Second Order Reaction

A **second-order reaction** is a chemical reaction in which the rate of reaction is proportional to the square of the concentration of a single reactant or to the product of the concentrations of two reactants, each raised to the first power. Second-order reactions are commonly encountered in bimolecular reactions where two reactant molecules collide to form products. As the concentration of the reactants decreases, the reaction rate decreases more rapidly than in a first-order reaction. The mathematical treatment of second-order reactions is important for determining the rate constant, predicting the concentration of reactants at any instant, and calculating the half-life of the reaction.

Rate Law

For a second-order reaction involving a single reactant,

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

the rate law is

$$-\frac{d[A]}{dt} = k[A]^2$$

where k is the second-order rate constant.

Derivation of the Integrated Rate Equation

Starting from the differential rate equation,

$$-\frac{d[A]}{dt} = k[A]^2$$

Rearranging,

$$\frac{d[A]}{[A]^2} = -k\,dt$$

Integrating both sides between the limits:

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

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

$$-\frac{1}{[A]} + \frac{1}{[A]_0} = -kt$$

Rearranging,

$$\boxed{\frac{1}{[A]} = \frac{1}{[A]_0} + kt}$$

or,

$$\boxed{k = \frac{1}{t}\left(\frac{1}{[A]} - \frac{1}{[A]_0}\right)}$$

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

Graphical Representation

A plot of $\frac{1}{[A]}$ versus time gives a straight line with a positive slope equal to k and an intercept equal to $\frac{1}{[A]_0}$.

$$\text{Slope} = k$$

$$\text{Intercept} = \frac{1}{[A]_0}$$

Units of the Rate Constant

Since

$$k = \frac{1}{\text{concentration} \times \text{time}}$$

the SI unit of the second-order rate constant is

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

Half-Life of a Second-Order Reaction

The half-life of a second-order reaction is the time required for the concentration of the reactant to become one-half of its initial value. Unlike a first-order reaction, the half-life of a

second-order reaction depends on the initial concentration of the reactant.

Derivation

The integrated rate equation is

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

At half-life,

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

Substituting,

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

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

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

Therefore,

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

Thus, the half-life of a second-order reaction is inversely proportional to the initial concentration of the reactant.

Second-Order Reaction Involving Two Reactants

A second-order reaction may also involve two different reactants, each having first-order dependence on its concentration. In such reactions, the overall order is two because the sum of the exponents of the concentration terms is equal to two. Such reactions are commonly encountered in bimolecular processes where two different reactant molecules collide to form products.

Consider the general reaction:

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

The rate law is

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

If the initial concentrations of the reactants are different, that is,

$$[A]_0 = a, \qquad [B]_0 = b$$

and after time t, let x be the amount reacted. Then,

$$[A] = a - x$$

$$[B] = b - x$$

The rate equation becomes

$$\frac{dx}{dt} = k(a - x)(b - x)$$

On integration, the integrated rate equation is

$$\boxed{k = \frac{2.303}{(a - b)t} \log\left(\frac{b(a - x)}{a(b - x)}\right)}$$

where a and b are the initial concentrations of reactants A and B, respectively, and x is the concentration reacted after time t.

Special Case: Equal Initial Concentrations

If the initial concentrations of both reactants are equal, that is,

$$[A]_0 = [B]_0 = a$$

then

$$[A] = [B] = a - x$$

The rate law becomes

$$\frac{dx}{dt} = k(a - x)^2$$

On integration,

$$\boxed{\frac{1}{a - x} = \frac{1}{a} + kt}$$

which is identical to the integrated rate equation for a second-order reaction involving a single reactant.

Half-Life for Equal Initial Concentrations

At half-life,

$$a - x = \frac{a}{2}$$

Substituting into the integrated rate equation,

$$\frac{2}{a} = \frac{1}{a} + kt_{1/2}$$

Therefore,

$$\boxed{t_{1/2} = \frac{1}{ka}}$$

Thus, when the initial concentrations of both reactants are equal, the half-life is inversely proportional to the initial concentration.

Mean Life of a Second-Order Reaction

The concept of **mean life** is generally not applicable to second-order reactions. Mean life is defined only for first-order reactions because it is derived from exponential decay. Since the concentration of a reactant in a second-order reaction does not decrease exponentially, there is no fixed expression for its mean life.

Characteristics of a Second-Order Reaction

- The reaction rate is proportional to the square of the concentration of a single reactant or to the product of the concentrations of two reactants.
- The integrated rate equation is expressed in reciprocal concentration.
- A plot of $1/[A]$ versus time gives a straight line.
- The rate constant has the unit $\mathrm{L\,mol^{-1}\,s^{-1}}$.
- The half-life depends on the initial concentration of the reactant.
- Mean life is not defined for second-order reactions.

Examples

- Dimerization of butadiene.
- Saponification of ethyl acetate by sodium hydroxide.
- Reaction between hydrogen and iodine under suitable conditions.

Important Points

- The integrated rate equation is written in terms of reciprocal concentration.
- The graph of $1/[A]$ versus time is linear.
- The half-life decreases as the initial concentration increases.
- Mean life is defined only for first-order reactions and not for second-order reactions.