Chapters 6 and 8

Systematic Treatment of Equilibrium

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

Table 6.1
Types of Equilibria

Equilibrium	Reaction	Equilibrium Constant
Acid–base dissociation	$HA + H_2O \rightleftharpoons H_3O^+ + A^-$	K_a, acidity constant
Solubility	$MA \rightleftharpoons M^{n+} + A^{n-}$	K_{sp}, solubility product
Complex formation	$M^{n+} + aL^{b-} \rightleftharpoons ML_a^{(n-ab)+}$	K_f, formation constant
Reduction–oxidation	$A_{red} + B_{ox} \rightleftharpoons A_{ox} + B_{red}$	K_{eq}, reaction equilibrium constant
Phase distribution	$A_{H_2O} \rightleftharpoons A_{organic}$	K_D, distribution coefficient

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.

n => charge, C => concentration

$$\sum_{i} n_i C_i^{Cation} = \sum_{j} n_j C_j^{anion}$$

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 NH_3 solution is saturated with AgCl.

$AgCl_{(s)} \Leftrightarrow Ag^{+}_{(aq)} + Cl^{-1}_{(aq)}$

$Ag^{+}_{(aq)} + 2\ NH_{3(aq)} \Leftrightarrow [Ag(NH_3)_2^{+}]_{(aq)}$

$NH_{3(aq)} + H_2O_{(l)} \Leftrightarrow NH_4^{+}{}_{(aq)} + OH^{-}_{(aq)}$

$H_2O_{(l)} \Leftrightarrow H^{+}_{(aq)} + OH^{-}_{(aq)}$

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$NH_{3(aq)} + H_2O_{(l)} \Leftrightarrow NH_4^+{}_{(aq)} + OH^-$
(aq)

Mass Balance Equations:

$[Ag+] + [Ag(NH_3)_2^+] = [Cl^-]$

$C_{NH3} = [NH_3] + [NH_4^+] + 2\,[Ag(NH_3)_2^+] = 0.010\ M$

$AgCl_{(s)} \Leftrightarrow Ag^+_{(aq)} + Cl^-_{(aq)}$

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$NH_{3(aq)} + H_2O_{(l)} \Leftrightarrow NH_4^+{}_{(aq)} + OH^-$
(aq)

Charge Balance Equation:

$[Cl^{-1}] + [OH^{-1}] = [NH_4^+] + [Ag(NH_3)_2^+] + [Ag^+] + [H^+]$

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.
9. Check validity of assumptions.

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 $[Ag(NH_3)_2]Cl$ solution.

EXAMPLE: Write the equation of charge balance for a solution of H_2S.

EXAMPLE: Write the equation of charge balance for a solution of 0.1 M Na_2HPO_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.

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Step 1.

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$$2H_2O \Leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$$

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$$K_w = [H_3O^+][OH^-] = 1 \times 10^{-14} M^2$$

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$K_{sp} = [Fe^{+2}][OH^-]^2 = 8 \times 10^{-16} M^3$ (1)

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Step 4. **Mass Balance Equation**

$[OH^-] = 2\ [Fe^{+2}] + [H_3O^+]$ (3)

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$2\ [Fe^{+2}] + [H_3O^+] = [OH^-]$ (4)

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Step 6. 3 unique equations 3 unknowns

exact solution possible

K_{sp} = $[Fe^{+2}][OH^-]^2$ = 8 X $10^{-16}M^3$ (1)

K_w = $[H_3O^+][OH^-]$ = 1 X $10^{-14}M^2$ (2)

$[OH^-]$ = 2 $[Fe^{+2}]$ + $[H_3O^+]$ (3)

Step 7. Simplify Algebra

assume $[OH^-]$ ~ 2 $[Fe^{+2}]$

i.e. 2 $[Fe^{+2}]$ >> $[H_3O^+]$

K_{sp} = $[Fe^{+2}][OH^-]^2$ = 8 X $10^{-16}M^3$ (1)

K_w = $[H_3O^+][OH^-]$ = 1 X $10^{-14}M^2$ (2)

$[OH^-]$ = 2 $[Fe^{+2}]$ + $[H_3O^+]$ (3)

Assume $[OH^-]$ ~ 2 $[Fe^{+2}]$ i.e. 2 $[Fe^{+2}]$ >> $[H_3O^+]$

Step 8. Solve Algebraic Expressions

Using equation (1)

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

$[Fe^{+2}] = \sqrt[3]{(8 \times 10^{-16}/4)M^3} = 6 \times 10^{-6}M$

Step 8. Solve Algebraic Expressions

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

Step 9. Check Assumption

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

$[H_3O^+] = K_w / [OH^-]$

$= (1 \times 10^{-14} M^2)/(1 \times 10^{-5} M) = 1 \times 10^{-9} M$

$2 [Fe^{+2}] >> [H_3O^+]$

Calculation of Chemical Equilibrium

Concentration calculation

(1) pH of Weak Acid

pH 0.1 M HAc.

A. Reaction equations

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

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

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

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

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

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

$$CKa > 20Kw,$$

$$C/Ka > 400$$

Or is $[H^+] < 0.05$ 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-}

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

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

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

Type	Keq	Formula	Example
Strong acids	Keq=∞	$[H_3O^+] = Ca$	HCl, HNO_3, H_2SO_4, HClO4
Strong Bases	Keq=∞	[OH-]=Cb	NaOH, KOH
Weak Acids	$Ka = \frac{[H_3O^+][A]}{HA}$	$[H_3O^+] = \sqrt{CKa}$	HAc, HCOOH, HClO
Weak Bases		$[OH^-] = \sqrt{CK_b}$	NH4OH
Buffer			HAc-NaAc, NH^{4+} - NH_3H_2O
Amphiprotic salt(NaHA)			$NaHCO_3$, $NaHPO_4$, NaH_2PO_4,
Polyprotic acids		Same as weak acid	

0.1 M H_2SO_4

$Ka_2=1.2X10^{-2}$

$[HSO_4^-]+[SO_4^{2-}]=C$

$[H^+]= [HSO_4^-]+2[SO_4^{2-}]$

$[H^+]= C+ [SO_4^{2-}]$

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 1.75×10^{-5})

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