Methods for determining order of the reaction

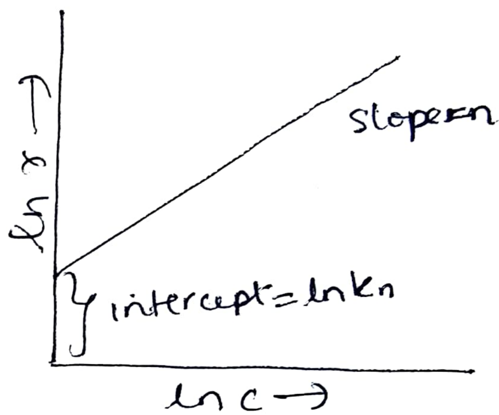
(1) The Use of Differential Rate Expression :

According to this method, which was devised by Vant Hoff, the rate of nth-order reaction is given by

$$r = k_n c^n \quad \text{—— (1)}$$

On taking the logs of this equation we get

$$\ln r = \ln k_n + n \ln c \quad \text{—— (2)}$$



Plot of ln r vs ln c for an n-th order reaction.

For a double logarithmic plot, of rate versus concentration gives a straight line, then slope gives the value of 'n' that is order of the reaction and intercept gives the value of k_n i.e. rate constant of the reaction.

For two different rates r_1 and r_2 at two concentration c_1 and c_2 then

$$\frac{r_1}{r_2} = \frac{-dc_1/dt}{-dc_2/dt} = \frac{k_n c_1^n}{k_n c_2^n} = \left(\frac{c_1}{c_2}\right)^n$$

or taking logs,

$$\ln \frac{r_1}{r_2} = n \ln \left(\frac{c_1}{c_2}\right) \quad \text{where } n = \frac{\ln (r_1/r_2)}{\ln (c_1/c_2)}$$

② The use of integrated rate law:-

The method can be used either analytically or graphically.
In analytical method, we assume a certain order for the reaction and calculate the rate constant from the given data.
The constancy of k-values obtained suggest that the assumed order is correct.
If the k-values obtained are not constant we assumed a different order for the reaction and again calculate k-values using the new rate expression to ~~ets~~ check if its constant.

In graphical method, if the plot of ln c vs t is a straight line, the reaction is first order.

Similarly for integrated rate law for the second order reaction can be utilized ~~using~~ graphically to ascertain if the reaction is second order or not.

3. The Half - life method:-

Assuming all the reactants to be present in equimolar concentrations, the half life on nth order of reaction can be given by equation,

$$t_{1/2} \propto \frac{1}{a_0^{n-1}} \quad \text{---} \ (1)$$

For two initial molar concentrations,

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

Taking ln for both the sides

$$\ln \frac{(t_{1/2})_1}{(t_{1/2})_2} = (n-1) \ln \left(\frac{a_2}{a_1}\right) \ \text{---} \ (3)$$

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

The method was suggested by Ostwald. The determination of half - lives of a reaction at two different initial concentration leads to the determination of n.

4. Isolation method:-

In this method kinetics of reactions are studied by keeping concentration of all but except one reactant in large excess so the result gives order with respect to reactant whose concentration is constantly changing.

For example,

In, $H_2 + I_2 \rightleftharpoons 2HI$

the reaction is pseudo-first order with respect to ~~HI~~ H_2 in presence of large excess of I_2

And also the reaction is pseudo first order when H_2 is in excess.

Hence the reaction was found to be second order reaction.

* Soon the Youtube lectures with respect to the topics will be uploaded, You can suggest your idea and suggestion in this regard on ankitaojha26@gmail.com.

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