UNIT 5

Acids and Bases

The study of acids and bases is fundamental in chemistry, leading to several theories over the years that attempt to explain their behaviour. The three main theories are the Arrhenius theory, the Bronsted-Lowry theory, and the Lewis theory. Each of these theories offers a different perspective on what constitutes an acid or a base and how they interact with each other.

Arrhenius Theory

Developed in the late 19th century by Svante Arrhenius, this theory was the first to provide a scientific basis for the properties of acids and bases. According to the Arrhenius theory:

- An **acid** is a substance that, when dissolved in water, increases the concentration of hydrogen ions (H^+) in the solution.
- A **base** is a substance that, when dissolved in water, increases the concentration of hydroxide ions (OH^-) in the solution.

Examples:

- Hydrochloric acid (HCl) is an Arrhenius acid because it dissociates in water to produce H^+ and Cl^- ions.

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

- Sodium hydroxide (NaOH) is an Arrhenius base because it dissociates in water to produce Na^+ and OH^- ions.

$$NaOH\ (aq) \xrightarrow{\text{Water}} Na^+\ (aq) + OH^-\ (aq)$$

Bronsted-Lowry Theory

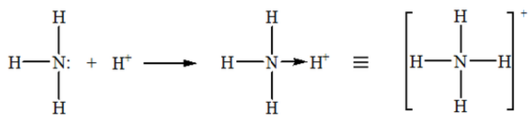
In the 1920s, Johannes Nicolaus Brønsted and Thomas Martin Lowry independently expanded upon Arrhenius's theory. The Bronsted-Lowry theory defines acids and bases in terms of their ability to donate or accept protons (H^+ ions):

- A **Bronsted-Lowry acid** is a substance that can donate a proton to another substance.
- A **Bronsted-Lowry base** is a substance that can accept a proton from another substance.

This theory broadened the definition of acids and bases beyond aqueous solutions to include reactions in other solvents and even gas-phase reactions.

Examples:

- Ammonia (NH_3) is a Bronsted-Lowry base because it can accept an H^+ ion to form ammonium (NH_4^+).



- Water can act as both a Bronsted-Lowry acid (by donating an H^+ to form OH^-) and a Bronsted-Lowry base (by accepting an H^+ to form H_3O^+).

$$\underset{\text{Acid}}{H_2O} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{OH^-}$$

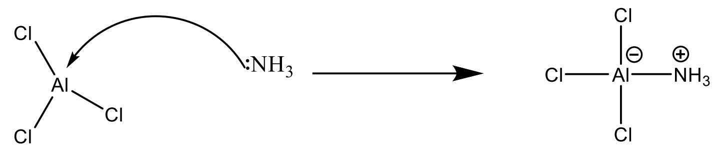
Lewis Theory

In 1923, Gilbert N. Lewis proposed a more general theory of acids and bases that focuses on the sharing of electron pairs rather than on protons specifically:

- A **Lewis acid** is an electron pair acceptor.
- A **Lewis base** is an electron pair donor.

This theory includes a wider range of chemical reactions, such as the formation of complexes and coordination compounds, and it does not require the acid or base to contain hydrogen.

Example:



Lewis acid **(electron pair acceptor)** **Lewis base** **(electron pair donor)**

- Aluminum trichloride ($AlCl_3$) is a Lewis acid because it can accept an electron pair from a donor molecule.
- Ammonia (NH_3) is a Lewis base because it has a lone pair of electrons that it can donate to an acceptor molecule, such as in the formation of an ammonium complex with a metal ion.

Solvent Systems:

Solvent systems are crucial in the field of chemistry, influencing the course and outcomes of reactions by acting as mediums in which reactants interact. These systems can significantly affect the rate, mechanism, and selectivity of chemical processes, making the choice of solvent a critical decision in both research and industrial applications.

Nonaqueous Solvents

Nonaqueous solvents are chemical solvents that do not contain water. They are used in chemical reactions where water is unsuitable, either because it might participate in undesirable side reactions, hydrolyze sensitive compounds, or because it might not dissolve the reactants or catalysts efficiently.

Classification of Nonaqueous Solvents

Nonaqueous solvents can be broadly classified into two categories based on their ability to donate or accept protons:

1. Protonic Solvents

Protonic solvents, also known as protic solvents, have the ability to donate protons (H^+ ions) during a chemical reaction. This property stems from the presence of acidic hydrogen atoms in their molecular structure, typically bonded to electronegative elements like oxygen or nitrogen. Protonic solvents are known for their ability to form hydrogen bonds, a characteristic that significantly influences their solvation properties.

