B. Sc. (Hons.) Part- I

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 concentrations 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) <u>When Concentrations of Reactants are Same :—</u>

Consider the following second order reactions

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

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

or, $A + B \longrightarrow \text{Product}$

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

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

On rearranging this equation we have

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

On integration it gives

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

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

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

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

	A	B	Products
at t = 0	a	b	0
at t = t	(a−x)	(b−x)	x

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

After rearranging this we get-

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

again using "partial fractions" ⊛ we get-

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

By integrating this equation we get-

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

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

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

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

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

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

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

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

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

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

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

Half - life of a Second Order Reaction:-

For a simple second order reaction of the type $2A \rightarrow$ Products, the integrated rate equation is

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

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

By definition, if $t = t_{1/2}$, $x = \frac{a}{2}$.

On putting these values in the above equation we get

$$t_{1/2} = \frac{1}{k} \cdot \frac{a/2}{a(a-a/2)}$$

$$= \frac{1}{k} \cdot \frac{1}{a}$$

$$\text{or} \quad t_{1/2} = \frac{1}{ka}$$

From this equation, we say that half-life period of a second order reaction is inversely proportional to the initial concentration of reactants.

In general, half-life of any reaction of nth order varies inversely as (n-1) power of the initial concentration of reactants, i.e. for the reaction $nA \rightarrow \text{Products}$

$$t_{1/2} = \frac{1}{k} \times \frac{1}{a^{n-1}} = \text{constant} \times \frac{1}{a^{n-1}}$$

$$\text{or,} \quad \boxed{t_{1/2} \propto \frac{1}{a^{n-1}} \quad \text{or,} \quad t_{1/2} \propto a^{1-n}}$$

Here the magnitude of the constant depends on the order of a reaction.

Examples of Second Order Reactions :-

A typical example of the second order reaction is the hydrolysis (or saponification) of an ester (e.g. ethyl acetate) with a strong base (e.g. NaOH). The reaction takes place as

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

The reaction mixture is prepared by mixing a known (generally equimolar) amount of ethylacetate with a known amount of NaOH. Let 'a' and 'b' be the initial concentrations of ester and base respectively. The course of the reaction is followed by removing a definite quantity of the reaction mixture from time to time and titrating with standard acid to know the concentration of NaOH left behind. As we see from reaction, the concentration of NaOH will decrease with time. If x is the decrease in concentration of NaOH at any time t, then $(b-x)$ is the amount of unreacted NaOH left behind. Similarly $(a-x)$ will be the amount of unreacted ester at time t. The specific rate constant k then be calculated using equation

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

Determination of Order of Reactions :-

The following methods are commonly used for determining the order of a reaction.

1. Intigrated Rate Equation Method :-

It is also known as "Hit and Trial Method". This method can be used either analytically or graphically.

a. Analytical Method :

In this method, experiments are made with different initial concentrations and concentrations at different intervals of time. By using integrated rate laws for different orders of reactions, value of k is calculated and the equation from which constant value of k is obtained gives the order of reaction. The different integrated rate laws are

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$ (First Order Reaction)

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

More simply the experimental values of a, (a-x) and t are substituted into the integrated rate equations for the first and second order reactions. The rate equation which yields a constant value of k corresponds to the correct order of the reaction.

b. Graphical Method :

In this method, we can determine

the order of reaction by seeing whether a graph of the data fits one of the integrated rate equations.

