Exam II--Redemption

- Wednesday Feb 13
- Bring blue book and calculator
- Be early or on time, Exam start time is 7AM.
- 14 multiple choice, 4 out of 5 problems, with 5th bonus.
- If you know the homework you will do well.
- Guarantee problems like those in Skoog 8 and 9 and like those in Chapter 19 Silberberg.
Exam II--Redemption

- Understand acid-base equilibria, buffers, how they work with equations, features of buffer.
- Calculating impact of H or OH on buffer
- Calculate how to preparing a buffer using the buffer equation
- How acid base indicators work.
- Titrations, equivalence point and end point with calculations
- Calculation pH after mixing acid and base together
- Molar solubility, $K_{sp}$ and expressions and calculations.
- Predicting precipitates, common ions or acid base on solubility.
- Gravimetric analysis, understanding of process, problems
- Activities, activity coefficient, ionic strength concepts
Chapter 9:

Effects of Electrolytes on Chemical Equilibria: Activities

Please do problems: 1, 2, 3, 6, 7, 8, 12

Exam II       February 13
Why Non-Idealism Occurs

- The presence of electrolytes alters electrostatic interactions (ion-ion and ion-solvent interactions).
- The extent of change depends on the concentration and to a larger extent the charge of the ions.
- We quantify this value using the concept of ionic strength.

\[
\text{ionic strength } = \mu = \frac{1}{2} \left( [A]Z_A^2 + [B]Z_B^2 + [C]Z_C^2 + \ldots \right)
\]

where \([A]\) is molarity of ion A, \([B]\) of ion B and \(Z\) is the charge of the ion.
Electrolyte Concentrations Impact $K_c$ Values

Molarity Works Fine Here

Must Use Activity

Increasing [electrolyte]
Activity of an ion is "effective concentration".

\[ \text{aA} + \text{bB} \rightleftharpoons \text{cC} + \text{dD} \]

At equilibrium:

\[ K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \]

\[ K_a = \frac{a_y^c a_z^d}{a_w^a b_x^b} \]

Equilibrium constant in terms of molar concentration.

Equilibrium constant in terms of activities.
Activity of An Ion is “effective concentration”

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

\[ K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

thermodynamic equilibrium constant (tables)

equilibrium constant in terms of activities

concentration equilibrium constant

activity coefficients

\[ K_c^o = \frac{a_y^c a_z^d}{a_w^a b_x^b} = \frac{([C] \gamma_c)^c ([D] \gamma_d)^d}{([A] \gamma_a)^a ([B] \gamma_b)^b} = K_c \times \frac{\gamma_c^c \gamma_d^d}{\gamma_a^a \gamma_b^b} \]
Activity of An Ion is “effective concentration”

In order to take into the effects of electrolytes on chemical equilibria we use “activity” instead of “concentration”.

The activity of an ion is defined as:

\[ a_i = [X_i] \gamma_i \]

where \([C_i]\) is the molarity of the \(i^{th}\) ion and \(\gamma_i\) is the ion’s activity coefficient (a dimensionless quantity). \(\gamma_i\) depends on the ionic strength of the solution.
The ionic strength of a solution is a measure of the total electrolyte concentration and is a function of both concentration and charge of the ions in solution.

\[
\mu = \frac{1}{2} \left( [A] Z_A^2 + [B] Z_B^2 + [C] Z_C^2 + \ldots \right)
\]

where \([X]\) is the molarity of ions A, B, C, ..., and \(Z_A, Z_B, Z_C\)

Recognize that the \textit{total ionic strength} of a solution is the \textit{sum of all ions in solution}!
Ionic Strength Worked Example

Calculate the ionic strength of (a) 0.1M solution of KNO₃ and (b) 0.1M solution of Na₂SO₄

(a) For the KNO₃ solution [K⁺] = [NO₃⁻] = 0.1M, the charge \( z = +1 \) and -1. We can substitute:

\[
\mu = \frac{1}{2} \left( [A] Z_A^2 + [B] Z_B^2 + [C] Z_C^2 + \ldots \right) 
\]

\[
(a) \quad \mu = \frac{1}{2} \left( [0.1] 1^2 + [0.1] (-1)^2 \right) = 0.1 M 
\]

