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Deg-I (H) - Chemical - Kinetics
Topics - Methods for the Determination of order of Reaction.

Methods for the determination of order of Reaction.

There are various method for the determination of order of Reaction.

① Methods of Integration (Hit & Trial Method)

The most simple method is one in which the value of a, x & t are determined & substituted in the kinetic equation of various order. The rate-equation which gives the most constant value for the specific rate-constant (K) for a series of time intervals they decide their order of Reaction.

Rate-expression for

First-order, $K = \frac{2.303}{t} \log \frac{a}{(a-x)}$

Second-order, $K = \frac{1}{t}\left[\frac{1}{a-x} - \frac{1}{a}\right]$

Third-order, $K = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$

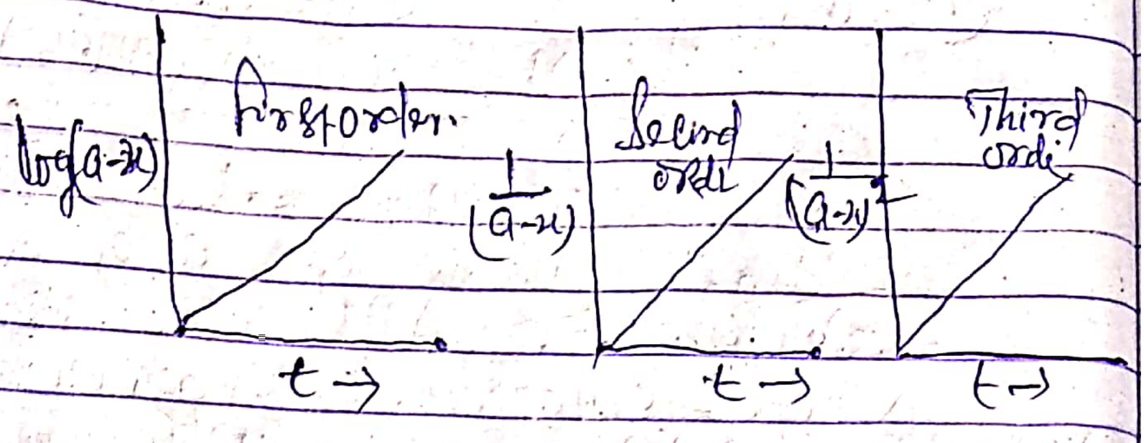
② Graphical-Method :-

By plotting graph for various order of Rkn rate expression.

(a) If the plot of $\log(a-x)$ Vs 't' is a straight-line, decided first-order

(b) If the plot of $\frac{1}{(a-x)}$ Vs 't' is straight line decided second order

(c) If plot of $\frac{1}{(a-x)^2}$ Vs 't' is straight line for third order



③ Half-life-Method :-

A general-expression for the half-life period ($t_{1/2}$) of a chemical-reaction is given by

$$t_{1/2} \propto \frac{1}{a_0^{n-1}}$$

a = Initial-Concn, n = order of Reaction

At two different initial concentration a_1 & a_2 for the same reaction, $t_{1/2}$ are $(t_{1/2})_1$ & $(t_{1/2})_2$ respectively are determined

$$(t_{1/2})_1 \propto \frac{1}{a_1^{n-1}} \quad \text{--- (1)}$$

$$(t_{1/2})_2 \propto \frac{1}{a_2^{n-1}} \quad \text{--- (2)}$$

Dividing eqn (I) by eqn (2)

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

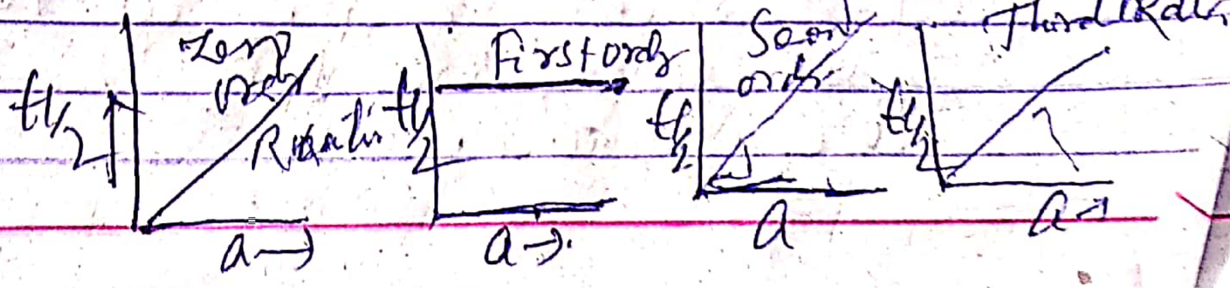
Taking log both side

$$\log(t_{1/2})_1 - \log(t_{1/2})_2 = (n-1)\left[\log a_2 - \log a_1\right]$$

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

$$\therefore n = 1 + \frac{\log(t_{1/2})_1 - \log(t_{1/2})_2}{\log a_2 - \log a_1}$$

Plot of $t_{1/2}$ vs a^{1-n}



(4) Vant Hoff Differential Rate Equation :-

In this method rate at different two different Concentration are determine at different instant of Time.

We know that

$$rate\ (r) \propto [Concn]^n$$

$$\frac{dx}{dt} \propto C^n \qquad n = \text{order of Reaction}$$

At two different Condition,

$$r_1 = K C_1^n$$

$$r_2 = K C_2^n$$

Thus, $$\frac{r_1}{r_2} = \left(\frac{C_1}{C_2}\right)^n$$

Taking log both side

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

Now $$\log r_1 - \log r_2 = n[\log C_1 - \log C_2]$$

$$\therefore\ n = \frac{\log r_1 - \log r_2}{\log C_1 - \log C_2}$$

By knowing r_1 & r_2 at two different Concentration C_1 & C_2, n can be Calculated.

(5) Ostwald's Isolation Method:-

This method is applicable for those reaction in which two or more reactants are involved. In this method the order of reaction does not depend upon the concentration of those reactant which are taken in large quantity.

Turn by turn, all reactant except one are taken to be in excess. The order of those reactant which are in very small quantity are calculated. One by one we determine over all order of reaction by sum of the order.

Considering a general type of Rxn.

$$aA + bB + cC \longrightarrow \text{Product}$$

including three reactant A, B & C whose coefficient is a, b & c respectively.

$\text{Rate} \propto [A]^x \rightarrow$ B & C are in excess

$\text{Rate} \propto [B]^y \rightarrow$ A & C are in excess

$\text{Rate} \propto [C]^z \rightarrow$ A & B are in exces.

Thus the over-all order of Reaction will be $x+y+z$.