In case of first-Order: The first order equation is given by

$$k = \frac{2.303}{t} \cdot \log \frac{a}{(a-x)}$$

On simplifying it, we get

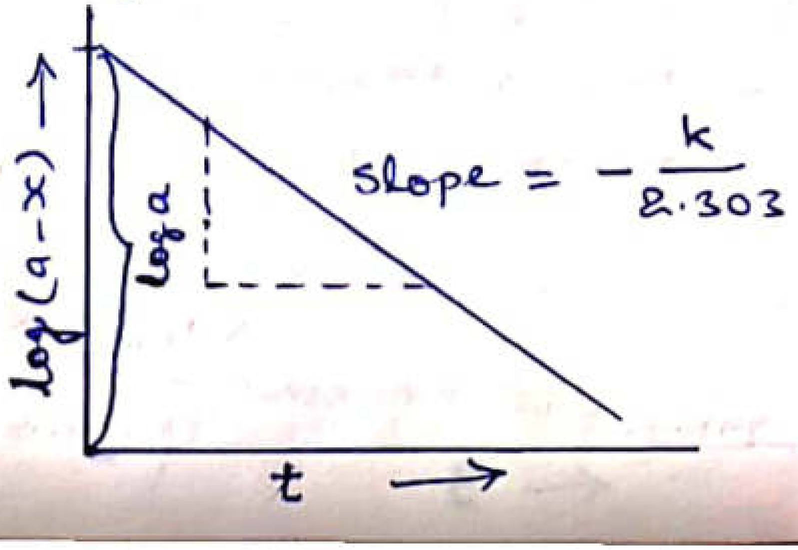
$$\log(a-x) = \left(-\frac{k}{2.303}\right)t + \log a$$

comparing this equation with the classical equation of a straight line, $y = mx + c$, the two variables are

$$y \Rightarrow \log(a-x) \quad \text{and}$$
$$x \Rightarrow t$$

And a plot of $\log(a-x)$ versus t for a first-order reaction should be a straight-line with a slope equal to $-\frac{k}{2.303}$ and intercept on the y-axis equal to $\log a$.

However, if a curve is obtained the reaction is not of the first-order.



The rate constant k can thus be calculated from measuring the slope

$$\text{slope} = -\frac{k}{2.303}$$

$$\text{or, } k = 2.303 \times \text{slope}$$

In case of Second Order :

The second order reaction of the type $2A \rightarrow \text{Products}$, the rate equation is given by

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

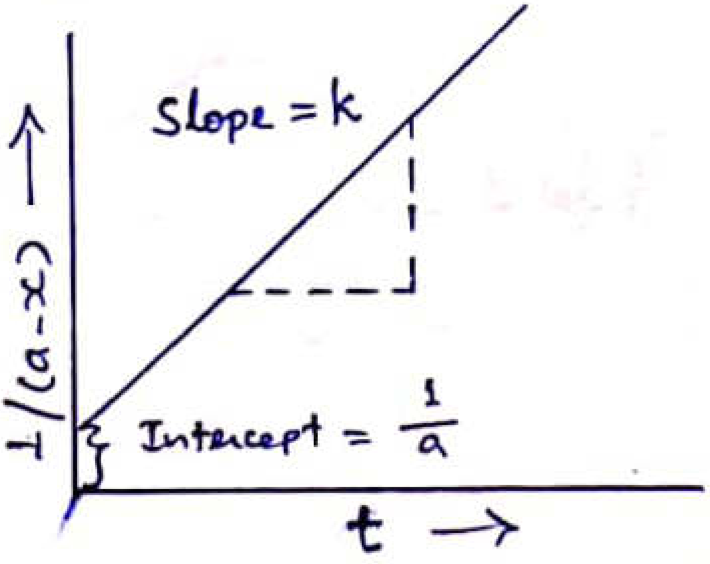
$$\text{or, } kt = \frac{1}{(a-x)} - \frac{1}{a}$$

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

This is comparable to the equation of straight line, $y = mx + c$ with two variables

$$y \Rightarrow \frac{1}{(a-x)} \quad \text{and} \quad x \Rightarrow t$$

Thus a plot of $1/(a-x)$ versus t for a second order reaction would be a straight line with a slope equal to k and intercept equal to $1/a$.



In case a curve is obtained, the reaction is not a second order reaction.

