effect
- The larger the ion charges, the bigger the equilibrium changes
 Ionic Strength

- A measure of total ion concentration in solution.
- A quantity required to calculate activity coefficients.
- Attempts to account for effects of both concentration and charge of ion on activity coefficients.

$$\mu = \frac{1}{2} \sum_{i=1}^{n} c_i Z_i^2$$

- Example: what is the ionic strength of a 0.050 M KCl solution?

$$\mu = \frac{1}{2} \left[ (0.050 \times 1^2) + (0.050 \times (-1)^2) \right] = 0.050 \text{ M}$$

- Example: what is the ionic strength of a 0.050 M Na$_2$SO$_4$ solution?

$$\mu = \frac{1}{2} \left[ (0.100 \times 1^2) + (0.050 \times (-2)^2) \right] = 0.30 \text{ M}$$

A strong electrolyte consisting solely of singly charged ions has the identical $\mu$ to its total molar concentration.
How do we apply this to the Equilibrium Expression?

- For the generic reaction:
  \[ aA + bB \rightleftharpoons cC + dD \]

- We have been writing the expression:
  \[ \frac{[C]^c[D]^d}{[A]^a[B]^b} = K \]

- A more accurate expression is:
  \[ \frac{a_i^{c_i} b_i^{d_i}}{a_i^{a_i} b_i^{b_i}} = K ; \text{ where } a_i \text{ is the activity of } i. \]
Activities

• For an aqueous species:

\[ a_i = [i] \gamma_i \]  

where \([i]\) is the concentration of \(i\), and \(\gamma_i\) is the activity coefficient.

• For the reaction:

\[ aA + bB \rightleftharpoons cC + dD \]

• We can write the expression:

\[ \frac{[C]^c \gamma_C^c [D]^d \gamma_D^d}{[A]^a \gamma_A^a [B]^b \gamma_B^b} = K \]

Properties of Activity Coefficients

• As \(\mu \to 0\), \(\gamma_x \to 1\), \(a_x \to [x]\), and \(K' \to K\).

• In solutions that are not too concentrated, \(\gamma_x = f(\mu)\).

• For a given \(\mu\), \(\gamma_x\) decreases as the ion charge increases.

• For neutral species, \(\gamma_x \to 1\)

• For a given \(\mu\), approximately same \(\gamma_x\) values for the same charge ions

Effect of \(\mu\) on \(\gamma_x\)
Calculating Activity Coefficients

- The three factors (ionic strength, ionic charge, and ionic radius) are related by the Debye-Hückel equation (valid to ~ 0.1 M):

\[ \log \gamma_x = -\frac{0.51z_x^2\sqrt{\mu}}{1 + (3.3\alpha_x\sqrt{\mu})} \text{ at } 25^\circ C \]

where \( \gamma_x \) is the activity of an ion \( x \) with charge \( z \) and hydrated radius \( \alpha_x \) (in nm) in a solution with an ionic strength of \( \mu \).

- Table 10-2 in the text gives activity coefficients for many common ions at various ionic strengths.

### An Example:

- What is the solubility of \( \text{Hg}_2(\text{IO}_3)_2(\text{s}) \) in pure water and in 0.050 M KNO\(_3\)?

\[ \text{Hg}_2(\text{IO}_3)_2(\text{s}) \rightleftharpoons \text{Hg}^{2+}(\text{aq}) + 2\text{IO}_3^-(\text{aq}) \]

<table>
<thead>
<tr>
<th></th>
<th>Hg(^{2+})</th>
<th>IO(_3^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>+x</td>
<td>+2x</td>
</tr>
<tr>
<td>End</td>
<td>x</td>
<td>2x</td>
</tr>
</tbody>
</table>

Use Excel to calculate the activity coefficients of various ions in different ionic strength solutions.
**Solubility of $\text{Hg}_2(\text{IO}_3)_2$ in pure $\text{H}_2\text{O}$**

\[
[x][2x]^2 = 1.3 \times 10^{-18}
\]

\[
4x^3 = 1.3 \times 10^{-18}
\]

\[
x = 6.9 \times 10^{-7}\text{M}
\]

- **the solubility of $\text{Hg}_2(\text{IO}_3)_2$ in 0.050 M $\text{KNO}_3$**
  - The ionic strength of 0.050 M $\text{KNO}_3$:
    \[
    \mu = \frac{1}{2} \left[ (0.050 \times x^2) + (0.050 \times (-1)^2) \right] = 0.050\text{ M}
    \]
  - From table 10-2:
    - The activity coefficient for $\text{Hg}_2^{2+} = 0.44$
    - The activity coefficient for $\text{IO}_3^{-} = 0.82$

- **The expression**:
  \[
  \frac{[\text{Hg}^{2+}][\text{IO}_3^{-}]}{[\text{Hg}_2(\text{IO}_3)_2]^2} = 1.3 \times 10^{-18}
  \]

  becomes:
  \[
  [\text{Hg}^{2+}][\text{Hg}^{2+}][\text{IO}_3^{-}][\text{IO}_3^{-}] = 1.3 \times 10^{-18}
  \]

  \[
  2x \frac{2x \cdot 0.44}{(0.82)^2} = 1.3 \times 10^{-18}
  \]

  \[
x = 1.0 \times 10^{-6}
  \]

  versus $6.9 \times 10^{-7}$ in pure water

  About 1.4X greater than in pure water

  *Relative Error = -31%*
Using Activity Coefficients

- We will normally not consider activity coefficients.
  - Usually, we are working at concentrations where \( \gamma \) is nearly 1.0
  - Usually, the difference that accounting for activity introduces is smaller than we can precisely measure.