

# UNIT 1: ACID-BASE EQUILIBRIA

**Introduction to Acids and Bases:** Acids and bases are fundamental concepts in chemistry, widely recognized for their use both in laboratories and at home. Common household acids include:

- **Acetic Acid ( $\text{CH}_3\text{COOH}$ ):** Found in vinegar.
- **Citric Acid ( $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ ):** Present in citrus fruits.
- **Phosphoric Acid ( $\text{H}_3\text{PO}_4$ ):** Used as a flavoring in carbonated beverages.

Common household bases include:

- **Sodium Hydroxide ( $\text{NaOH}$ ):** Found in drain cleaners.
- **Ammonia ( $\text{NH}_3$ ):** Used in glass cleaners.

**Importance of Weak Acids and Bases:** Weak acids and bases are crucial in many chemical and biological processes. For instance, amino acids are both weak acids and weak bases. In this unit, you will learn how to express the concentrations of hydronium ions ( $\text{H}_3\text{O}^+$ ) and hydroxide ions ( $\text{OH}^-$ ) in solutions, explore equilibria involving weak electrolytes, and understand the role of indicators like phenolphthalein in titrations.

## Acid-Base Concepts

By the end of this subunit, you will be able to:

- Define acids and bases according to the Brønsted-Lowry and Lewis concepts.
- Identify conjugate acid-base pairs.
- Write equations for the self-ionization of water and ammonia.
- Explain the concept of amphiprotic species and provide examples.
- Calculate pH and pOH from the concentrations of  $\text{H}^+$  and  $\text{OH}^-$  ions.

## Arrhenius Concept of Acids and Bases:

Svante Arrhenius, a Swedish chemist, first defined acids and bases based on their behavior in water:

- **Acids** increase the concentration of  $\text{H}^+$  ions in an aqueous solution. Example:  $\text{HClO}_4 \rightarrow \text{H}^+ + \text{ClO}_4^-$ .
- **Bases** increase the concentration of  $\text{OH}^-$  ions. Example:  $\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$ .

## Brønsted-Lowry Concept:

In 1923, J.N. Brønsted and T.M. Lowry independently proposed that acids are proton donors and bases are proton acceptors. This concept is broader than Arrhenius's and applies to reactions not limited to aqueous solutions.

### Example:

- The ionization of ammonia in water:  $\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$ 
  - Here, water acts as an acid, donating a proton to ammonia, which acts as a base.

## Conjugate Acid-Base Pairs:

In a Brønsted-Lowry reaction, acids and bases form conjugate pairs:

- **Conjugate Base:** The species remaining after an acid donates a proton.
- **Conjugate Acid:** The species formed when a base accepts a proton.

### Example:

- $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$
- Acetic acid ( $\text{CH}_3\text{COOH}$ ) is an acid, and its conjugate base is acetate ( $\text{CH}_3\text{COO}^-$ ). Water ( $\text{H}_2\text{O}$ ) acts as a base, and its conjugate acid is the hydronium ion ( $\text{H}_3\text{O}^+$ ).

## Strengths of Conjugate Acid-Base Pairs:

The strength of an acid or base determines the direction of the reaction. A strong acid has a weak conjugate base, and a strong base has a weak conjugate acid. For example, HCl is a strong acid with a weak conjugate base ( $\text{Cl}^-$ ), while  $\text{CH}_3\text{COOH}$  is a weak acid with a relatively stronger conjugate base ( $\text{CH}_3\text{COO}^-$ ).

## Self-Ionization of Water:

Water can ionize itself, a process called autoionization:  $2\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$

Here, water acts as both an acid and a base, a characteristic known as being **amphiprotic**.

## Amphiprotic Species:

Amphiprotic species can either donate or accept a proton, depending on the reaction context. For example, water can act as an acid in the presence of a base (like  $\text{NH}_3$ ) or as a base in the presence of an acid (like  $\text{CH}_3\text{COOH}$ ).

## Lewis Concept of Acids and Bases:

G.N. Lewis expanded the definition of acids and bases:

- **Lewis Acid:** Accepts an electron pair to form a bond.
- **Lewis Base:** Donates an electron pair to form a bond.

### Example:

- In the reaction  $\text{BF}_3 + \text{NH}_3 \rightarrow \text{BF}_3\text{NH}_3$ , boron trifluoride ( $\text{BF}_3$ ) is the Lewis acid, and ammonia ( $\text{NH}_3$ ) is the Lewis base.

Understanding these concepts will provide a strong foundation for exploring more complex acid-base equilibria and titration techniques.

## Ionic Equilibria of Weak Acids and Bases

This section explains important concepts about weak acids and bases, including their ionization, the ion-product constant for water ( $K_w$ ), and how to use these to calculate pH, pOH, and the strengths of acids and bases.