(b) For the Na₂SO₄ solution [Na⁺] = 0.2M and [SO₄²⁻] = 0.1M, the charge \( z = +1 \) and -2, respectively. We can substitute:

\[
(b) \quad \mu = \frac{1}{2} \left( [0.2] 1^2 + [0.1] (-2)^2 \right) = 0.3 M 
\]
### Ionic Strength = Molar Concentration for Mono

<table>
<thead>
<tr>
<th>Type Electrolyte</th>
<th>Example</th>
<th>Ionic Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>NaCl</td>
<td>c</td>
</tr>
<tr>
<td>1:2</td>
<td>Ba(NO$_3$)$_2$ or Na$_2$(SO$_4$)</td>
<td>3c</td>
</tr>
<tr>
<td>1:3</td>
<td>Al(NO$_3$)$_3$ or Na$_3$(PO$_4$)</td>
<td>6c</td>
</tr>
<tr>
<td>2:2</td>
<td>Mg(SO$_4$)</td>
<td>4c</td>
</tr>
</tbody>
</table>

Ionic strength increases rapidly with charge of ions (increases as the square of the charge.)
1923--Debye and Huckel derive an expression that allows calculation of activity coefficients, $\Upsilon_\chi$ for ions from knowledge of charge, $Z$, the ionic strength of the solution, $\mu$ and average diameter of hydrated ion in nm, $\alpha$ (at 25°C).

$$-\log \gamma_\chi = \frac{0.51 Z^2_\chi \sqrt{\mu}}{1 + 3.3 \alpha_\chi \sqrt{\mu}}$$
### Activity Coefficients for Ions at 25°C

<table>
<thead>
<tr>
<th>Ion</th>
<th>Activity Coefficient at Indicated Ionic Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O⁺</td>
<td>0.9</td>
</tr>
<tr>
<td>Li⁺, C₆H₅COO⁻</td>
<td>0.6</td>
</tr>
<tr>
<td>Na⁺, IO₃⁻, HSO₃⁻, HCO₃⁻, H₂PO₄⁻, H₂AsO₄⁻, OAc⁻</td>
<td>0.4–0.45</td>
</tr>
<tr>
<td>OH⁻, F⁻, SCN⁻, HS⁻, ClO₃⁻, ClO₄⁻, BrO₃⁻, IO₃⁻, MnO₄⁻</td>
<td>0.35</td>
</tr>
<tr>
<td>K⁺, Cl⁻, Br⁻, I⁻, CN⁻, NO₂⁻, NO₃⁻, HCOO⁻</td>
<td>0.3</td>
</tr>
<tr>
<td>Rb⁺, Cs⁺, Ti⁺, Ag⁺, NH₄⁺</td>
<td>0.25</td>
</tr>
<tr>
<td>Mg²⁺, Be²⁺</td>
<td>0.8</td>
</tr>
<tr>
<td>Ca²⁺, Cu²⁺, Zn²⁺, Sn²⁺, Mn²⁺, Fe²⁺, Ni²⁺, Co²⁺, Phtalate²⁻</td>
<td>0.6</td>
</tr>
<tr>
<td>Sr²⁺, Ba²⁺, Cd²⁺, Hg²⁺, S²⁻</td>
<td>0.5</td>
</tr>
<tr>
<td>Pb²⁺, CO₂⁻, SO₃⁻, C₂O₄⁻</td>
<td>0.45</td>
</tr>
<tr>
<td>Hg₂⁺, SO₄²⁻, S₂O₃⁻, Cr₂⁺, HPO₄²⁻</td>
<td>0.40</td>
</tr>
<tr>
<td>Al³⁺, Fe³⁺, Cr³⁺, La³⁺, Ce³⁺</td>
<td>0.9</td>
</tr>
<tr>
<td>PO₄³⁻, Fe(CN)₆³⁻</td>
<td>0.4</td>
</tr>
<tr>
<td>Th⁴⁺, Zr⁴⁺, Ce⁴⁺, Sn⁴⁺</td>
<td>1.1</td>
</tr>
<tr>
<td>Fe(CN)₆⁴⁻</td>
<td>0.5</td>
</tr>
</tbody>
</table>


