

B.Sc. Part II (Subsidiary)

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Paper : Physical Chemistry

Topic : Chemical Kinetics

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In case of Second Order :

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

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

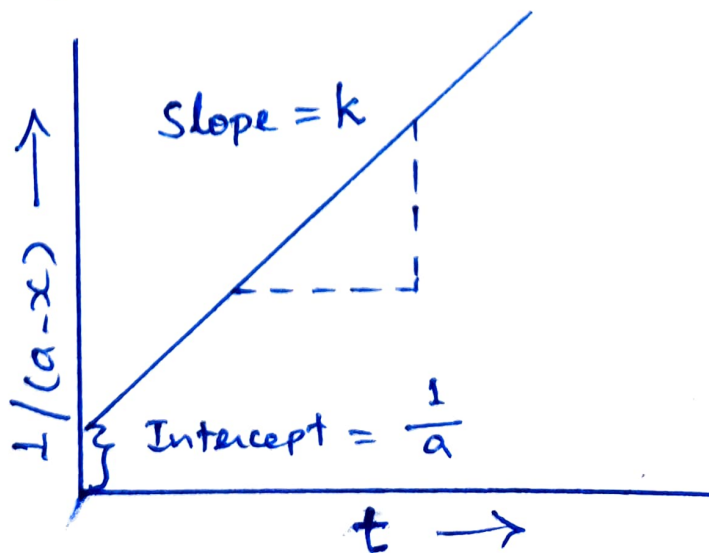
$$\text{or, } kt = \frac{1}{(a-x)} - \frac{1}{a}$$

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

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 $A + B \rightarrow \text{Products}$, the rate equation is given by

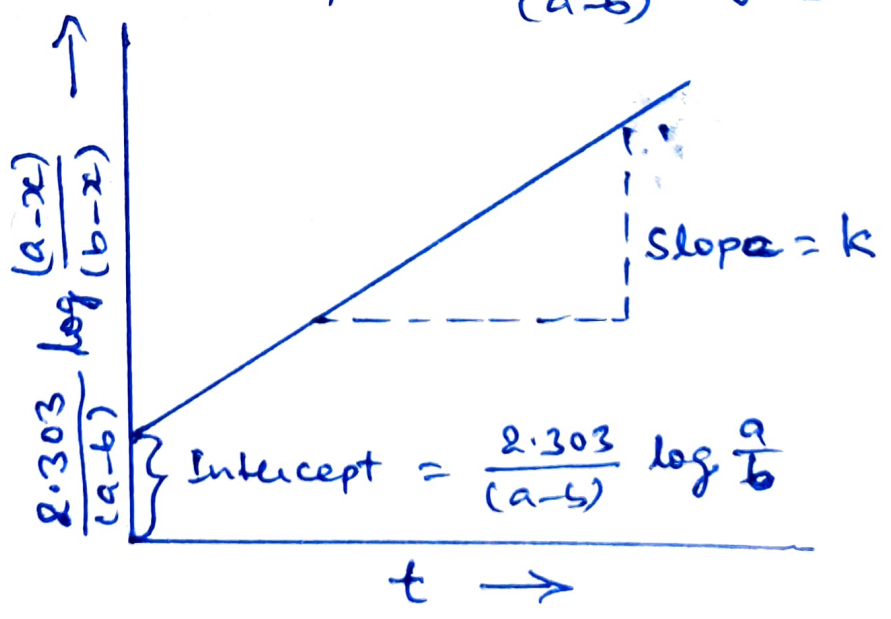
$$k = \frac{2.303}{t(a-b)} \cdot \log \frac{b(a-x)}{a(b-x)}$$

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

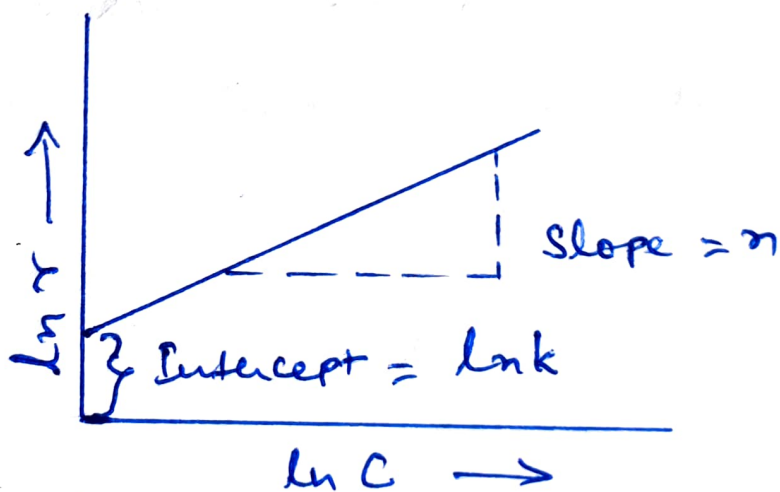
$$\text{Rate, } r = -\frac{dC}{dt} = k C^n$$

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

$$\ln r = \ln k + n \ln C$$

\uparrow \uparrow \uparrow (compare it- with)
 y C mx $y = mx + c$

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

$$r_1 = k C_1^n \quad \text{and} \quad r_2 = k C_2^n$$

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

Taking logs, we have

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

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

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

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

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 $(-dC_2/dt)$ 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 $nA \rightarrow \text{Products}$ type of reaction, the half-life is inversely propo-

proportional 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

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

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

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

After taking logs we get-

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

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

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

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



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.