### 1. Ionization of Water

Water undergoes a slight ionization, where it self-ionizes to produce hydronium ions ( $\text{H}_3\text{O}^+$ ) and hydroxide ions ( $\text{OH}^-$ ). The reaction can be written as:



### 2. Ion-Product Constant for Water ( $K_w$ )

The ionization of water is described by the ion-product constant,  $K_w$ , which at  $25^\circ\text{C}$  is:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

This constant is temperature-dependent and increases as temperature rises.

### 3. Weak Electrolyte Nature of Water

Water is a weak electrolyte because it only partially ionizes, producing very few ions in solution. This partial ionization results in the low  $K_w$  value.

### 4. Using $K_w$ to Calculate $[H_3O^+]$ or $[OH^-]$

Given  $K_w$  and either  $[H_3O^+]$  or  $[OH^-]$ , you can calculate the other:

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

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

For pure water at 25°C:  $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} M$

### 5. Percent Ionization of Weak Acids and Bases

The percent ionization shows how much of an acid or base ionizes in solution:

$$\text{Percent Ionization} = \frac{\text{Ionized concentration at equilibrium}}{\text{Initial concentration}} \times 100\%$$

Weak acids and bases have low percent ionization, meaning they ionize only slightly in water.

### 6. Acid-Dissociation Constant ( $K_a$ ) and Base-Dissociation Constant ( $K_b$ )

- **$K_a$**  : Represents the strength of a weak acid. The larger the  $K_a$  the stronger the acid.
- **$K_b$**  : Represents the strength of a weak base. The larger the  $K_b$  , the stronger the base.

The dissociation constant expressions are:

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

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

### 7. Calculating pH and pOH

- **pH**: Measure of acidity. Calculated as:  $pH = -\log[H_3O^+]$
- **pOH**: Measure of basicity. Calculated as:  $pOH = -\log[OH^-]$

Relationship between pH and pOH:  $pH + pOH = 14$  at 25°C

## Practical Applications

1. **Example Calculation for pH:**
  - Given  $[\text{H}_3\text{O}^+] = 3.0 \times 10^{-4} \text{M}$ :
  - $\text{pH} = -\log(3.0 \times 10^{-4}) \approx 3.52$
2. **Determining Acidic, Basic, or Neutral Solutions:**
  - **Neutral:**  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$  and  $\text{pH} = 7$ .
  - **Acidic:**  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$  and  $\text{pH} < 7$ .
  - **Basic:**  $[\text{OH}^-] > [\text{H}_3\text{O}^+]$  and  $\text{pH} > 7$ .

Understanding these concepts is crucial for analyzing the behavior of weak acids and bases in various chemical reactions and real-world applications, such as in biological systems and environmental chemistry.

## Common Ion Effect and Buffer Solution

### *The Common Ion Effect*

The common-ion effect refers to the shift in the equilibrium of an ionic solution when an ion already present in the solution is added from another source. This effect is crucial in understanding how the addition of a common ion can suppress the ionization of a weak acid or base.

**Example:** Consider a solution of acetic acid ( $\text{CH}_3\text{COOH}$ ) in water, which partially ionizes according to the following equilibrium:



If you add hydrochloric acid ( $\text{HCl}$ ) to this solution, it dissociates completely, providing additional  $\text{H}_3\text{O}^+$  ions. According to LeChâtelier's principle, the equilibrium shifts to the left, reducing the degree of ionization of acetic acid. This suppression of ionization due to the addition of a common ion ( $\text{H}_3\text{O}^+$  in this case) is known as the common-ion effect.

**Another Example:** If sodium acetate ( $\text{CH}_3\text{COONa}$ ) is added to the acetic acid solution, the acetate ions ( $\text{CH}_3\text{COO}^-$ ) increase, which further shifts the equilibrium to the left, decreasing the ionization of acetic acid.

## Buffer Solution

A buffer solution is one that resists changes in pH when small amounts of an acid or base are added. Buffers are essential in maintaining a stable pH in chemical and biological systems, which is crucial for processes like enzyme activity.

**Components of a Buffer:** A buffer is usually made from a weak acid and its conjugate base or a weak base and its conjugate acid. The weak acid/base can neutralize any added OH or H<sup>+</sup> ions, maintaining the pH of the solution.

