First-Order Reaction

A **first-order reaction** is a chemical reaction in which the rate of reaction is directly proportional to the first power of the concentration of a single reactant. In other words, as the concentration of the reactant decreases, the reaction rate decreases proportionally. First-order reactions are among the most common reactions in chemistry and are widely encountered in radioactive decay, decomposition reactions, hydrolysis reactions, and pharmaceutical degradation. One of the most important characteristics of a first-order reaction is that its half-life is independent of the initial concentration of the reactant.

Rate Law

For a first-order reaction,

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

the rate law is

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

where k is the first-order rate constant.

Derivation of the Integrated Rate Equation

Starting from the differential rate equation,

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

Rearranging,

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

Integrating both sides between the limits:

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

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

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

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt$$

or,

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

Converting the natural logarithm into the common logarithm,

$$\boxed{k = \frac{2.303}{t} \log\left(\frac{[A]_0}{[A]}\right)}$$

This equation is known as the **integrated rate equation for a first-order reaction**.

Graphical Representation

A plot of $\ln[A]$ versus time gives a straight line with a slope of $-k$ and an intercept of $\ln[A]_0$. Similarly, a plot of $\log[A]$ versus time also gives a straight line with a slope of $-k/2.303$.

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

Units of the Rate Constant

For a first-order reaction,

$$k = \frac{1}{t}$$

Hence, the SI unit of the first-order rate constant is

$$\boxed{\text{s}^{-1}}$$

Half-Life of a First-Order Reaction

The half-life of a reaction is the time required for the concentration of the reactant to decrease to one-half of its initial value. For a first-order reaction, the half-life is constant and does not depend on the initial concentration of the reactant.

Derivation

Using the integrated rate equation,

$$k = \frac{2.303}{t} \log\left(\frac{[A]_0}{[A]}\right)$$

At half-life,

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

Substituting,

$$k = \frac{2.303}{t_{1/2}} \log\left(\frac{[A]_0}{[A]_0/2}\right)$$

$$k = \frac{2.303}{t_{1/2}} \log 2$$

Since

$$\log 2 = 0.3010$$

$$k = \frac{2.303 \times 0.3010}{t_{1/2}}$$

$$k = \frac{0.693}{t_{1/2}}$$

Therefore,

$$\boxed{t_{1/2} = \frac{0.693}{k}}$$

This equation shows that the half-life of a first-order reaction is independent of the initial concentration.

Mean Life of a First-Order Reaction

The **mean life** of a first-order reaction is the average lifetime of a reactant molecule before it undergoes a chemical change. It is represented by the symbol τ.

Derivation

The mean life is related to the rate constant by

$$\boxed{\tau = \frac{1}{k}}$$

Since

$$t_{1/2} = \frac{0.693}{k}$$

therefore,

$$\boxed{\tau = 1.443\, t_{1/2}}$$

Thus, the mean life of a first-order reaction is approximately 1.443 times its half-life.

Characteristics of a First-Order Reaction

- The reaction rate is directly proportional to the concentration of the reactant.
- The integrated rate equation is logarithmic in nature.
- A plot of $\ln[A]$ versus time is a straight line.
- The rate constant has the unit s^{-1}.
- The half-life is constant and independent of the initial concentration.
- Mean life is defined only for first-order reactions.

Examples

- Radioactive decay.
- Decomposition of hydrogen peroxide.
- Decomposition of nitrogen pentoxide (N_2O_5).
- Hydrolysis of sucrose in dilute acid.

Important Points

- Only first-order reactions have a constant half-life.
- Mean life is defined only for first-order reactions.
- The integrated rate equation is used to calculate the rate constant from experimental data.
- Many decomposition and radioactive processes follow first-order kinetics.