Examples:

- **Acetic Acid (CH_3COOH):** Used in esterification reactions due to its acidic nature.
- **Methanol (CH_3OH) and Ethanol (C_2H_5OH):** Commonly used as solvents in organic synthesis due to their moderate polarity and ability to dissolve a wide range of compounds.

2. Aprotic Solvents

Aprotic solvents lack acidic hydrogen, meaning they cannot donate protons in a reaction. These solvents are characterized by their inability to form hydrogen bonds with solutes, a feature that makes them particularly useful for reactions involving highly reactive anionic species. Aprotic solvents can be further divided into polar and non-polar types based on their dielectric constant.

Examples:

- **Dimethyl Sulfoxide (DMSO, $(CH_3)_2SO$):** A polar aprotic solvent known for its ability to dissolve both polar and non-polar compounds, making it invaluable in many organic reactions.
- **Acetone (CH_3COCH_3):** A widely used polar aprotic solvent, effective for the dissolution of many organic compounds and used in various chemical processes.

Liquid ammonia as a solvent:

Liquid ammonia is a unique solvent with distinct properties that make it an interesting medium for a variety of chemical reactions, particularly those involving alkali and alkaline earth metals. Its ability to dissolve a wide range of substances, combined with its peculiar solvation properties and reactivity, offers a versatile environment for exploring novel chemistry.

Properties of Liquid Ammonia

- **Physical Characteristics:** At atmospheric pressure, ammonia boils at -33.34°C and freezes at -77.73°C. It has a high dielectric constant (about 22 at -33°C), making it a good solvent for ionic compounds.
- **Solvation Properties:** Ammonia can form hydrogen bonds, which contributes to its ability to dissolve many organic and inorganic compounds. However, its ability to solvate ions comes also from its relatively high dielectric constant.

- **Reactivity:** Liquid ammonia can act both as a Brønsted base, accepting protons, and as a Lewis base, donating a pair of electrons.

Solutions of Alkali and Alkaline Earth Metals in Ammonia

The dissolution of alkali and alkaline earth metals in liquid ammonia is a fascinating area of study due to the unique properties of these solutions.

1. **Alkali Metals (Li, Na, K, Rb, Cs):**
   - **General Observations:** These metals dissolve readily in liquid ammonia, giving solutions that can range from blue to bronze in color, depending on the concentration and the metal used.
   - **Conductivity:** These solutions are excellent conductors of electricity, indicating the presence of free electrons.
   - **Metal-Ammonia Solutions:** At low metal concentrations, the solution contains solvated electrons, which impart a characteristic blue color. At higher concentrations, the solutions become bronze-colored due to the formation of metal cations and solvated electrons.
2. **Alkaline Earth Metals (Mg, Ca, Sr, Ba):**
   - **Solubility:** Alkaline earth metals are less soluble in liquid ammonia than alkali metals. Their solubility and the properties of their solutions vary significantly among the group.
   - **Reactivity and Solutions:** These solutions tend to be more reactive than those of alkali metals. They can also form amides (e.g., $Mg(NH_2)_2Mg(NH_2)_2$ from magnesium) with ammonia, releasing hydrogen gas.

Types of chemical reactions:

Chemical reactions are central to the study of chemistry, allowing the transformation of substances into different substances through the breaking and forming of chemical bonds. Among the various types of chemical reactions, acid-base and oxidation-reduction (redox) reactions are foundational.

Acid-Base Reactions

Acid-base reactions involve the transfer of protons (H^+ ions) between reactants. These reactions are governed by the principles of Brønsted-Lowry, which define acids as proton donors and bases as proton acceptors.

Examples:

1. **Neutralization Reaction:**
   - **Example:** Hydrochloric acid reacts with sodium hydroxide to form sodium chloride and water.

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$

This reaction is a classic example of an acid (HCl) reacting with a base (NaOH) to produce a salt (NaCl) and water, illustrating the neutralization process.

2. **Gas Formation Reaction:**

Example: Sulfuric acid reacts with sodium bicarbonate to form carbon dioxide gas, water, and sodium sulfate.

$$H_2SO_{4(aq)} + 2NaHCO_{3(aq)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} + Na_2SO_{4(aq)}$$

This reaction showcases an acid reacting with a carbonate base, leading to the evolution of carbon dioxide gas.

