

Chem Kinetics Overview



First-Order Reactions

Definition and Characteristics

A first-order reaction is one in which the rate of reaction is directly proportional to the concentration of one reactant. This means that if the concentration of the reactant is doubled, the rate of the reaction also doubles.

Rate Law

For a first-order reaction, the rate law can be written as:

$$\text{Rate} = k[A]$$

Where:

- Rate is the rate of the reaction.
- k is the rate constant.
- $[A]$ is the concentration of the reactant.

Integrated Rate Law

To derive the integrated rate law for a first-order reaction, we start from the rate equation:

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

Rearranging and integrating both sides:

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

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

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

$$[A] = [A]_0 e^{-kt}$$

This equation indicates that the concentration of the reactant decreases exponentially with time.

Half-Life of a First-Order Reaction

The half-life ($t_{1/2}$) of a first-order reaction is the time required for the concentration of the reactant to decrease to half of its initial concentration. For first-order reactions, the half-life is given by:

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

This shows that the half-life of a first-order reaction is independent of the initial concentration and depends only on the rate constant k .

Graphical Representation

For a first-order reaction, plotting $\ln[A]$ versus time t gives a straight line with a slope of $-k$ and a y-intercept of $\ln[A]_0$.

Slope = $-k$

Y-intercept = $\ln[A]_0$

 First-Order Reaction Plot

Alternatively, plotting $[A]$ versus time t gives an exponential decay curve.

Determination of Rate Constant

The rate constant k for a first-order reaction can be determined using the integrated rate law. By rearranging the equation, we get:

$$k = -\frac{\ln([A]/[A]_0)}{t}$$

Examples of First-Order Reactions

- 1. Radioactive Decay:** The decay of radioactive isotopes follows first-order kinetics. For example, the decay of Carbon-14:
$$\text{C}^{14} \rightarrow \text{N}^{14} + \beta$$
- 2. Hydrolysis of Esters:** The hydrolysis of esters in an acidic medium follows first-order kinetics. For example, the hydrolysis of methyl acetate:
$$\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{CH}_3\text{OH}$$
- 3. Decomposition of Hydrogen Peroxide:** The decomposition of hydrogen peroxide in the presence of iodide ions follows first-order kinetics:
$$2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$$
- 4. Formation of Product in Enzyme Reactions:** Many enzyme-catalyzed reactions show first-order kinetics at low substrate concentrations.

Summary

- **First-Order Reaction:** Rate is directly proportional to reactant concentration.
- **Rate Law:** $\text{Rate} = k[A]$
- **Integrated Rate Law:** $[A] = [A]_0 e^{-kt}$
- **Graph:** $\ln[A]$ vs. t is a straight line with slope $-k$, and $[A]$ vs. t is an exponential decay.
- **Half-Life:** $t_{1/2} = \frac{0.693}{k}$, independent of initial concentration.
- **Examples:** Radioactive decay, hydrolysis of esters, decomposition of hydrogen peroxide, enzyme-catalyzed reactions.

Understanding first-order reactions is crucial in various fields such as chemistry, biology, and environmental science, where the rate of reactions and their mechanisms play a significant role.