## 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:

$$
\begin{array}{ll}
k=\frac{2.303}{t} \log _{10} \frac{a}{(a-x)} & \text { (For first order reactions) } \\
k=\frac{1}{t}\left[\frac{1}{a}-\frac{1}{a-x}\right] & \text { (For second order reactions) } \\
k=\frac{1}{2 t}\left[\frac{1}{(a-x)^{2}}-\frac{1}{a^{2}}\right] & \text { (For third order reactions) }
\end{array}
$$

(2) Half-lifemethod: This method is employed only when the rate law involved only one concentration term.
$t_{1 / 2} \propto a^{1-n} ; t_{1 / 2}=k a^{1-n} ; \quad \log t_{1 / 2}=\log k+(1-n) \log a$, 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.

$$
\begin{aligned}
& \left(t_{1 / 2}\right)_{1} \propto \frac{1}{a_{1}^{n-1}} ;\left(t_{1 / 2}\right)_{2} \propto \frac{1}{a_{2}^{n-1}} ; \frac{\left(t_{1 / 2}\right)_{1}}{\left(t_{1 / 2}\right)_{2}}=\left(\frac{a_{2}}{a_{1}}\right)^{n-1} \\
& \log _{10}\left(t_{1 / 2}\right)_{1}-\log _{10}\left(t_{1 / 2}\right)_{2}=(n-1)\left[\log _{10} a_{2}-\log _{10} a_{1}\right]
\end{aligned}
$$

$$
n=1+\frac{\log _{10}\left(t_{1 / 2}\right)_{1}-\log _{10}\left(t_{1 / 2}\right)_{2}}{\left(\log _{10} a_{2}-\log _{10} a_{1}\right)} ; \text { This relation can be used to determine order of }
$$

reaction ' n '
Plots of half-lives Vs concentrations $\left(\mathbf{t}_{1 / 2} \propto \mathbf{a}^{1-\mathrm{n}}\right)$

(3) Graphical method:A graphical method based on the respective rate laws, can also be used.
(i) If the plot of $\log (a-x) \vee s t$ is a straight line, the reaction follows first order.
(ii) If the plot of $\frac{1}{(a-x)} \vee \mathrm{s} t$ is a straight line, the reaction follows second order.
(iii) If the plot of $\frac{1}{(a-x)^{2}} \mathrm{Vs} t$ is a straight line, the reaction follows third order.
(iv) In general, for a reaction of nth order, a graph of $\frac{1}{(a-x)^{n-1}} \mathrm{~V} t$ must be a straight line.

Graphical determination of order of the reaction

| Order | Equation | Straight line plot |  | Slope | Intercept <br> on Y-axis |
| :--- | :--- | :--- | :--- | :--- | :--- |
|  | $x=k_{0} t$ | $\mathbf{Y - a x i s}$ | $\mathbf{X}$-axis |  | $k_{0}$ |
| First | $\log _{10}(a-x)=\frac{-k_{1} t}{2.303}+\log _{10} a$ | $x$ | $t$ | 0 |  |
| Second | $(a-x)^{-1}=k_{2} t+a^{-1}$ | $\log _{10}(a-x)$ | $t$ | $\frac{-k}{2.303}$ | $\log _{10} a$ |
| $n^{\text {th }}$ | $(a-x)^{1-n}=(n-1) k_{n} t+a^{1-n}$ | $(a-x)^{-1}$ | $t$ | $k_{2}$ | $a^{-1}$ |
|  | $(a-x)^{1-n}$ | $t$ | $(n-1) k_{n}$ | $a^{1-n}$ |  |

Plots from integrated rate equations


Plots of rate Vs concentrations [Rate $=k(\text { conc. })^{\mathrm{n}}$ ]

(4) Van't Haff differential Method:The rate of reaction varies as the $\mathrm{n}^{\text {th }}$ 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, $\frac{-d C_{1}}{d t}=k C_{1}^{n}$ and $\frac{-d C_{2}}{d t}=k C_{2}^{n}$ Taking logarithms, $\log _{10}\left(\frac{-d C_{1}}{d t}\right)=\log _{10} k+n \log _{10} C_{1}$
and $\log _{10}\left(\frac{-d C_{2}}{d t}\right)=\log _{10} k+n \log _{10} C_{2}$
Subtracting equation (ii) from (i),

$$
\begin{equation*}
n=\frac{\log _{10}\left(\frac{-d C_{1}}{d t}\right)-\log _{10}\left(\frac{-d C_{2}}{d t}\right)}{\log _{10} C_{1}-\log _{10} C_{2}} \tag{iii}
\end{equation*}
$$

$\frac{-d C_{1}}{d t}$ and $\frac{-d C_{2}}{d t}$ are determined from concentration $V$ s 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, $n_{1} A+n_{2} B+n_{3} C \rightarrow$ Products .

This method consists in finding the initial rate of the reaction taking known concentrations of the different reactants ( $\mathrm{A}, \mathrm{B}, \mathrm{C}$ ). 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 $=k[A]^{2}[B][C]^{0}$
$\therefore$ Overall order of reaction $=2+1+0=3$.