Oxidation-Reduction (Redox) Reactions

Redox reactions are characterized by the transfer of electrons between substances, with oxidation referring to the loss of electrons and reduction to the gain of electrons. These reactions are crucial in energy transfer processes in chemical and biological systems.

Examples:

1. **Combustion Reaction:**

Example: Methane combustion in oxygen to produce carbon dioxide and water.

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$$

In this reaction, methane is oxidized (loses electrons) and oxygen is reduced (gains electrons), releasing energy in the form of heat and light.

2. **Displacement Reaction:**

Example: Zinc metal reacts with copper(II) sulfate to produce zinc sulfate and copper metal.

$$Zn_{(s)} + CuSO_{4(aq)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)}$$

Zinc displaces copper from its sulfate salt, illustrating a transfer of electrons from zinc (which is oxidized) to copper(II) ions (which are reduced).

Calculation of oxidation number:

The oxidation number (or oxidation state) is a concept in chemistry that describes the degree of oxidation of an atom in a chemical compound. It is a theoretical charge that an atom would have if all bonds to atoms of different elements were completely ionic.

Rules for Calculating Oxidation Numbers

1. The Oxidation Number of a Free Element is Zero.
   - For example, in O_2, H_2, or S_8, the oxidation number of oxygen, hydrogen, and sulfur is 0.
2. For Monoatomic Ions, the Oxidation Number is Equal to the Charge of the Ion.

- Na^+ has an oxidation number of +1, and Cl^- has an oxidation number of -1.

3. Oxygen Usually has an Oxidation Number of -2, Except in Peroxides like H_2O_2 (where it is -1) and in compounds with fluorine (OF_2) where it is +2.
4. Hydrogen Usually has an Oxidation Number of +1 When Combined with Nonmetals, and -1 When Combined with Metals in Hydrides like NaH.
5. The Sum of the Oxidation Numbers in a Neutral Compound is Zero; in a Polyatomic Ion, It Equals the Charge of the Ion.
6. Fluorine Always has an Oxidation Number of -1 in its Compounds. Other Halogens (Cl, Br, I) Generally have an Oxidation Number of -1, Unless They're Combined with Oxygen or Other Halogens More Electronegative Than Them.

Examples of Calculating Oxidation Numbers

Sl.No	Oxidation number of the element	In the compound	Calculation
1	C	CO_2	$x + 2(-2) = 0$ $x = +4$
2	S	H_2SO_4	$2(+1) + x + 4(-2) = 0$ $2 + x - 8 = 0$ $x = +6$
3	Cr	$Cr_2O_7^{2-}$	$2x + 7(-2) = -2$ $2x - 14 = -2$ $x = +6$
4	C	CH_2F_2	$x + 2(+1) + 2(-1) = 0$ $x = 0$
5	S	SO_2	$x + 2(-2) = 0$ $x = +4$

Definition of p^H, p^{K_a}, p^{K_b}:

Definition of pH

p^H is a measure of the hydrogen ion concentration $[H^+]$ in a solution, reflecting its acidity or basicity. The pH scale ranges from 0 to 14, with 7 being neutral. pH values less than 7 indicate acidic solutions, whereas values greater than 7 indicate basic (alkaline) solutions.

The pH is defined mathematically as:

$$p^H = -\log_{10}[H^+]$$

This logarithmic scale means that each unit change in pH represents a tenfold change in $[H^+]$ concentration.

Definition of pKa

p^{K_a} is the negative base-10 logarithm of the acid dissociation constant (K_a) of a solution. It quantifies the strength of an acid in a solution, indicating how easily the acid donates a proton

(H^+) to a base. The lower the $p^K{}_a$ value, the stronger the acid, as it more readily donates protons. The pKa value is derived from the equilibrium constant for the dissociation of an acid (HA) into its conjugate base (A^-) and a proton:

$$HA \rightleftharpoons A^- + H^+$$

$$Ka=[A^-][H^+] / [HA]$$

$$p^K{}_a = -\log_{10}K_a$$

Definition of pKb

$p^K{}_b$ is the negative base-10 logarithm of the base dissociation constant (K_b) of a solution. It measures the strength of a base in terms of its ability to accept a proton. Similar to $p^K a$, a lower $p^K b$ value indicates a stronger base. $p^K b$ is derived from the equilibrium constant for the dissociation of a base (B) into its conjugate acid (BH^+) and hydroxide ion (OH^-):

