B. Sc. (Hons.) Part- I

CHEMICAL KINETICS

(Continued from page no. 25)

Dr. Om Prakash Singh
Department of Chemistry,
Maharaja College, Ara.

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

$$Rate = k[A]^2$$

or $$Rate = k[A][B]$$

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

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

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

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

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

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

..........to be continued