Chapters 6 and 8

Systematic Treatment of Equilibrium

Equilibrium constants may be written for dissociations, associations, reactions, or distributions.

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<th>Table 6.1</th>
<th>Types of Equilibria</th>
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<td>Reaction</td>
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<tr>
<td>Acid–base dissociation</td>
<td>$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$</td>
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<tr>
<td>Solubility</td>
<td>$\text{MA} \rightleftharpoons \text{M}^{n+} + \text{A}^{-}$</td>
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<tr>
<td>Complex formation</td>
<td>$\text{M}^{n+} + \text{aL}^{b-} \rightleftharpoons \text{ML}^{(n-\alpha b)+}$</td>
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<tr>
<td>Reduction-oxidation</td>
<td>$\text{A}<em>{\text{red}} + \text{B}</em>{\text{ox}} \rightleftharpoons \text{A}<em>{\text{ox}} + \text{B}</em>{\text{red}}$</td>
</tr>
<tr>
<td>Phase distribution</td>
<td>$\text{A}<em>{\text{org}} \rightleftharpoons \text{A}</em>{\text{org}}$</td>
</tr>
</tbody>
</table>
Types of Chemical Equations

- **Balanced Chemical Equation**
- **Charge Balance Equation**
- **Mass Balance Equation**

**Charge Balance**

The sum of the positive charges in solution equals the sum of the negative charges in solution.

\[ \sum_{i} n_{i}C_{i}^{\text{Cation}} = \sum_{j} n_{j}C_{j}^{\text{Anion}} \]
Mass Balance

The sum of the amounts of all species in a solution containing a particular atom (or group of atoms) must equal the amount of that atom (or group) delivered to the solution.

**EXAMPLE:** Write the mass-balance & charge balance equations for the system formed when a 0.010 M NH₃ solution is saturated with AgCl.

\[ \text{AgCl}(s) \rightleftharpoons \text{Ag}^{+}(aq) + \text{Cl}^{-}(aq) \]

\[ \text{Ag}^{+}(aq) + 2 \text{NH}_3(aq) \rightleftharpoons [\text{Ag(NH}_3)_2]^+(aq) \]

\[ \text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \]

\[ \text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq) \]
\[
\text{AgCl}(s) \leftrightarrow \text{Ag}^{+}(aq) + \text{Cl}^{-}(aq) \\
\text{Ag}^{+}(aq) + 2 \text{NH}_3(aq) \leftrightarrow [\text{Ag(NH}_3)_2]^+ (aq) \\
\text{NH}_3(aq) + \text{H}_2\text{O}(l) \leftrightarrow \text{NH}_4^+(aq) + \text{OH}^- (aq)
\]

**Mass Balance Equations:**

\[
[\text{Ag}^+] + [\text{Ag(NH}_3)_2^+] = [\text{Cl}^-]
\]

\[
C_{\text{NH}_3} = [\text{NH}_3] + [\text{NH}_4^+] + 2 [\text{Ag(NH}_3)_2^+] = 0.010 \text{ M}
\]

\[
\text{AgCl}(s) \leftrightarrow \text{Ag}^{+}(aq) + \text{Cl}^{-}(aq) \\
\text{Ag}^{+}(aq) + 2 \text{NH}_3(aq) \leftrightarrow [\text{Ag(NH}_3)_2]^+ (aq) \\
\text{NH}_3(aq) + \text{H}_2\text{O}(l) \leftrightarrow \text{NH}_4^+(aq) + \text{OH}^- (aq)
\]

**Charge Balance Equation:**

\[
[\text{Cl}^-] + [\text{OH}^-] = [\text{NH}_4^+] + [\text{Ag(NH}_3)_2^+] + [\text{Ag}^+] + [\text{H}^+]
\]
Systematic Approach to Equilibrium Problems

1. Balanced chemical equations
2. What quantity is being sought.
3. Equilibrium-constant expressions
4. Mass-balance expressions for the system
5. Charge balance expression
6. Count equations vs. unknowns. If more unknowns than equations, seek additional equations, or make appropriate approximations.

Systematic Approach to Equilibrium Problems

7. Make suitable approximations to simplify the algebra.
8. Solve algebraic equations.
EXAMPLE: Write the equation of mass balance for a 0.100 M solution of acetic acid.

EXAMPLE: Write the equations of mass balance for a 1.00X10\(^{-5}\) M \([\text{Ag(NH}_3\text{)}_2\text{]}\text{Cl}\) solution.
EXAMPLE: Write the equation of charge balance for a solution of H$_2$S.

EXAMPLE: Write the equation of charge balance for a solution of 0.1 M Na$_2$HPO$_4$. 
**EXAMPLE:** Calculate the pH of a 0.100 M solution of acetic acid in water.

