## CHEMICAL KINETICS

## 1. Rate of Reaction :

The rate of a reaction means the speed with which the reaction takes place. This is expressed either in terms of decrease in the concentration of a reactant per unit time or increase in the concentration of a product per unit time. Hence the rate of a reaction may be defined as follows:
The rate of reaction is the change in the concentration of any one of the reactants or products per unit time i.e.,

$$
\begin{aligned}
\text { Rate of reaction }= & \frac{\text { Decrease in the concentration of a reactant }}{\text { Time interval }} \\
\text { or } & =\frac{\text { Increase in the concentration of a product }}{\text { Time interval }}
\end{aligned}
$$

For example, consider the reaction,

$$
\mathrm{PCl}_{5} \longrightarrow \mathrm{PCl}_{3}+\mathrm{Cl}_{2}
$$

Suppose in a time interval $\Delta \mathrm{t}$, decrease in concentration of $\mathrm{PCl}_{5}$ is $\Delta\left[\mathrm{PCl}_{5}\right]$ and increase in the concentration of $\mathrm{PCl}_{3}$ and $\mathrm{Cl}_{2}$ are $\Delta\left[\mathrm{PCl}_{3}\right]$ and $\Delta\left[\mathrm{Cl}_{2}\right]$ respectively, where square brackets indicate molar concentrations (moles/litre) of the substances involved. Then we have,
Rate of reaction $=-\frac{\Delta\left[\mathrm{PCl}_{5}\right]}{\Delta \mathrm{t}}=+\frac{\Delta\left[\mathrm{PCl}_{3}\right]}{\Delta \mathrm{t}}=+\frac{\Delta\left[\mathrm{Cl}_{2}\right]}{\Delta \mathrm{t}}$
It may be emphasized that the rate of reaction is always positive. The minus sign alongwith the first term is used simply to show that the concentration of the reactant $\left(\mathrm{PCl}_{5}\right)$ is decreasing while plus sign along with the other two terms is used to show that the concentration of the products $\left(\mathrm{PCl}_{3}\right)$ and $\left(\mathrm{Cl}_{2}\right)$ is increasing.
In general, for any reaction of the type

$$
\begin{aligned}
& \mathrm{A}+\mathrm{B} \longrightarrow \mathrm{C}+\mathrm{D} \\
& \text { Rate of reaction }=-\frac{\Delta[\mathrm{A}]}{\Delta \mathrm{t}}=-\frac{\Delta[\mathrm{B}]}{\Delta \mathrm{t}}=+\frac{\Delta[\mathrm{C}]}{\Delta \mathrm{t}}=+\frac{\Delta[\mathrm{D}]}{\Delta \mathrm{t}}
\end{aligned}
$$

## Units of the Rate of Reaction :

Since concentration is usually expressed in moles/litre and the time is taken in seconds or minutes, the unit of the rate of reaction is moles litre ${ }^{-1} \sec ^{-1}\left(\mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}\right)$ or moles litre $\mathrm{min}^{-1}$ ( $\mathrm{mol} \mathrm{L}^{-1} \mathrm{~min}^{-1}$ ).
In case of gaseous reactions, pressures are used in place of molar concentrations. As pressures are expressed in atmospheres, therefore the units of the rate of reaction are atm $\mathrm{min}^{-1}$ or atm s ${ }^{-1}$ etc. The relationship between partial pressure of a gas in a reaction mixture and its molar concentration follows from the relationship $P V=n R T$ i.e. $\frac{n}{V}=\frac{P}{R T}$

Where partial pressure, $\mathrm{P}=\frac{\text { No. of moles of the gas }}{\text { Total no. of moles }} \times$ Total pressure