**Example:** Consider a buffer solution made by mixing acetic acid (CH<sub>3</sub>COOH) and sodium acetate (CH<sub>3</sub>COONa) in water. The sodium acetate fully dissociates, providing acetate ions (CH<sub>3</sub>COO<sup>-</sup>):



In this buffer system:

- If an acid (providing H<sup>+</sup>) is added, the acetate ions neutralize it:  
 $\text{CH}_3\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{CH}_3\text{COOH (aq)}$
- If a base (providing OH<sup>-</sup>) is added, the acetic acid neutralizes it:  
 $\text{CH}_3\text{COOH (aq)} + \text{OH}^-(\text{aq}) \rightarrow \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O (l)}$

This ability to neutralize added acids or bases allows the buffer to maintain a relatively constant pH.

## Henderson-Hasselbalch Equation

The pH of a buffer solution can be calculated using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{Conjugate base}]}{[\text{Weak acid}]}\right)$$

For a buffer made from a weak base and its conjugate acid, the pOH is calculated as:

$$\text{pOH} = \text{pK}_b + \log\left(\frac{[\text{Conjugate acid}]}{[\text{Weak base}]}\right)$$

**Example Calculation:** For a buffer made by mixing 0.060 M NH<sub>3</sub> (ammonia) with 0.040 M NH<sub>4</sub>Cl (ammonium chloride), where K<sub>b</sub> for ammonia is 1.8×10<sup>-5</sup>:

1. Calculate pOH using Henderson-Hasselbalch equation:

$$\text{pOH} = 4.745 + \log\left(\frac{0.04}{0.06}\right)$$

$$\text{pOH} = 4.745 - 0.1761 = 4.5689$$

2. Convert pOH to pH:

$$\text{pH} = 14 - \text{pOH} = 14 - 4.5689 = 9.4311$$

This buffer would maintain a pH around 9.4, resisting changes when small amounts of acid or base are added.

### ***Importance of Buffers***

Buffers are vital in various systems, especially in biological contexts. For example, human blood is buffered to maintain a pH of about 7.4, ensuring that enzymes function correctly and vital processes are regulated properly.

Understanding the common-ion effect and buffer solutions is crucial for managing pH in chemical reactions and biological systems.

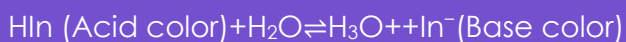
## **Acid-Base Indicators and Titrations**

### ***Acid-Base Indicators***

Acid-base indicators are substances that change color depending on the pH of the solution they are in. These indicators are usually weak acids or bases. They help us determine whether a solution is acidic, basic, or neutral.

- **How Indicators Work:** An indicator exists in two forms: an acidic form (HIn) and a basic form (In<sup>-</sup>). The color of the solution changes based on the pH, which influences whether the indicator is in its acidic or basic form.

#### **Reaction:**



- In an acidic solution, there is a high concentration of H<sub>3</sub>O<sup>+</sup> ions, causing the equilibrium to shift to the left, and the indicator shows its acid color.

- In a basic solution, the concentration of  $\text{H}_3\text{O}^+$  is lower, so the equilibrium shifts to the right, and the indicator shows its base color.

- **Common Indicators:**

- **Methyl violet:** Yellow in acid (pH 0.0 – 1.6), violet in base.
- **Methyl orange:** Red in acid (pH 3.2 – 4.4), yellow in base.
- **Litmus:** Red in acid (pH 5.0 – 8.0), blue in base.
- **Phenolphthalein:** Colorless in acid (pH 8.2 – 10.0), pink in base.

### **Acid-Base Titrations**

Titration is a laboratory technique used to determine the concentration of an unknown acid or base by reacting it with a solution of known concentration.

- **Titration Setup:**

- **Titrand (Analyte):** The solution with an unknown concentration, typically placed in a flask.
- **Titrant:** The solution of known concentration, typically added from a burette.
- **Indicator:** A few drops of an appropriate indicator are added to the analyte to signal the end point.

- **Process:**

- The titrant is added to the analyte until the indicator changes color, signaling the **end point** of the titration.
- The **equivalence point** is when the amount of titrant added is just enough to completely neutralize the analyte. At this point, the moles of acid equal the moles of base.

- **Calculations:**

- The normality (N) of a solution is the number of equivalents of solute per liter of solution.
- To find the concentration of an unknown solution after titration, use the formula:

$$\text{Normality of acid (N}_1\text{)} \times \text{Volume of acid (V}_1\text{)} = \text{Normality of base (N}_2\text{)} \times \text{Volume of base (V}_2\text{)}$$

- This equation helps in determining the unknown concentration after titration by rearranging it as:

$$\text{Unknown concentration of acid} = \frac{\text{Volume of base} \times \text{Concentration of base}}{\text{Volume of acid}}$$



## ***Titration Curves***

A titration curve is a graph that shows the change in pH as the titrant is added to the analyte. The curve helps in understanding how the pH of the solution changes during the titration and locating the equivalence point accurately.