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

$$K_b=[BH^+][OH^-] / [B]$$

$$p^K b = -\log_{10} K_b$$

Types of Salts

Salts can be categorized based on several criteria, including the acidity and basicity of the ions they contain, their solubility, and the presence of complex ions. Major types include:

1. **Normal Salts:** Formed by the complete neutralization of an acid with a base. They do not contain replaceable hydrogen atoms or hydroxyl groups. Examples include sodium chloride (NaCl) and potassium sulfate (K_2SO_4).
2. **Acid Salts:** Result from the partial neutralization of a polybasic acid by a base, containing replaceable hydrogen atoms. An example is sodium hydrogen sulfate ($NaHSO_4$).
3. **Basic Salts:** Produced by the incomplete neutralization of a polyacidic base by an acid, containing replaceable hydroxyl groups. An example is basic copper carbonate ($CuCO_3 \cdot Cu(OH)_2$).
4. **Complex Salts:** Contain complex ions, where a central metal atom is bonded to one or more ligands. An example is potassium hexacyanoferrate(II) ($K_4[Fe(CN)_6]$).
5. **Hydrated Salts:** Incorporate water molecules in their crystal structure, known as water of crystallization. An example is copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$).

Salt Hydrolysis

Salt hydrolysis is the reaction of a salt with water to form an acidic or basic solution. The process involves the salt's anion or cation reacting with water to produce hydroxide ions (OH^-) or hydronium ions (H_3O^+), leading to a change in the pH of the solution. The extent of hydrolysis and the resulting pH depend on the strengths of the parent acid and base from which the salt is derived:

- Salts from a strong acid and a weak base undergo cationic hydrolysis, creating an acidic solution.
- Salts from a weak acid and a strong base undergo anionic hydrolysis, leading to a basic solution.
- Salts from strong acids and strong bases do not hydrolyze significantly and result in a neutral solution.

Pearson's Concept of Hard and Soft Acids and Bases (HSAB)

Pearson's HSAB theory categorizes acids and bases as "hard" or "soft" based on their polarizability and charge density. This concept helps predict the stability and reactivity of acid-base pairs, including those forming salts:

- **Hard Acids and Bases:** Have small, highly charged ions with low polarizability. Hard acids prefer to bind to hard bases, leading to ionic interactions. Examples include Na^+ (hard acid) and F^- (hard base).
- **Soft Acids and Bases:** Feature larger, less charged ions with high polarizability. Soft acids prefer to bind to soft bases, resulting in covalent bonding. Examples include Cu^+ (soft acid) and I^- (soft base).

Importance of the HSAB Principle

The HSAB principle is important in various fields of chemistry for several reasons:

1. **Predicting Reaction Mechanisms:** It helps in predicting the mechanism of chemical reactions, especially in organic synthesis and coordination chemistry.
2. **Stability of Complexes:** It provides insights into the stability of complexes, explaining why certain ligands preferentially bind to specific metal ions.
3. **Bioavailability of Metals:** In biochemistry, it explains the bioavailability and toxicity of metals, as organisms often differentiate between hard and soft metal ions.
4. **Catalysis:** In catalysis, understanding the nature of the acid and base can help design more effective catalysts for specific reactions.
5. **Material Science:** It aids in materials science, particularly in the synthesis of new materials with desired properties by controlling the hardness or softness of the components.

Bonding in Hard-Hard and Soft-Soft Combinations

The HSAB principle asserts that hard-hard and soft-soft acid-base interactions are more favorable due to the nature of the bonding:

- **Hard-Hard Combinations:** These interactions are typically ionic, with high lattice energies due to the strong electrostatic attraction between ions. For example, the interaction between magnesium ions (Mg^{2+}, a hard acid) and hydroxide ions (OH^-, a hard base) results in the formation of magnesium hydroxide, $Mg(OH)_2$. This compound is relatively insoluble in water, a characteristic feature of many hard-hard combinations.

- **Soft-Soft Combinations:** Soft-soft interactions tend to be covalent, with significant electron sharing. An example is the bonding between mercury (II) ions (Hg^{2+}, a soft acid) and sulfur ions (S^{2-}, a soft base), leading to the formation of mercury sulfide (HgS). HgS has a low solubility in water and is characterized by its strong covalent bonding, typical of soft-soft interactions.