B. Sc. Part II (Subsidiary)

Paper : Physical Chemistry

Topic : Chemical Kinetics

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Second Order Reactions

The rate of second order reactions is proportional to the square of concentration of one reactant or product of concentrations of two reactants having power unity. i.e.

$$\text{Rate} = k[A]^2$$

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

Here we see that (i) the rate depends on two variable concentration terms which may or may not be same and (ii) the rate increases by n^2 times if concentration of reactants is increased by n times.

For a second order reaction, there may be two cases:

(a) when concentrations of reactants are same, and

(b) when concentrations of reactants are different. Now,

(a) When Concentrations of Reactants are Same :-

Consider the following second order reactions

	$2A$	$\longrightarrow$	Product
at $t=0$	a		0
at $t=t$	$(a-x)$		x

or,

	A	$+\ B$	$\longrightarrow$ Product
at $t=0$	a	a	0
at $t=t$	$(a-x)$	$(a-x)$	x

So, Rate $= \frac{dx}{dt} = k(a-x)^2$ —— ①

On rearranging this equation we have

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

On integration it gives

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

where I is integration constant. The value of I can be determined by putting t = 0 and x = 0. Thus

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

substituting for I in equation (2) we get

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

or $$k.t = \frac{1}{(a-x)} - \frac{1}{a}$$

or $$k = \frac{1}{t} \cdot \frac{x}{a(a-x)} \quad \text{——— (3)}$$

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

(b.) When Concentrations of Reactants are Different :—

Consider the following second order reaction starting with different initial concentrations of reactants

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

at t = 0	a	b	0
at t = t	(a-x)	(b-x)	x

and Rate $= \frac{dx}{dt} = k(a-x)(b-x)$ ——— (1)

After rearranging this we get

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

again using "partial fractions" (*) we get

$$\frac{1}{(a-b)}\left[\frac{dx}{(b-x)} - \frac{dx}{(a-x)}\right] = k.dt \quad \text{— (3)}$$

By integrating this equation we get

$$\frac{1}{(a-b)}\left[-\ln(b-x) + \ln(a-x)\right] = kt + I \quad \text{— (4)}$$

or $$\frac{1}{(a-b)}\left[\ln\frac{(a-x)}{(b-x)}\right] = kt + I \quad \text{— (5)}$$

The integration constant I can be evaluated by putting t = 0 and x = 0, then

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

Substituting the value of I in equation (5) we get

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

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

or, $$k = \frac{1}{t(a-b)}\left[\ln\frac{b(a-x)}{a(b-x)}\right] \quad \text{—— (6)}$$

or $$k = \frac{2.303}{t(a-b)}\log\frac{b(a-x)}{a(b-x)} \quad \text{—— (7)}$$

Equations ⑥ and ⑦ are the integrated rate equation for second order reaction.

✱ Partial Fractions:-

The term $\frac{1}{(a-x)(b-x)}$ can be broken into partial fraction as shown below

$$\frac{1}{(a-x)(b-x)} = \frac{A}{(a-x)} + \frac{B}{(b-x)}$$

or $$A(b-x) + B(a-x) = 1$$

If $x = a$, then $A(b-a) = 1$

or, $A = \frac{1}{(b-a)}$

If $x = b$, then $B(a-b) = 1$

or, $B = \frac{1}{(a-b)}$

On putting the values of A and B in above equation we have

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

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

Units of Second Order Rate Constant:-

The rate constant for a second order reaction is expressed as

$$k = \frac{1}{t} \times \frac{x}{a(a-x)}$$

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

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

$$= \frac{1}{\text{second}} \times \frac{1}{\text{moles/litre}}$$

$$= \text{litre/mole/second}$$

∴ Units of k ⇒ $L \cdot mol^{-1} s^{-1}$
for second order reaction

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