**EXAMPLE:** Calculate the molar solubility of Fe(OH)\(_2\) in water.
**EXAMPLE:** Calculate the molar solubility of Fe(OH)$_2$ in water.

**Step 1.**

Fe(OH)$_2$(s) $\rightleftharpoons$ Fe$^{2+}$(aq) + 2 OH$^-$ (aq)

$2H_2O$ $\rightleftharpoons$ H$_3$O$^+$(aq) + OH$^-$ (aq)

**Step 2.**  
let x = molar solubility = [Fe$^{2+}$]
Step 1.

\[
\text{Fe(OH)}_2(s) \rightleftharpoons \text{Fe}^{2+}(aq) + 2 \text{OH}^-(aq)
\]
\[
2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)
\]

Step 2.

let \( x \) = molar solubility = \([\text{Fe}^{2+}]\)

Step 3.

\[K_{sp} = [\text{Fe}^{2+}][\text{OH}^-]^2 = 8 \times 10^{-16}M^3\]  

\[K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14}M^2\]

Step 4. Mass Balance Equation

\[\text{[OH}^-\text{]} = 2 \times [\text{Fe}^{2+}] + [\text{H}_3\text{O}^+]\]  

(3)
Step 1. \[ \text{Fe(OH)}_2(s) \leftrightarrow \text{Fe}^{+2} \text{(aq)} + 2 \text{OH}^{-\text{aq}} \]
\[ 2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^{+\text{aq}} + \text{OH}^{-\text{aq}} \]

Step 2. let \( x = \text{molar solubility} = [\text{Fe}^{+2}] \)

Step 3.
\[ K_{sp} = [\text{Fe}^{+2}][\text{OH}^{-}]^2 = 8 \times 10^{-16} \text{M}^3 \quad (1) \]
\[ K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14} \text{M}^2 \quad (2) \]

Step 4. Mass Balance Equation
\[ [\text{OH}^-] = 2 [\text{Fe}^{+2}] + [\text{H}_3\text{O}^+] \quad (3) \]

Step 5. Charge Balance Equation
\[ 2 [\text{Fe}^{+2}] + [\text{H}_3\text{O}^+] = [\text{OH}^-] \quad (4) \]

Step 6. 3 unique equations 3 unknowns
exact solution possible
\[ K_{sp} = [Fe^{+2}][OH^-]^2 = 8 \times 10^{-16} \text{M}^3 \quad (1) \]
\[ K_w = [H_3O^+][OH^-] = 1 \times 10^{-14} \text{M}^2 \quad (2) \]
\[ [OH^-] = 2[Fe^{+2}] + [H_3O^+] \quad (3) \]

**Step 7. Simplify Algebra**

Assume \([OH^-] \sim 2[Fe^{+2}]\)

i.e. \(2[Fe^{+2}] \gg [H_3O^+]\)

**Step 8. Solve Algebraic Expressions**

Using equation (1)

\[ K_{sp} = [Fe^{+2}][OH^-]^2 = [Fe^{+2}](2[Fe^{+2}])^2 = 8 \times 10^{-16} \text{M}^3 \]

\[ [Fe^{+2}] = \sqrt{3 \left( 8 \times 10^{-16}/4 \right) \text{M}^3} = 6 \times 10^{-6} \text{M} \]
Step 8. Solve Algebraic Expressions

\[[\text{Fe}^{+2}] = 6 \times 10^{-6} \text{M}\]

Step 9. Check Assumption

\[[\text{OH}^-] \approx 2 \times [\text{Fe}^{+2}] = 2(6 \times 10^{-6} \text{M}) = 1.2 \times 10^{-5} \text{M} \sim 1 \times 10^{-5} \text{M}\]

\[[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}\]

\[= \frac{(1 \times 10^{-14} \text{M}^2)}{1 \times 10^{-5} \text{M}} = 1 \times 10^{-9} \text{M}\]

\[2 \times [\text{Fe}^{+2}] \gg [\text{H}_3\text{O}^+]\]

Calculation of Chemical Equilibrium

Concentration calculation

(1) pH of Weak Acid

\[\text{pH} 0.1 \text{ M HAc.}\]

A. Reaction equations

\[\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+\]

\[2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-\]
A. Reaction equations

\[ HA + H_2O \rightleftharpoons A^- + H_3O^+ \]

\[ 2H_2O \rightleftharpoons H_3O^+ + OH^- \]

B. Equilibrium Constant

\[ Ka = \frac{[A^-][H_3O^+]}{[HA]} \]

\[ Kw = [H_3O^+][OH^-] = 10^{-14} \]

