

## 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	$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$	$K_a$ , acidity constant
Solubility	$\text{MA} \rightleftharpoons \text{M}^{n+} + \text{A}^{m-}$	$K_{sp}$ , solubility product
Complex formation	$\text{M}^{n+} + a\text{L}^{b-} \rightleftharpoons \text{ML}_a^{(n-ab)+}$	$K_f$ , formation constant
Reduction–oxidation	$\text{A}_{\text{red}} + \text{B}_{\text{ox}} \rightleftharpoons \text{A}_{\text{ox}} + \text{B}_{\text{red}}$	$K_{eq}$ , reaction equilibrium constant
Phase distribution	$\text{A}_{\text{H}_2\text{O}} \rightleftharpoons \text{A}_{\text{organic}}$	$K_D$ , distribution coefficient

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## 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.*

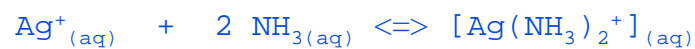
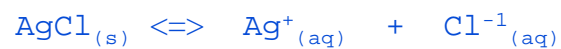
n => charge,      C => concentration

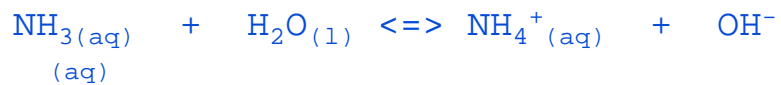
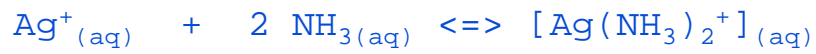
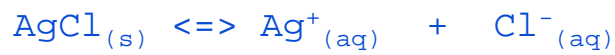
$$\sum_i n_i C_i^{\text{Cation}} = \sum_j n_j C_j^{\text{anion}}$$

## 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  $\text{NH}_3$  solution is saturated with  $\text{AgCl}$ .

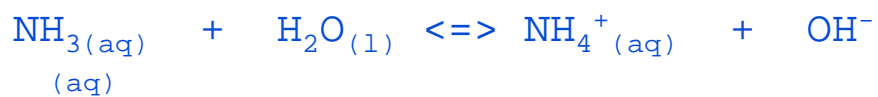
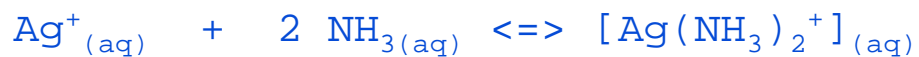
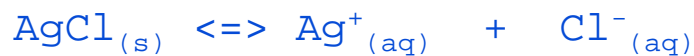




### Mass Balance Equations:

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

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



### Charge Balance Equation:

$$[\text{Cl}^-] + [\text{OH}^-] = [\text{NH}_4^+] + [\text{Ag}(\text{NH}_3)_2^+] + [\text{Ag}^+] + [\text{H}^+]$$

## **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.
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  $1.00 \times 10^{-5}$  M  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$  solution.

**EXAMPLE:** Write the equation of charge balance for a solution of  $\text{H}_2\text{S}$ .

**EXAMPLE:** Write the equation of charge balance for a solution of 0.1 M  $\text{Na}_2\text{HPO}_4$ .

**EXAMPLE:** Calculate the pH of a 0.100 M solution of acetic acid in water.

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

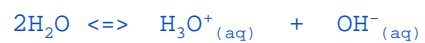
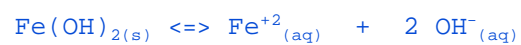


**EXAMPLE:** Calculate the molar solubility of  $\text{Fe}(\text{OH})_2$  in water.

**Step 1.**

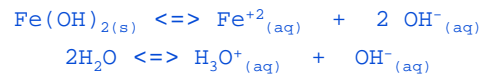


**Step 1.**



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

**Step 1.**

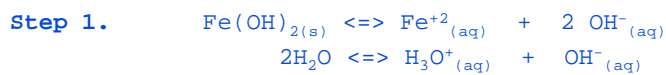


**Step 2.** let  $x$  = molar solubility =  $[\text{Fe}^{2+}]$

**Step 3.**

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

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



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

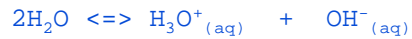
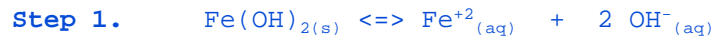
**Step 3.**

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

$$K_{\text{w}} = [\text{H}_3\text{O}^{+}][\text{OH}^{-}] = 1 \times 10^{-14}\text{M}^2 \quad (2)$$

**Step 4. Mass Balance Equation**

$$[\text{OH}^{-}] = 2 [\text{Fe}^{2+}] + [\text{H}_3\text{O}^{+}] \quad (3)$$



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

**Step 3.**

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

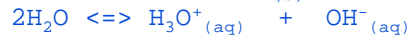
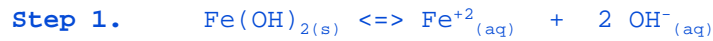
$K_w = [\text{H}_3\text{O}^{+}][\text{OH}^{-}] = 1 \times 10^{-14}\text{M}^2$  (2)

