Topic ⇒ Second order Reaction

Name ⇒ Dr. Amarendra Kumar,
Deptt. of Chemistry,
Jain College, Ara.

Second order Reaction

A reaction is said to be of the second order if the rate of reaction depends upon two concentration terms.

Case 1 ⇒ When only one reactant is involved

Let us consider a general reaction involving one reactant

$$2A \longrightarrow \text{Products}$$

Suppose the initial concentration of A = a moles/litre
If after time t, x moles of A have reacted, the concentration of A = (a−x) moles/litre.

We know that for such a second order reaction, rate of reaction is proportional to the square of the concentration of the reactant. Thus,

$$\frac{dx}{dt} \propto [A]^2$$

or $$\frac{dx}{dt} \propto (a-x)^2$$

or, $$\frac{dx}{dt} = K(a-x)^2 \quad \text{———} \quad (1)$$

Where K is the rate constant for the 2nd order reaction

Rearranging eqn. (1) we have

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

Integrating this eqn. we get

$$\int \frac{dx}{(a-x)^2} = \int Kdt$$

i.e. $$\frac{(a-x)^{-1}}{-1} \times (-1) = Kt + I$$

or $$\frac{1}{(a-x)} = Kt + I \quad \text{——— ②}$$

Where I is integration constant

In the beginning i.e. at time $t=0$, $x=0$

Putting this value in eqn. ② we get

$$\frac{1}{a} = I$$

Substituting this value of I in eqn ② we get

$$\frac{1}{a-x} = Kt + \frac{1}{a}$$

or $$Kt = \frac{1}{a-x} - \frac{1}{a} \quad \text{——— ③}$$

or $$Kt = \frac{a-(a-x)}{a(a-x)}$$

or $$Kt = \frac{x}{a(a-x)}$$

$$\therefore K = \frac{1}{t} \frac{x}{a(a-x)}$$

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

If the initial concentration is written as C_0 and concentration at any instant of time t as C_t, then $a = C_0$ and $(a-x) = C_t$ Putting this value in eqn ③, we get

$$K = \frac{1}{t}\left[\frac{1}{C_t} - \frac{1}{C_0}\right]$$

This is another form of the expression for the rate constant of second order reaction.

Case 2 ⟹ When two different reactants with different initial concentrations are involved

General equation for such reaction is

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

Suppose the initial concentration of A = a moles/litre, the initial concentration of B = b moles/litre, amount of A that reacts in time t = x moles/litre, then the amount of B that would react in the same time would also be x moles/litre.

∴ At any instant of time t

Concentration of A = (a−x) moles/litre

Concentration of B = (b−x) moles/litre

We know that,

$$\text{Rate of reaction } \frac{dx}{dt} \propto [A][B]$$

$$\text{or } \frac{dx}{dt} \propto (a-x)(b-x)$$

$$\therefore \frac{dx}{dt} = K(a-x)(b-x) \quad \text{——— (1)}$$

Where K is the rate constant.

Equation (1) may be rewritten as

$$\frac{dx}{(a-x)(b-x)} = K\,dt \quad \text{——— (2)}$$

Resolving the left hand side into partial fractions equation (2) may be rewritten as

$$\frac{1}{(a-b)}\left[\frac{1}{(b-x)} - \frac{1}{(a-x)}\right]dx = K\,dt$$

Integrating this equation, we get

$$\frac{1}{(a-b)}\left(\int\frac{dx}{(b-x)} - \int\frac{dx}{(a-x)}\right) = \int K\,dt$$

$$\text{or, } \frac{1}{(a-b)}\left[-\ln(b-x) - \{-\ln(a-x)\}\right] = Kt + I$$

or, $\frac{1}{(a-b)}\left[\ln(a-x) - \ln(b-x)\right] = Kt + I$

$\therefore \quad \frac{1}{(a-b)}\left(\ln \frac{a-x}{b-x}\right) = Kt + I$ ——— (3)

Where I is the constant of Integration.
But at $t=0$, $x=0$
Putting these values in eqn (3), we get

$\frac{1}{(a-b)}\left(\ln \frac{a}{b}\right) = I$ ——— (4)

Putting this value in eqn (3), we get

$\frac{1}{(a-b)} \ln \frac{a-x}{b-x} = Kt + \frac{1}{(a-b)} \ln \frac{a}{b}$

or $Kt = \frac{1}{(a-b)} \ln \frac{a-x}{b-x} - \frac{1}{(a-b)} \ln \frac{a}{b}$

or $Kt = \frac{1}{(a-b)}\left[\ln \frac{a-x}{b-x} - \ln \frac{a}{b}\right]$

or $Kt = \frac{1}{(a-b)} \ln\left(\frac{a-x}{b-x} \times \frac{b}{a}\right)$

$\therefore K = \frac{2.303}{t(a-b)} \log \frac{b\,(a-x)}{a\,(b-x)}$

This is the rate equation for a second order reaction.

unit ⇒ The unit of K for second order reactions are

conc^{-1} time^{-1}

—x—

SPM