Chapter 7
Ionic equilibria

1. How do we identify acids and bases?

Arrhenius Definition

- An acid as a substance that librates hydrogen ions .
- A base as a substance that supplies hydroxyl ions on dissociation.

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$, $NaOH + H_2O \rightarrow OH^- + Na^+$

Bronsted-Lowry Definition

- An acid is a proton (H^+) donor.
- A base is proton acceptor.
- $PhOH + H_2O \rightarrow PhO^- + H_3O^+$, $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$
- In an acid-base reaction, the transfer of protons occurs from an acid to a base.

- The relative strengths of acids and bases are measured by the tendencies of these substances to give up and take on protons

- the strength of an acid depends not only on its ability to give up a proton but also on the ability of the solvent to accept the proton from the acid.
- This is called the basic strength of the solvent

2-Classification of Solvents

- Solvents can be classified as protophilic, protogenic, amphiprotic, and aprotic.
- **A protophilic** or basic solvent is one that is capable of accepting protons from the solute. Such as acetone, ether and liquid ammonia a protophilic solvent.
- **A protogenic** solvent is a proton donating compound and is represented by acids such as formic acid, acetic acid, sulfuric acid, liquid HCl, and liquid HF.

- **Amphiprotic** solvents act as both proton acceptors and proton donors, and this class includes water and the alcohols.

- **Aprotic** solvents, such as the hydrocarbons, neither accept nor donate protons.

3-Brönsted–Lowry classification

- acids and bases may be anions such as HSO_4^- and CH_3COO^-,cations such asNH_4^+ and H_3O^+, or neutral molecules such as HCl and NH_3
- Acid–base reactions occur when an acid reacts with a base to form a new acid and a new base.
- In the reaction between HCl and water, HCl is the acid and water the base:

$$\underset{Acid_1}{HCl} + \underset{Base_2}{H_2O} \rightarrow \underset{Acid_2}{H_3O^+} + \underset{Base_1}{Cl^-} \qquad (7\text{–}1)$$

- Strong acids/ bases ionize completely in aqueous solution
- Weak acids/ bases ionize partially in aqueous solution.

4-Acid–Base Equilibria

The ionization or proteolysis of a weak electrolyte, acetic acid, in water can be written in the Brönsted– Lowry manner as:

$$\underset{Acid_1}{HAc} + \underset{Base_2}{H_2O} \rightleftharpoons \underset{Acid_2}{H_3O^+} + \underset{Base_1}{Ac^-} \qquad (7\text{–}4)$$

- The arrows pointing in the forward and reverse directions indicate that the reaction is proceeding to the right and left simultaneously.
- According to the concept of equilibrium, the rate of the forward reaction decreases with time as acetic acid is depleted, whereas the rate of the reverse reaction begins at zero and increases as larger quantities of hydrogen ions and acetate ions are formed. Finally, a balance is attained when the two rates are equal.

5-Ionization of Weak Acids

$$\underset{\text{Acid}_1}{HAc} + \underset{\text{Base}_2}{H_2O} \rightleftharpoons \underset{\text{Acid}_2}{H_3O^+} + \underset{\text{Base}_1}{Ac^-} \quad (7\text{–}4)$$

$$R_f = k_1 \times [HAc]^1 \times [H_2O]^1 \quad (7\text{–}5) \qquad R_r = k_2 \times [H_3O^+]^1 \times [Ac^-]^1 \quad (7\text{–}6)$$

$$k_1 \times [HAc] \times [H_2O] = k_2 \times [H_3O^+] \times [Ac^-] \quad (7\text{–}8) \qquad k = \frac{k_1}{k_2} = \frac{[H_3O^+][Ac^-]}{[HAc][H_2O]} \quad (7\text{–}9)$$

$$K_a = 55.3k = \frac{[H_3O^+][Ac^-]}{[HAc]} \quad (7\text{–}10)$$

Ka is Dissociation constant

- In general, the acidity constant for an uncharged weak acid HB can be expressed by:

$$HB + H_2O \rightleftharpoons H_3O^+ + B^- \quad (7\text{–}11) \qquad K_a = \frac{[H_3O^+][B^-]}{[HB]} \quad (7\text{–}12)$$

Example 7-1

In a liter of a 0.1 M solution, acetic acid was found by conductivity analysis to dissociate into 1.32×10^{-3} g ions ("moles") each of hydrogen and acetate ion at 25°C. What is the acidity or dissociation constant K_a for acetic acid?

$$K_a = \frac{(1.32 \times 10^{-3})^2}{0.1}$$

$$K_a = \frac{1.74 \times 10^{-6}}{1 \times 10^{-1}} = 1.74 \times 10^{-5}$$

- In general, for charged acids BH^+, the reaction is written as

$$BH^+ + H_2O \rightleftharpoons H_3O^+ + B \qquad (7\text{–}20)$$

$$K_a = \frac{[H_3O^+][B]}{[BH^+]} \qquad (7\text{–}21)$$

6-Ionization of Weak Bases

- weak bases B, exemplified by NH3, react with water as follows:

$$B + H_2O \rightleftharpoons OH^- + BH^+ \qquad (7\text{–}22)$$

$$K_b = \frac{[OH^-][BH^+]}{[B]} \qquad (7\text{–}23)$$

- In general, for an anionic base B-

$$B^- + H_2O \rightleftharpoons OH^- + HB$$

$$K_b = \frac{[OH^-][HB]}{[B^-]} \qquad (7\text{–}27)$$

7-The Ionization of Water

- In a manner corresponding to the dissociation of weak acids and bases, water ionizes slightly to yield hydrogen and hydroxyl ions.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \qquad (7\text{–}28)$$

$$\frac{[H_3O^+][OH^-]}{[H_2O]^2} = k \qquad (7\text{–}29)$$

$$K_w = k \times [H_2O]^2 \qquad (7\text{–}30)$$

Kw, known as the dissociation constant, the auto protolysis constant, or the **ion product** of water:

- The value of the ion product is approximately 1×10^{-14} at 25°C; it depends strongly on temperature
- Substituting equation (7-30) into (7-29) gives the common expression for the ionization of water:

$$[H_3O^+] \times [OH^-] = K_w \cong 1 \times 10^{-14} \text{ at } 25°C \quad (7\text{–}31)$$

In *pure* water, the hydrogen and hydroxyl ion concentrations are equal, and each has the value of approximately 1×10^{-7} mole/liter at 25°C.*

$$[H_3O^+] = [OH^-] \cong \sqrt{1 \times 10^{-14}}$$

$$\cong 1 \times 10^{-7} \quad (7\text{–}32)$$

EXAMPLE 7-3

- A quantity of HCl (1.5×10^{-3}M) is added to water at 25°C to increase the hydrogen ion concentration from 1×10^{-7} to 1.5×10^{-3} mole/liter. What is the new hydroxyl ion concentration?

$$[OH^-] = \frac{1 \times 10^{-14}}{1.5 \times 10^{-3}}$$

$$= 6.7 \times 10^{-12} \text{ mole/liter}$$