C. Mass Balance Equations

\[ C = [HA] + [A^-] \]

D. Charge Balance

\[ [H_3O^+] = [A^-] + [OH^-] \]

E. Conversion

Known item: C

\[ [H_3O^+] = [A^-] + \frac{Kw}{[H_3O^+]} \]

\[ [A^-] = \frac{CKa}{[H_3O^+]} \]

\[ [H_3O^+] = \frac{CKa}{Kw + [H_3O^+] + [H_3O^+]^2} \]

\[ CKa > 20Kw, \]

\[ C/Ka > 400 \quad \text{Or is } [H^+] < 0.05 \text{ F} \]

\[ [H_3O^+] = \sqrt{CKa} \]
Fraction of Dissociation

For HA = A^- + H^+,

\[ \alpha_{HA} = \frac{[HA]}{[HA] + [A^-]} = \frac{[HA]}{F} = \frac{[H^+]}{[H^+]+K_a} \]

\[ \alpha_{A^-} = \frac{[A^-]}{[HA] + [A^-]} = \frac{[A^-]}{F} = \frac{K_a}{[H^+]+K_a} \]

For diprotic weak acid

For H_2A = H^+ + HA^- and HA^- = H^+ + A^{2-},

\[ \alpha_{H_2A} = \frac{[H_2A]}{[H_2A] + [HA^-] + [A^{2-}]} = \frac{[H^+]^2}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \]

\[ \alpha_{HA} = \frac{[HA^-]}{[H_2A] + [HA^-] + [A^{2-}]} = \frac{K_{a1}[H^+]^2}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \]

\[ \alpha_{A^{2-}} = \frac{[A^{2-}]}{[H_2A] + [HA^-] + [A^{2-}]} = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \]
<table>
<thead>
<tr>
<th>Type</th>
<th>Keq</th>
<th>Formula</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong acids</td>
<td>Keq=∞</td>
<td>[H₃O⁺] = Ca</td>
<td>HCl, HNO₃, H₂SO₄, HClO₄</td>
</tr>
<tr>
<td>Strong Bases</td>
<td>Keq=∞</td>
<td>[OH⁻] = Cb</td>
<td>NaOH, KOH</td>
</tr>
<tr>
<td>Weak Acids</td>
<td>Ka = \frac{[H₃O⁺][A]}{HA}</td>
<td>\left[H₃O⁺\right] = \sqrt{CK_a}</td>
<td>HAc, HCOOH, HClO</td>
</tr>
<tr>
<td>Weak Bases</td>
<td></td>
<td>\left[OH⁻\right] = \sqrt{CK_b}</td>
<td>NH₄OH</td>
</tr>
<tr>
<td>Buffer</td>
<td></td>
<td></td>
<td>HAc-NaAc, NH₄⁺ - NH₃H₂O</td>
</tr>
<tr>
<td>Amphiprotic salt(NaHA)</td>
<td></td>
<td></td>
<td>NaHCO₃, NaHPO₄, NaH₂PO₄</td>
</tr>
<tr>
<td>Polyprotic acids</td>
<td></td>
<td>Same as weak acid</td>
<td></td>
</tr>
</tbody>
</table>

0.1 M H₂SO₄

\( Ka_2 = 1.2 \times 10^{-2} \)

\[ [HSO_4^-] + [SO_4^{2-}] = C \]
\[ [H^+] = [HSO_4^-] + 2[SO_4^{2-}] \]
\[ [H^+] = C + [SO_4^{2-}] \]
Calculations related to weak acid and base dissociations

Example 1. Calculate the pH of a 0.010 M acetic acid solution. 
$K_a$ of acetic acid is $1.75 \times 10^{-5}$

Example 2. What is the pH of a solution of guanidine, $(H_2N)_2CNH$? 
$K_a$ for $(H_2N)CNH_2^+$ is $2.9 \times 10^{-14}$.

Buffers and pH values in buffer solutions

A buffer solution resists changes in pH when acids or bases are added or when dilution occurs. A buffer solution generally consists of a mixture of an acid and its conjugate base.

Henderson-Hasselbalch Equation:
For a buffer solution containing a weak acid and its conjugate base:

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

For a buffer solution containing a weak base and its conjugate acid,

$$pH = pK_a + \log \frac{[B]}{[HB^+]} \quad \text{or} \quad pOH = pK_b + \log \frac{[HB^+]}{[B]}$$
Effect of addition of some amount of acid to a buffer solution

Example 1. Calculate the pH of a buffer prepared by adding 10.00 mL of 0.10 M acetic acid and 20.00 mL of 0.10 M sodium acetate.

Example 2. What is the pH if 10.00 mL of 0.0050 M HCl is added to the above buffer solution?