Chem Kinetics

Zero-Order Reactions

Definition and Characteristics

A zero-order reaction is one in which the rate of reaction is independent of the concentration of the reactants. This means that the rate remains constant throughout the reaction as long as the reactant is present.

Rate Law

For a zero-order reaction, the rate law can be written as:
$\text{Rate} = k[A]^0 = k$
Where:

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

Since $[A]^0 = 1$, the rate of reaction is simply equal to the rate constant k.

Integrated Rate Law

To derive the integrated rate law for a zero-order reaction, we start from the rate equation:
$-\frac{d[A]}{dt} = k$
Integrate both sides with respect to time t from the initial concentration $[A]_0$ at $t = 0$ to the concentration $[A]$ at time t:
$\int_{[A]_0}^{[A]} d[A] = -k \int_0^t dt$
$[A] - [A]_0 = -kt$
$[A] = [A]_0 - kt$
This equation indicates that the concentration of the reactant decreases linearly with time.

Graphical Representation

For a zero-order reaction, plotting the concentration $[A]$ versus time t gives a straight line with a slope of $-k$ and a y-intercept of $[A]_0$.
$\text{Slope} = -k$
$\text{Y-intercept} = [A]_0$
Zero-Order Reaction Plot

Half-Life of a Zero-Order Reaction

The half-life ($t_{1/2}$) of a zero-order reaction is the time required for the concentration of the reactant to decrease to half of its initial concentration. For zero-order reactions, the half-life is given by:
$t_{1/2} = \frac{[A]_0}{2k}$
This shows that the half-life of a zero-order reaction is directly proportional to the initial concentration $[A]_0$ and inversely proportional to the rate constant k.

Examples of Zero-Order Reactions

1. **Photochemical Reactions**: The decomposition of certain compounds under the influence of light can follow zero-order kinetics. For example, the photochemical reaction between hydrogen and iodine:
   $\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \xrightarrow{hv} 2\mathrm{HCl}(g)$
2. **Catalytic Reactions on Surfaces**: Many reactions that occur on the surface of solid catalysts exhibit zero-order kinetics. For instance, the decomposition of ammonia on a platinum surface or the decomposition of nitrous oxide ($\mathrm{N_2O}$) on hot platinum.
3. **Iodination of Acetone**: In acid medium, the reaction between acetone and iodine shows zero-order kinetics with respect to iodine.
   $\mathrm{CH_3COCH_3} + \mathrm{I_2} \rightarrow \mathrm{ICH_2COCH_3} + \mathrm{HI}$
   $\mathrm{Rate} = k[\mathrm{CH_3COCH_3}][\mathrm{H^+}]$

Summary

- **Zero-Order Reaction**: Rate is constant and independent of reactant concentration.
- **Rate Law**: $\mathrm{Rate} = k$
- **Integrated Rate Law**: $[A] = [A]_0 - kt$
- **Graph**: Straight line, slope $-k$, y-intercept $[A]_0$
- **Half-Life**: $t_{1/2} = \frac{[A]_0}{2k}$
- **Examples**: Photochemical reactions, catalytic surface reactions, iodination of acetone.

Understanding zero-order reactions helps in various fields like industrial chemistry, where maintaining a constant reaction rate is essential for processes involving surface catalysts or photochemical reactions .