## Methods for Determination of Order of a reaction.

## (1) Substitution method in integrated rate equation (Hit and Trial method)

- (i) The method can be used with various sets of a, x and t with integrated rate equations.
- (ii) The value of k is determined and checked for all sets of a, x and t.
- (iii) If the value of k is constant, the used equation gives the order of reaction.
  - (iv) If all the reactants are at the same molar concentration, the kinetic equations are:

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$
 (For first order reactions)  

$$k = \frac{1}{t} \left[ \frac{1}{a} - \frac{1}{a-x} \right]$$
 (For second order reactions)  

$$k = \frac{1}{2t} \left[ \frac{1}{(a-x)^2} - \frac{1}{a^2} \right]$$
 (For third order reactions)

(2) **Half-lifemethod:** This method is employed only when the rate law involved only one concentration term.

 $t_{1/2} \propto a^{1-n}$ ;  $t_{1/2} = ka^{1-n}$ ;  $\log t_{1/2} = \log k + (1-n)\log a$ , a plotted graph of  $\log t_{1/2}$  vs log a gives a straight line with slope (1-n), determining the slope we can find the order n. If half-life at different concentration is given then.

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

$$\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2 = (n-1) [\log_{10} a_2 - \log_{10} a_1]$$

 $n = 1 + \frac{\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2}{(\log_{10} a_2 - \log_{10} a_1)}$ ; This relation can be used to determine order of

reaction 'n'



## Plots of half-lives Vs concentrations ( $t_{1/2} \propto a^{1-n}$ )

(3) Graphical method: A graphical method based on the respective rate laws, can also be used.

(i) If the plot of log(a - x) Vs t is a straight line, the reaction follows first order.

- (ii) If the plot of  $\frac{1}{(a-x)}$  Vs *t* is a straight line, the reaction follows second order.
- (iii) If the plot of  $\frac{1}{(a-x)^2}$  Vs *t* is a straight line, the reaction follows third order.
- (iv) In general, for a reaction of nth order, a graph of  $\frac{1}{(a-x)^{n-1}}$  Vs *t* must be a straight line.

Graphical determination of order of the reaction

Order	Equation	Straight line plot		Slope	Intercept
		Y- axis	X-axis		on Y-axis
Zero	$x = k_0 t$	x	t	k <sub>0</sub>	0
First	$\log_{10}(a-x) = \frac{-k_1 t}{2.303} + \log_{10} a$	$\log_{10}(a-x)$	t	$\frac{-k}{2.303}$	$\log_{10} a$
Second	$(a-x)^{-1} = k_2 t + a^{-1}$	$(a-x)^{-1}$	t	<i>k</i> <sub>2</sub>	$a^{-1}$
n <sup>th</sup>	$(a-x)^{1-n} = (n-1)k_n t + a^{1-n}$	$(a-x)^{1-n}$	t	$(n-1)k_n$	$a^{1-n}$

Plots from integrated rate equations



Plots of rate Vs concentrations [Rate =  $k (conc.)^n$ ]



(4) **Van't Haff differential Method:** The rate of reaction varies as the n<sup>th</sup> power of the concentration where '*n*' is the order of the reaction. Thus for two different initial concentrations  $C_1$  and  $C_2$  equation, can be written in the form,  $\frac{-dC_1}{dt} = kC_1^n$  and  $\frac{-dC_2}{dt} = kC_2^n$ Taking logarithms,  $\log_{10}\left(\frac{-dC_1}{dt}\right) = \log_{10}k + n\log_{10}C_1$  .....(i)

and 
$$\log_{10}\left(\frac{-dC_2}{dt}\right) = \log_{10} k + n \log_{10} C_2$$
 .....(ii)

Subtracting equation (ii) from (i),

$$n = \frac{\log_{10}\left(\frac{-dC_1}{dt}\right) - \log_{10}\left(\frac{-dC_2}{dt}\right)}{\log_{10} C_1 - \log_{10} C_2} \qquad \dots \dots (iii)$$

 $\frac{-dC_1}{dt}$  and  $\frac{-dC_2}{dt}$  are determined from concentration Vs time graphs and the value of 'n' can be determined.

(5) **Ostwald's isolation method** (Initial rate method): This method can be used irrespective of the number of reactants involved e.g., consider the reaction,  $n_1A + n_2B + n_3C \rightarrow$  Products.

This method consists in finding the initial rate of the reaction taking known concentrations of the different reactants (A, B, C). Now the concentration of one of the reactants is changed (say that of A) taking the concentrations of other reactants (B and C) same as before. The initial rate of the reaction is determined again. This gives the rate expression with respect to A and hence the order with respect to A. The experiment is repeated by changing the concentrations of B and taking the same concentrations of A and C and finally changing the concentration of C and taking the same concentration of A and B. These will give rate expressions with respect to B and

C and hence the orders with respect to B and C respectively. Combining the different rate expressions, the overall rate expression and hence the overall order can be obtained.

Suppose it is observed as follows:

(i) Keeping the concentrations of B and C constant, if concentration of A is doubled, the rate of reaction becomes four times. This means that, Rate  $\propto [A]^2$  i.e., order with respect to A is 2

(ii) Keeping the concentrations of A and C constant, if concentration of B is doubled, the rate of reaction is also doubled. This means that,  $Rate \propto [B]$  i.e., order with respect to B is 1

(iii) Keeping the concentrations of A and B constant, if concentration of C is doubled, the rate of reaction remains unaffected. This means that rate is independent of the concentration of C i.e., order with respect to C is zero. Hence the overall rate law expression will be, Rate =  $k[A]^2$  [B] [C]<sup>0</sup>

 $\therefore$  Overall order of reaction = 2 + 1 + 0 = 3.