Zero-Order Reaction

A **zero-order reaction** is a chemical reaction in which the rate of reaction is independent of the concentration of the reactant. This means that changing the concentration of the reactant does not affect the reaction rate, provided that other conditions remain constant. Such reactions generally occur when the surface of a catalyst becomes completely saturated with reactant molecules or when the reactant is supplied at a constant rate. In a zero-order reaction, the reaction proceeds at a constant rate until the reactant is nearly exhausted.

Rate Law

For a zero-order reaction,

$$A \longrightarrow \text{Products}$$

the rate law is

$$-\frac{d[A]}{dt} = k$$

where k is the zero-order rate constant.

Derivation of the Integrated Rate Equation

Starting from the differential rate equation,

$$-\frac{d[A]}{dt} = k$$

Rearranging,

$$d[A] = -k\,dt$$

Integrating between the limits:

- At $t = 0$, concentration $= [A]_0$
- At time t, concentration $= [A]$

$$\int_{[A]_0}^{[A]} d[A] = -k \int_0^t dt$$

$$[A] - [A]_0 = -kt$$

or,

$$[A] = [A]_0 - kt$$

This equation is known as the **integrated rate equation for a zero-order reaction**. It shows that the concentration of the reactant decreases linearly with time.

Graphical Representation

A plot of reactant concentration $[A]$ versus time t gives a straight line with a negative slope equal to $-k$ and an intercept equal to the initial concentration $[A]_0$.

$$\text{Slope} = -k$$

$$\text{Intercept} = [A]_0$$

Units of the Rate Constant

Since

$$k = \frac{\text{concentration}}{\text{time}}$$

the SI unit of the zero-order rate constant is

$$\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}$$

Half-Life of a Zero-Order Reaction

The **half-life** of a reaction is the time required for the concentration of a reactant to decrease to one-half of its initial value. It is denoted by $t_{1/2}$. In a zero-order reaction, the half-life depends directly on the initial concentration of the reactant. Therefore, unlike a first-order reaction, the half-life of a zero-order reaction is not constant and decreases as the reaction proceeds.

Derivation

The integrated rate equation for a zero-order reaction is

$$[A] = [A]_0 - kt$$

At half-life,

$$[A] = \frac{[A]_0}{2}$$

Substituting this value into the integrated rate equation,

$$\frac{[A]_0}{2} = [A]_0 - kt_{1/2}$$

Rearranging,

$$kt_{1/2} = [A]_0 - \frac{[A]_0}{2}$$

$$kt_{1/2} = \frac{[A]_0}{2}$$

Therefore,

$$\boxed{t_{1/2} = \frac{[A]_0}{2k}}$$

Important Points

- The half-life of a zero-order reaction is directly proportional to the initial concentration of the reactant.
- As the initial concentration increases, the half-life also increases.
- The half-life is not constant throughout the reaction.

Mean Life of a Zero-Order Reaction

The concept of **mean life** is generally not applicable to zero-order reactions. Mean life is derived from exponential decay and is therefore defined only for first-order reactions. Since the concentration of a reactant in a zero-order reaction decreases linearly with time rather than exponentially, there is no fixed expression for its mean life.

Important Note

For examination purposes, remember that **mean life is defined only for first-order reactions**. It is **not defined for zero-order or second-order reactions**.

Characteristics of a Zero-Order Reaction

- The reaction rate is independent of reactant concentration.
- The concentration of the reactant decreases linearly with time.
- The rate remains constant throughout most of the reaction.
- A plot of concentration versus time is a straight line.
- The unit of the rate constant is concentration per unit time.

Examples

- Photochemical reactions carried out under constant light intensity.
- Catalytic reactions when the catalyst surface is completely saturated with reactant molecules.
- Decomposition of ammonia on a hot platinum surface at high pressure.