

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

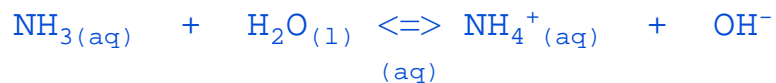
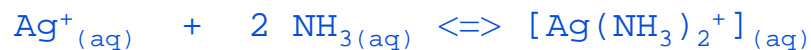
n => charge,      C => concentration

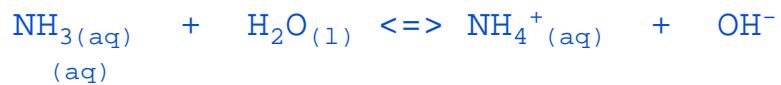
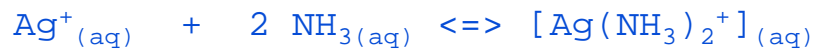
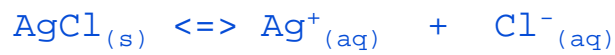
$$\sum_i n_i C_i^{\text{Cation}} = \sum_j n_j C_j^{\text{anion}}$$

## 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  $\text{AgCl}$ .

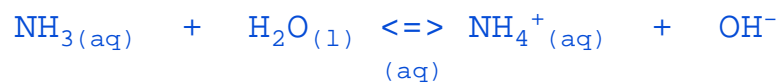
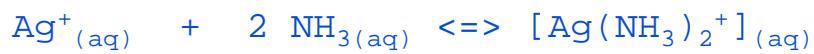
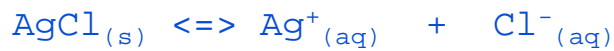




### Mass Balance Equations:

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

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



### Charge Balance Equation:

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

## **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  $\text{Na}_2\text{HPO}_4$ .

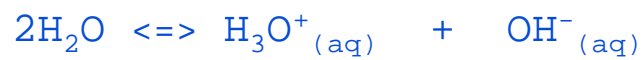
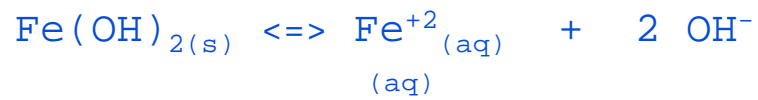
**EXAMPLE:** Calculate the pH of a 0.100 M solution of acetic acid in water.

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

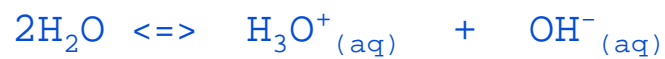
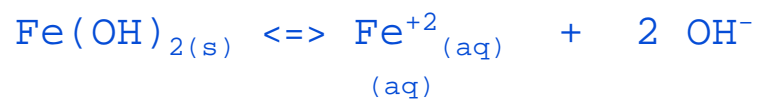


**EXAMPLE:** Calculate the molar solubility of  $\text{Fe}(\text{OH})_2$  in water.

**Step 1.**

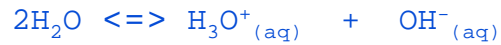
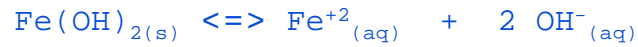


**Step 1.**



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

**Step 1.**

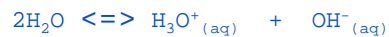


**Step 2.** let  $x$  = molar solubility =  $[\text{Fe}^{+2}]$

**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 =  $[\text{Fe}^{+2}]$

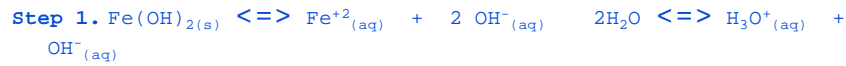
**Step 3.**

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

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

**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.**

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

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**Step 5.    Charge Balance Equation**

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

**Step 6.** 3 unique equations        3  
          unknowns

          exact solution possible

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

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

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

### Step 7. Simplify Algebra

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

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

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

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

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

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

### 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**

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

$$\begin{aligned} [\text{H}_3\text{O}^+] &= K_w / [\text{OH}^-] \\ &= (1 \times 10^{-14}\text{M}^2) / (1 \times 10^{-5}\text{M}) = 1 \times 10^{-9}\text{M} \end{aligned}$$

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

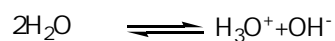
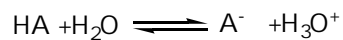
## Calculation of Chemical Equilibrium

### Concentration calculation

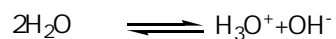
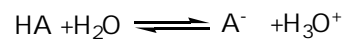
#### (1) pH of Weak Acid

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

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

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

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

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

$$CK_a > 20K_w,$$

$$C/K_a > 400$$

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

| Type                   | Keq  | Formula                                | Example  |
|------------------------|--|--|--|
| Strong acids           | Keq=°  | $[H_3O^+] = Ca$                        | HCl, HNO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> , HClO <sub>4</sub>   |
| Strong Bases           | Keq=°  | $[OH^-]=Cb$                            | NaOH, KOH  |
| Weak Acids             | $Ka = \frac{[H_3O^+][A]}{HA}$  | $[H_3O^+] = \sqrt{CKa}$                | HAc, HCOOH, HClO   |
| Weak Bases             | $Kb = \frac{[OH^-][B]}{[BOH]}$   | $[OH^-] = \sqrt{CK_b}$                 | NH <sub>4</sub> OH   |
| Buffer                 | $Ka = \frac{[H_3O^+][A]}{HA}$  | $[H_3O^+] = Ka \frac{C_{HA}}{C_{NaA}}$ | HAc-NaAc, NH <sub>4</sub> <sup>+</sup> - NH <sub>3</sub> H <sub>2</sub> O    |
| Amphiprotic salt(NaHA) | $Ka_1 = \frac{[H_3O^+][HA]}{H_2A}$<br>$Ka_2 = \frac{[H_2O^+][A^{2-}]}{HA^-}$ | $[H_3O^+] = \sqrt{Ka_1Ka_2}$           | NaHCO <sub>3</sub> , NaHPO <sub>4</sub> , NaH <sub>2</sub> PO <sub>4</sub> , |
| Polyprotic acids       |  | Same as weak acid                      |  |