© 2004 Thomson - Brooks/Cole

**NOTE:** Deybye-Huckel fails beyond ionic strengths of 0.1M. We then must use experimentally derived activity coefficients.
The Debye-Huckel Equation Calculates Activity Coefficients

- Over range of ionic strengths from 0 to 0.1M the effect of each variable on activity coefficient is as follows:

  1. As the ionic strength, $\mu$ increases the activity coefficient ($\gamma$) decreases ($<1$).

  2. As the ionic strength approaches 0, the activity coefficient ($\gamma$) decreases => 1.

  3. As the charge of ion increases the departure of away from ideal behavior (when $\gamma = 1$). Highly charged ions cause deviations.

  4. The smaller the hydrated radius of an ion the more it causes non-ideality in the solution (must use activities).
Properties of Activity vs Concentration

- For Dilute Solutions (IDEAL SOLUTIONS)
  ✓ When $\mu < 0.01$ then $\gamma_X \to 1$ then $a_i \to [i]$

- For NON-IDEAL SOLUTIONS
  ✓ When $\mu < 0.1$ then $\gamma_X < 1$ then $a_i < [i]$
  ✓ When $\mu > 0.1$ then things get complicated
  ✓ In general when we try to keep ionic strength $< 0.1$ so that we can use concentration instead of activities.
Calculate the activity coefficients for $K^+$ and $SO_4^{2-}$ in a 0.20 M solution of $K_2SO_4$. Assume $\alpha_{K^+} = 0.3$ nm and $\alpha_{SO_4} = 4.0$ nm

$$\log \gamma_{\chi} = \frac{0.51 Z^2 \chi \sqrt{\mu}}{1 + 3.3 \alpha_{\chi} \sqrt{\mu}}$$

get this from a table provided or given data

calculate this first
Equilibrium Calculations With Activities

Calculate the activity coefficients for $K^+$ and $SO_4^{2-}$ in a 0.020 M solution of $K_2SO_4$.

$$\mu = \frac{1}{2} ([A]Z_A^2 + [B]Z_B^2 + [C]Z_C^2 + ...)$$

$$\mu = \frac{1}{2} ([K]1^2 + [SO_4](-2)^2)$$

$$\mu = \frac{1}{2} ([2 \times 0.020]1^2 + [0.020](-2)^2) = 0.060$$

$$- \log \gamma_{K^+} = \frac{0.51 \ 1^2 \ \sqrt{0.060}}{1 + 3.3 \ 0.3 \ \sqrt{0.060}} = 0.1005 \quad \gamma_{K^+} = 10^{-0.101} = 0.79$$

$$- \log \gamma_{SO_4} = \frac{0.51 \ (-2)^2 \ \sqrt{0.060}}{1 + 3.3 \ 0.4 \ \sqrt{0.060}} = 0.463 \quad \gamma_{SO_4} = 10^{-0.463} = 0.344$$
Activity of an ion is “effective concentration”

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

\[ K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

- thermodynamic equilibrium constant (tables)
- equilibrium constant in terms of activities
- concentration equilibrium constant
- activity coefficients

\[ K_c^o = \frac{a_y^c a_z^d}{a_w^a b_x^b} = \frac{([C] \gamma_c)^c ([D] \gamma_d)^d}{([A] \gamma_a)^a ([B] \gamma_b)^b} = K_c \times \frac{\gamma_c^c \gamma_d^d}{\gamma_a^a \gamma_b^b} \]
Activity of An Ion is "effective concentration"