**Step 4. Mass Balance Equation**

$[\text{OH}^{-}] = 2 [\text{Fe}^{2+}] + [\text{H}_3\text{O}^{+}]$  (3)

**Step 5. Charge Balance Equation**

$2 [\text{Fe}^{2+}] + [\text{H}_3\text{O}^{+}] = [\text{OH}^{-}]$  (4)



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

**Step 3.**

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

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

**Step 4. Mass Balance Equation**

$[\text{OH}^{-}] = 2 [\text{Fe}^{2+}] + [\text{H}_3\text{O}^{+}]$  (3)

**Step 5. Charge Balance Equation**

$2 [\text{Fe}^{2+}] + [\text{H}_3\text{O}^{+}] = [\text{OH}^{-}]$  (4)

**Step 6.** 3 unique equations 3 unknowns  
exact solution possible

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

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

$$[\text{OH}^-] = 2 [\text{Fe}^{+2}] + [\text{H}_3\text{O}^+] \quad (3)$$

**Step 7. Simplify Algebra**

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

i.e.  $2 [\text{Fe}^{+2}] \gg [\text{H}_3\text{O}^+]$

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

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

$$[\text{OH}^-] = 2 [\text{Fe}^{+2}] + [\text{H}_3\text{O}^+] \quad (3)$$

Assume  $[\text{OH}^-] \sim 2 [\text{Fe}^{+2}]$  i.e.  $2 [\text{Fe}^{+2}] \gg [\text{H}_3\text{O}^+]$

**Step 8. Solve Algebraic Expressions**

Using equation (1)

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

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



**Step 8. Solve Algebraic Expressions**

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

**Step 9. Check Assumption**

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

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

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

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

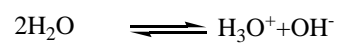
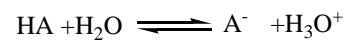
## Calculation of Chemical Equilibrium

### Concentration calculation

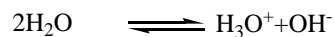
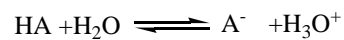
#### (1) pH of Weak Acid

pH 0.1 M HAc.

##### A. Reaction equations



A. Reaction equations



B. Equilibrium Constant

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

$$K_w = [H_3O^+][OH^-] = 10^{-14}$$

C. Mass Balance Equations

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

D. Charge Balance

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

E. Conversion

Known item: C

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

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

$$[H_3O^+] = \frac{CK_a}{K_a + [H_3O^+]} + \frac{K_w}{[H_3O^+]}$$

$$[H_3O^+] = \frac{CK_a}{K_a + [H_3O^+]} + \frac{K_w}{[H_3O^+]}$$

$$CK_a > 20K_w,$$

$$C/K_a > 400$$

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

Or is  $[H^+] < 0.05 F$

## Fraction of Dissociation

For  $\text{HA} = \text{A}^- + \text{H}^+$ ,

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

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

## For diprotic weak acid

For  $\text{H}_2\text{A} = \text{H}^+ + \text{HA}^-$  and  $\text{HA}^- = \text{H}^+ + \text{A}^{2-}$

$$\alpha_{\text{H}_2\text{A}} = \frac{[\text{H}_2\text{A}]}{[\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}]} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}}$$

$$\alpha_{\text{HA}^-} = \frac{[\text{HA}^-]}{[\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}]} = \frac{K_{a1}[\text{H}^+]}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}}$$

$$\alpha_{\text{A}^{2-}} = \frac{[\text{A}^{2-}]}{[\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}]} = \frac{K_{a1}K_{a2}}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}}$$

Type	Keq	Formula	Example
Strong acids	Keq= $\infty$	$[H_3O^+] = C_a$	HCl, HNO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> , HClO <sub>4</sub>
Strong Bases	Keq= $\infty$	$[OH^-]=C_b$	NaOH, KOH
Weak Acids	$K_a = \frac{[H_3O^+][A^-]}{[HA]}$	$[H_3O^+] = \sqrt{CK_a}$	HAc, HCOOH, HClO
Weak Bases		$[OH^-] = \sqrt{CK_b}$	NH <sub>4</sub> OH
Buffer			HAc-NaAc, NH <sub>4</sub> <sup>+</sup> - NH <sub>3</sub> H <sub>2</sub> O
Amphiprotic salt(NaHA)			NaHCO <sub>3</sub> , NaHPO <sub>4</sub> , NaH <sub>2</sub> PO <sub>4</sub> ,
Polyprotic acids		Same as weak acid	

## 0.1 M H<sub>2</sub>SO<sub>4</sub>

$$K_{a2} = 1.2 \times 10^{-2}$$

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

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

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



## 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?