The second order reaction of the type $A + B \rightarrow$ Products, the rate equation is given by

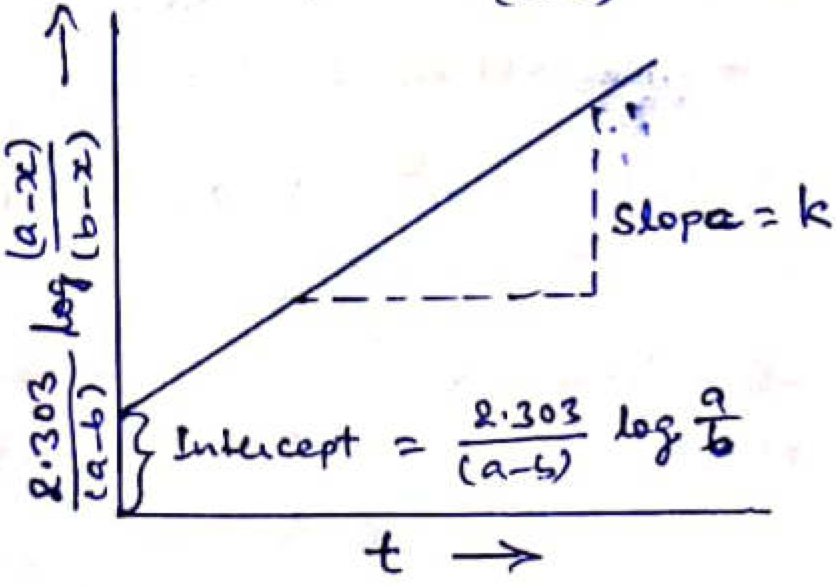
$$k = \frac{2.303}{t\,(a-b)} \cdot \log \frac{b(a-x)}{a(b-x)}$$

On simplifying it becomes

$$\frac{2.303}{(a-b)} \log \frac{(a-x)}{(b-x)} = kt + \frac{2.303}{(a-b)} \log \frac{a}{b}$$

This is similar to an equation for a straight line (i.e. $y = mx + c$). Therefore, for a second order reaction, the plot between $\frac{2.303}{(a-b)} \log \frac{(a-x)}{(b-x)}$ versus t should be a straight line with a slope equal to k and intercept equal to $\frac{2.303}{(a-b)} \log \frac{a}{b}$.

However, if a curve is obtained, the reaction is not second order.



2. Differential Method :-

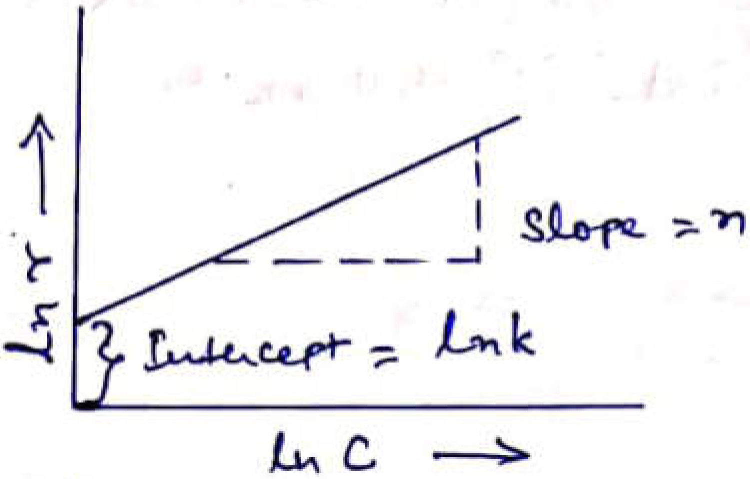
This method was suggested by van't Hoff, therefore, it is also called van't Hoff differential method. According to this method, the rate of a reaction of the n^{th} order is proportional to the n^{th} power of concentration

$$\text{Rate}, \ r = -\frac{dC}{dt} = kC^n$$

(a.) If we take logs of it, we get

$$\underset{\underset{y}{\uparrow}}{\ln r} = \underset{\underset{c}{\uparrow}}{\ln k} + \underset{\underset{mx}{\uparrow}}{n \ln C} \quad \left(\text{compare it with } Y = mx + c\right)$$

If we plot $\ln r$ versus $\ln C$, it gives a straight line with the slope equal to n and intercept equal to $\ln k$.