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

\[
K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}
\]

\[
a_i = [X_i] \gamma_i
\]

if we now substitute for \([a_i]\) we get:

\[
K_c = \frac{a_y^c a_z^d}{a_w^a b_x^b} = \frac{([C] \gamma_c)^c ([D] \gamma_d)^d}{([A] \gamma_a)^a ([B] \gamma_b)^b}
\]

Concentrations expressed in molarity!

\[K_c\] expressed in activity coefficients and \([X]\)
Equilibrium Calculations With Activities

Use activities to calculate the $\text{H}_3\text{O}^+$ concentration in a 0.120M solution of $\text{HNO}_2$ that is also 0.050M $\text{NaCl}$ (The thermodynamic equilibrium constant $K_a^\circ = 7.1 \times 10^{-4}$)

$$
\mu = \frac{1}{2} \left( [A] Z_A^2 + [B] Z_B^2 + [C] Z_C^2 + \ldots \right)
$$

$$
\mu = \frac{1}{2} \left( [0.050](1)^2 + [0.050](-1)^2 \right) = 0.0500
$$

We look up in the table the activity coefficients based on this ionic strength: $\gamma_{\text{H}_3\text{O}^+} = 0.85$ and $\gamma_{\text{NO}_2} = 0.81$ and $\gamma_{\text{HNO}_2} = 1.00$ (rule 3)

$$
\text{HNO}_2 \leftrightarrow \text{H}^+ + \text{NO}_3^-
$$

$$
K_a^\circ = \frac{a_{\text{H}^+} a_{\text{NO}_3^-}}{a_{\text{HNO}_2}} = \frac{[\text{H}^+] \gamma_{\text{H}^+} [\text{NO}_3^-] \gamma_{\text{NO}_3^-}}{[\text{HNO}_2] \gamma_{\text{HNO}_2}} = K_a \times \frac{\gamma_{\text{H}^+} \gamma_{\text{NO}_3^-}}{\gamma_{\text{HNO}_2}}
$$

$$
K_a = K_a^\circ \times \frac{\gamma_{\text{HNO}_2}}{\gamma_{\text{H}^+} \gamma_{\text{NO}_3^-}} = 7.1 \times 10^{-4} \times \frac{1}{0.85 \times 0.81} = 1.03 \times 10^{-3}
$$
Equilibrium Calculations With Activities

Calculate the pH of pure water using activities and do the same thing when pure water has 0.10 M KCl at 25°C.

\[ K_w = a_{H^+} a_{OH^-} = [H^+] \gamma_{H^+} [OH^-] \gamma_{OH^-} \]

Because KCl is monvalent its ionics strength = molarity = 0.10. If we now look up the \( \gamma_i \) for H\(^+\) and OH\(^-\) we find their values to be 0.83 and 0.76 respectively. We can now solve as we did before.

\[ 1.0 \times 10^{-14} = (x)0.83(x)0.76 \]

\[ pH = -\log[H^+] = -\log[1.26 \times 10^{-7}] = 6.90 \]
### Activity Coefficients For Ions 25 °C

