Half-Life Method

The **Half-Life Method** is a simple experimental method used to determine the order of a chemical reaction by studying the relationship between the half-life of the reaction and the initial concentration of the reactant. The half-life, denoted by $t_{1/2}$, is the time required for the concentration of a reactant to decrease to one-half of its initial value. Since the expression for half-life is different for reactions of different orders, the order of a reaction can be identified by observing how the half-life changes with the initial concentration.

Principle

The dependence of half-life on the initial concentration is different for zero-order, first-order, and second-order reactions. By experimentally determining the half-life at different initial concentrations and comparing the results with the known half-life equations, the order of the reaction can be established.

Zero-Order Reaction

For a zero-order reaction,

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

Thus,

$$t_{1/2} \propto [A]_0$$

The half-life is directly proportional to the initial concentration. Therefore, increasing the initial concentration increases the half-life.

First-Order Reaction

For a first-order reaction,

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

Thus,

$$t_{1/2} \propto [A]_0^0$$

The half-life is independent of the initial concentration and remains constant throughout the reaction. This is the characteristic feature of a first-order reaction.

Second-Order Reaction

For a second-order reaction,

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

Thus,

$$t_{1/2} \propto \frac{1}{[A]_0}$$

The half-life is inversely proportional to the initial concentration. Therefore, increasing the initial concentration decreases the half-life.

Summary of Half-Life Expressions

Order of Reaction	Half-Life Expression	Dependence on Initial Concentration
Zero Order	$t_{1/2} = \frac{[A]_0}{2k}$	Directly proportional to $[A]_0$
First Order	$t_{1/2} = \frac{0.693}{k}$	Independent of $[A]_0$
Second Order	$t_{1/2} = \frac{1}{k[A]_0}$	Inversely proportional to $[A]_0$

Procedure

1. Prepare the reaction with a known initial concentration.
2. Determine the time required for the reactant concentration to become half of its initial value.
3. Repeat the experiment using different initial concentrations.
4. Observe how the half-life changes with the initial concentration.

5. Compare the observations with the standard half-life expressions to determine the reaction order.

Advantages

- Simple and easy to perform.
- Requires only concentration and time measurements.
- Particularly useful for identifying first-order reactions.
- No measurement of instantaneous reaction rate is required.

Limitations

- Applicable only when the half-life can be measured accurately.
- Not suitable for reactions with very short or very long half-lives.
- Less reliable for complex reactions involving multiple steps.

Important Points

- The half-life of a zero-order reaction increases with the initial concentration.
- The half-life of a first-order reaction is constant and independent of the initial concentration.
- The half-life of a second-order reaction decreases with increasing initial concentration.
- The Half-Life Method is one of the simplest methods for determining the order of a reaction experimentally.