(b) If two experiments are performed with different initial concentrations, we can write

$$r_1 = kC_1^n \quad \text{and} \quad r_2 = kC_2^n$$

Now $$\frac{r_1}{r_2} = \frac{kC_1^n}{kC_2^n} = \left(\frac{C_1}{C_2}\right)^n$$

Taking logs, we have

$$\ln \frac{r_1}{r_2} = n \ln \frac{C_1}{C_2}$$

$$\text{or,} \quad n = \frac{\ln (r_1/r_2)}{\ln (C_1/C_2)} \quad \text{— (i)}$$

$$\text{or} \quad n = \frac{\ln r_1 - \ln r_2}{\ln C_1 - \ln C_2} \quad \text{— (ii)}$$

$$\text{or,} \quad n = \frac{\ln \left(-\frac{dC_1}{dt}\right) - \ln \left(-\frac{dC_2}{dt}\right)}{\ln C_1 - \ln C_2} \quad \text{— (iii)}$$

To find n in above expressions, we plot concentrations against time for the two experiments which will be a straight line. The slope measured will give $-\frac{dC}{dt}$ for each. By using the values of slopes $(-dC_1/dt)$ and $\left(-\frac{dC_2}{dt}\right)$ in above expression, n can be calculated.

3. Half-life Method :—

By definition and by evaluating a general expression of half-life of an n^{th} order reaction, we get

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

i.e. For a $nA \longrightarrow$ Products type of reaction, the half-life is inversely propoortional to the (n-1)th power of the initial concentration of reactants, provided that all reactants are present in same initial molar concentrations. Thus

$$t_{1/2} = \frac{1}{k} \cdot \frac{1}{a^{n-1}}$$

where k is the rate constant and depends on the order of reaction.

If two experiments are carried out at different initial molar concentrations, then

$$(t_{1/2})_1 = \frac{1}{k}\left(\frac{1}{a_1^{n-1}}\right) \quad \text{and}$$

$$(t_{1/2})_2 = \frac{1}{k}\left(\frac{1}{a_2^{n-1}}\right)$$

Now, $$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{a_2^{n-1}}{a_1^{n-1}} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

After taking logs we get

$$\ln\left(\frac{(t_{1/2})_1}{(t_{1/2})_2}\right) = (n-1)\ln\frac{a_2}{a_1}$$

or, $$n = 1 + \frac{\ln\left\{(t_{1/2})_1/(t_{1/2})_2\right\}}{\ln(a_2/a_1)}$$

or, $$n = 1 + \frac{\ln(t_{1/2})_1 - \ln(t_{1/2})_2}{\ln a_2 - \ln a_1}$$

Thus, the determination of half-lives of a reaction at two different initial molar concentrations leads to the determination of the order of a reaction (n).

4. Ostwald's Isolation Method :-

This method is used mostly in those cases where more than one reactant is present. In this method the kinetics of a reaction are studied in successive experiments by keeping the concentrations of all but one reactant in large excess so that the result gives the order with respect to the reactant whose concentration is changing significantly.

Suppose the reactant under consideration is $A + B + C \longrightarrow$ Products

The order of the reaction with respect to A, B and C is determined. For the determination of the order of reaction with respect to A, amounts of B and C are taken in a large excess so that their concentrations are not affected during the course of reaction. The order of the reaction is then determined by using any of the methods described earlier. Likewise, the order of the reaction with respect to B and C is determined. If

n_A, n_B and n_C are the orders of the reaction with respect to A, B and C resp; the order of the reaction (overall) n is given by the expression.

$$n = n_A + n_B + n_C$$

For example, the synthesis of HI from H_2 and I_2 is pseudo first order with respect to H_2 in presence of large excess of I_2 and also pseudo first order with respect to I_2 in the presence of large excess of H_2. Hence, overall it is a second order reaction.

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