#### Table 10-2

<table>
<thead>
<tr>
<th>Ion</th>
<th>Activity Coefficient at Indicated Ionic Strength</th>
<th>$\alpha_y, \text{ nm}$</th>
<th>0.001</th>
<th>0.005</th>
<th>0.01</th>
<th>0.05</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$^+$</td>
<td></td>
<td></td>
<td>0.9</td>
<td>0.967</td>
<td>0.934</td>
<td>0.913</td>
<td>0.85</td>
</tr>
<tr>
<td>Li$^+$, C$_6$H$_5$COO$^-$</td>
<td></td>
<td></td>
<td>0.6</td>
<td>0.966</td>
<td>0.930</td>
<td>0.907</td>
<td>0.83</td>
</tr>
<tr>
<td>Na$^+$, IO$_3^-$, HSO$_3^-$, HCO$_3^-$, H$_2$PO$_4^-$, H$_2$AsO$_4^-$, OAc$^-$</td>
<td></td>
<td></td>
<td>0.4-0.45</td>
<td>0.965</td>
<td>0.927</td>
<td>0.902</td>
<td>0.82</td>
</tr>
<tr>
<td>OH$^-$, F$^-$, SCN$^-$, HS$^-$, ClO$_3^-$, ClO$_4^-$, BrO$_3^-$, IO$_3^-$, MnO$_4^-$</td>
<td></td>
<td></td>
<td>0.35</td>
<td>0.965</td>
<td>0.926</td>
<td>0.900</td>
<td>0.81</td>
</tr>
<tr>
<td>K$^+$, Cl$^-$, Br$^-$, I$^-$, CN$^-$, NO$_2^-$, NO$_3^-$, HCOO$^-$</td>
<td></td>
<td></td>
<td>0.3</td>
<td>0.965</td>
<td>0.925</td>
<td>0.899</td>
<td>0.81</td>
</tr>
<tr>
<td>Rb$^+$, Cs$^+$, TI$^+$, Ag$^+$, NH$_4^+$</td>
<td></td>
<td></td>
<td>0.25</td>
<td>0.965</td>
<td>0.925</td>
<td>0.897</td>
<td>0.80</td>
</tr>
<tr>
<td>Mg$^{2+}$, Be$^{2+}$</td>
<td></td>
<td></td>
<td>0.8</td>
<td>0.872</td>
<td>0.756</td>
<td>0.690</td>
<td>0.52</td>
</tr>
<tr>
<td>Ca$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Sn$^{2+}$, Mn$^{2+}$, Fe$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Phthalate$^{2-}$</td>
<td></td>
<td></td>
<td>0.6</td>
<td>0.870</td>
<td>0.748</td>
<td>0.676</td>
<td>0.48</td>
</tr>
<tr>
<td>Sr$^{2+}$, Ba$^{2+}$, Cd$^{2+}$, Hg$^{2+}$, S$^{2-}$</td>
<td></td>
<td></td>
<td>0.5</td>
<td>0.869</td>
<td>0.743</td>
<td>0.668</td>
<td>0.46</td>
</tr>
<tr>
<td>Pb$^{2+}$, CO$_3^{2-}$, SO$_3^{2-}$, C$_2$O$_4^{2-}$</td>
<td></td>
<td></td>
<td>0.45</td>
<td>0.868</td>
<td>0.741</td>
<td>0.665</td>
<td>0.45</td>
</tr>
<tr>
<td>Hg$^{2+}$, SO$_4^{2-}$, S$_2$O$_3^{2-}$, Cr$^{2+}$, HPO$_4^{2-}$</td>
<td></td>
<td></td>
<td>0.40</td>
<td>0.867</td>
<td>0.738</td>
<td>0.661</td>
<td>0.44</td>
</tr>
<tr>
<td>Al$^{3+}$, Fe$^{3+}$, Cr$^{3+}$, La$^{3+}$, Ce$^{3+}$</td>
<td></td>
<td></td>
<td>0.9</td>
<td>0.737</td>
<td>0.540</td>
<td>0.443</td>
<td>0.24</td>
</tr>
<tr>
<td>PO$_4^{3-}$, Fe(CN)$_6^{3-}$</td>
<td></td>
<td></td>
<td>0.4</td>
<td>0.726</td>
<td>0.505</td>
<td>0.394</td>
<td>0.16</td>
</tr>
<tr>
<td>Th$^{4+}$, Zr$^{4+}$, Ce$^{4+}$, Sn$^{4+}$</td>
<td></td>
<td></td>
<td>1.1</td>
<td>0.587</td>
<td>0.348</td>
<td>0.252</td>
<td>0.10</td>
</tr>
<tr>
<td>Fe(CN)$_6^{3-}$</td>
<td></td>
<td></td>
<td>0.5</td>
<td>0.569</td>
<td>0.305</td>
<td>0.200</td>
<td>0.047</td>
</tr>
</tbody>
</table>


© 2004 Thomson - Brooks/Cole

---

**NOTE:** Deybye-Huckel fails beyond ionic strengths of 0.1M. We then must use experimentally derived activity coefficients.