Unit 4

CHEMICAL KINETICS

Introduction

Chemical reactions occur at different rates, varying from very slow to extremely fast. For instance, the rusting of iron is a slow process, while the ripening of fruits takes a few days, and the weathering of stone may take decades. On the other hand, reactions like the combustion of gasoline or the explosion of gunpowder happen within seconds. The study of these reaction rates is known as chemical kinetics, which focuses on understanding how fast a reaction occurs by measuring the change in concentration of reactants or products over time.

The Rate of a Reaction

The rate of a chemical reaction is a measure of how quickly the concentration of a reactant decreases or the concentration of a product increases over time. For a general reaction where reactants are converted into products:

Reactants→Products

we can monitor the reaction's progress by observing the concentration changes of either the reactants or the products. Consider the reaction:

$A \rightarrow B$

As the reaction proceeds, the concentration of A decreases while the concentration of B increases. The rate of this reaction can be expressed as:

Rate of reaction=$\frac{\Delta[A]}{\Delta t}$ or $\frac{\Delta[B]}{\Delta t}$

Here, $\Delta[A]$ and $\Delta[B]$ represent the changes in concentration of A and B, respectively, over a time interval Δt. Since the concentration of A decreases, $\Delta[A]$ is negative, so a minus sign is included in the expression to ensure that the rate is a positive quantity.

For more complex reactions, the rate expression must account for the stoichiometry. For example, consider the reaction:

$2A \rightarrow B$

In this case, two moles of A disappear for every mole of B formed, so the rate of formation of B is half the rate at which A disappears. The rate expression becomes:

$$\text{Rate}=-\frac{1}{2}\frac{\Delta[A]}{\Delta t}=\frac{1}{\Delta t}\frac{\Delta[B]}{\Delta t}$$

For a general reaction:

$aA+bB \rightarrow cC+dD$

The rate can be expressed as:

$$\text{Rate}=-\frac{1}{a}\frac{\Delta[A]}{\Delta t}=-\frac{1}{b}\frac{\Delta[B]}{\Delta t}=\frac{1}{c}\frac{\Delta[C]}{\Delta t}=\frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Determination of Rate of Reaction

The rate of a reaction can be determined by measuring changes in an observable property over time. This property could be a color change, temperature change, pressure change, mass change, or the formation of a new substance.

For example, consider the thermal decomposition of dinitrogen pentoxide (N_2O_5):

$2N_2O_5 \rightarrow 4NO_2+O_2$

This reaction can be monitored by measuring the increase in pressure as more gas molecules are formed or by observing the intensity of the brown color due to the formation of NO_2. The rate of the reaction is calculated by observing changes in concentration over time.

Example Calculation

For the reaction:

$2NO(g)+2H_2(g) \rightarrow N_2(g)+2H_2O(g)$

If the rate of disappearance of NO is 5.0×10^{-5} mol $L^{-1}s^{-1}$, the rate of formation of N_2 is:

$$\text{Rate}=-\frac{1}{2}\times(-5.0\times10^{-5}\ \text{mol L}^{-1}\text{s}^{-1})=2.5\times10^{-5}\ \text{mol L}^{-1}\text{s}^{-1}$$

This means that the reaction proceeds at a rate of 2.5×10^{-5} mol $L^{-1}s^{-1}$ for the formation of nitrogen gas (N_2).

Conditions Needed for a Chemical Reaction

Chemical reactions occur when reactant molecules collide with each other. However, not all collisions result in a chemical reaction. The conditions necessary for a chemical reaction to take place are explained by the collision theory, which emphasizes the importance of proper orientation and sufficient energy in collisions.

1. Collisions Between Reactants: For a chemical reaction to occur, reacting species (atoms, ions, or molecules) must collide. The rate of reaction depends on the number of collisions per second—the more collisions, the higher the reaction rate. However, only collisions with the correct orientation and sufficient energy lead to a reaction.
2. Proper Orientation: The molecules must collide in a specific orientation that allows the necessary bonds to break and new bonds to form. Only effective collisions, where the molecules are correctly aligned, result in a chemical reaction.
3. Activation Energy: For a collision to lead to a reaction, the molecules must collide with enough energy to overcome the activation energy barrier. Activation energy is the minimum amount of energy needed to initiate the reaction. If the molecules do not have sufficient energy, they will simply bounce off each other without reacting.
4. Factors Affecting Reaction Rate:
    - Nature of Reactants: Different substances react at different rates due to their chemical nature. For instance, reactions involving oppositely charged ions usually occur rapidly, whereas reactions that involve rearranging molecular structures may proceed more slowly.
    - Surface Area of Reactants: In reactions involving solids, the rate of reaction increases with the surface area of the solid. Finely divided materials react faster than larger chunks because more particles are exposed to react with the other reactants.
    - Concentration of Reactants: Higher concentrations of reactants lead to more frequent collisions, which increases the reaction rate. In gas reactions, an increase in pressure can also raise the concentration of gases, thereby speeding up the reaction.
    - Temperature of Reactants: Increasing the temperature raises the kinetic energy of the molecules, leading to more frequent and energetic collisions. Generally, a 10°C increase in temperature approximately doubles the reaction rate.

- Presence of a Catalyst: Catalysts are substances that increase the rate of a reaction by providing an alternative pathway with a lower activation energy. Catalysts are not consumed in the reaction, and they do not affect the equilibrium position of the reaction.

By ensuring these conditions—sufficient collisions, correct orientation, and enough energy—are met, chemical reactions can occur more efficiently and at a faster rate.