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	$HA + H_2O \ 7 \ H_3O^+ + A^-$	K_a, acidity constant
Solubility	$MA \ 7 \ M^{n+} + A^{n-}$	K_{sp}, solubility product
Complex formation	$M^{n+} + aL^{b-} \ 7 \ ML_a^{(n-ab)+}$	K_f, formation constant
Reduction–oxidation	$A_{red} + B_{ox} \ 7 \ A_{ox} + B_{red}$	K_{eq}, reaction equilibrium constant
Phase distribution	$A_{H_2O} \ 7 \ A_{organic}$	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.

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

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

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

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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

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

(aq)

Charge Balance Equation:

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

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.

$Fe(OH)_{2(s)}$ <=> $Fe^{+2}_{(aq)}$ + 2 OH^-
(aq)

$2H_2O$ <=> $H_3O^+_{(aq)}$ + $OH^-_{(aq)}$

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

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Step 3.

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

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

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

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

Step 4. Mass Balance Equation

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

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Step 6. 3 unique equations 3 unknowns

exact solution possible

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

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

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

Step 7. Simplify Algebra

assume $[OH^-] \sim 2\,[Fe^{+2}]$

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

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

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

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

assume $[OH^-] \sim 2\,[Fe^{+2}]$ i.e. $2\,[Fe^{+2}] >> [H_3O^+]$

Step 8. Solve Algebraic Expressions

Using equation (1)

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

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

Step 8. Solve Algebraic Expressions

$[Fe^{+2}]$ = 6×10^{-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

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

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

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

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

$$CKa > 20Kw,$$

$$C / Ka > 400$$

$$[H_3O^+] = \sqrt{CKa}$$

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	$Kb = \frac{[OH^-][B]}{[BOH]}$	$[OH^-] = \sqrt{CK_b}$	NH4OH
Buffer	$Ka = \frac{[H_3O^+][A]}{HA}$	$[H_3O^+] = Ka\frac{C_{HA}}{C_{NaA}}$	HAc-NaAc, NH^{4+} - NH_3H_2O
Amphiprotic salt(NaHA)	$Ka_1 = \frac{[H_3O^+][HA]}{H_2A}$ $Ka_2 = \frac{[H_3O^+][A^{2-}]}{HA^-}$	$[H_3O^+] = \sqrt{Ka_1Ka_2}$	$NaHCO_3$, $NaHPO_4$, NaH_2PO_4,
Polyprotic acids		Same as weak acid	

0.1 M H_2SO_4

Ka_2=1.2X10^{-2}

$$H_2SO_4 \longrightarrow HSO_4^- + H^+$$

$$HSO_4^- \rightleftharpoons SO_4^{2-} + H^+$$

$$Ka_2 = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$$

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

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

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

$$[HSO_4^-] = \frac{[H^+][SO_4^{2-}]}{Ka_2}$$

$$C = \frac{[H^+][SO_4^{2-}]}{Ka_2} + [SO_4^{2-}]$$

$$C = (\frac{[H^+]}{Ka_2} + 1)[SO_4^{2-}]$$

$$[SO_4^{2-}] = \frac{CKa_2}{[H+] + Ka_2}$$

$$[H^+] = C + \frac{CKa_2}{[H^+] + Ka_2}$$