## Average Rate and Instantaneous Rate of Reaction :

A difficulty arises in stating the rate of reaction as above. This is because according to the Law of Mass Action, the rate of reaction depends upon the molar concentrations of reactants which keep on decreasing with the passage of time (while those of the products keep on increasing). Therefore, the rate of reaction does not remain constant throughout. Thus the rate of reaction as defined above is the 'average rate of reaction' during the time interval chosen.
To know the rate of reaction at any instant of time during the course of a reaction, we introduce the term 'instantaneous rate of reaction' which may be defined as follows :
The rate of reaction at any instant of time is the rate of change of concentration (i.e. change of concentration per unit time) of any one of the reactants or products at that particular instant of time.
To express the instantaneous rate of reaction, as small interval of time (dt) is chosen at that particular instant of time during which the rate of reaction is supposed to be almost constant. Suppose the small change in concentration is dx in the small interval of time dt . Then the rate of reaction at that instant is given by $\frac{\mathrm{dx}}{\mathrm{dt}}$.

## Measurement of the Rate of Reaction :

In order to measure the rate of a reaction, the progress of the reaction is followed by studying the concentration of one of the reactants or products at different intervals of time. the most common practice to do so is to withdraw small amount of the reaction mixture ( $2 \mathrm{~cm}^{3}$ or $5 \mathrm{~cm}^{3}$ ) at different intervals of time, cool it down immediately to nearly $0^{\circ} \mathrm{C}$ to arrest the reaction (called freezing the reaction) and then find out the concentration of the reactant or the product by suitable method usually by titration against a suitable reagent. However, this method is not preferred when some observable property like volume, pressure, optical rotation etc. changes with time and can be observed directly at different intervals of time without stopping the reaction. it is important to mention that except concentration, all other factors (like temperature etc.) which affect the rate of the reaction are kept constant during the kinetic study of the reaction.


If concentration of one of the reactants is studied at different intervals of time and these values are plotted against the corresponding times, a graph of the type shown in figure is obtained.

## Calculation of instantaneous rate of reaction :

To know the rate of the reaction at any time $t$, a tangent is drawn to the curve at the point corresponding to that time figure and it is extended on either side so as to cut the axes, say at the points A and B. then

$$
\begin{aligned}
\text { Rate of reaction } & =\frac{\text { Change in the concentration }}{\text { Time }} \\
& =\frac{\Delta \mathrm{x}}{\Delta \mathrm{t}}=\frac{\mathrm{OA}}{\mathrm{OB}} \text { Slope of the tangent }
\end{aligned}
$$

Thus the slope of the tangent gives the rate of reaction.
For example, from the (figure) in the present case, at time $t=10$ minutes, $\Delta x=0.04$ mole and $\Delta \mathrm{t}=20$ minutes $=20 \times 60=1200$ seconds, therefore, rate of reaction at the end of 10 minutes will be $0.04 / 1200=3.33 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}$.

## Calculation of the average rate of reaction :

To calculate the average rate of reaction between any two instants of time say $t_{1}$ and $t_{2}$, the corresponding concentrations $\mathrm{x}_{1}$ and $\mathrm{x}_{2}$ are noted from the graph. Then

$$
\text { Average rate of reaction }=\frac{x_{2}-x_{1}}{t_{2}-t_{1}}
$$

For example, from the (figure) between the time interval 5 to 15 minutes,

$$
\text { Average rate }=\frac{0.03-0.012}{15-5}=\frac{0.018}{10}=0.0018 \text { and } \mathrm{mol} \mathrm{~L}^{-1} \mathrm{~min}^{-1}
$$

If concentration of one of the products is plotted against time, the type of curve obtained and the rate of reaction at any instant of time are calculated as shown in the figure.


## Example 1:

In a reaction the concentration of a reactant (A) changes from 0.200 mol litre ${ }^{-1}$ to 0.150 mol litre ${ }^{-1}$ in 10 minutes. What is the average rate of reaction during this interval? Solution :

$$
\begin{aligned}
\Delta[\mathrm{A}] & =[\mathrm{A}]_{\text {final }}-[\mathrm{A}]_{\text {initial }} \\
& =[0.150-0.200] \\
& =-0.050 \mathrm{~mol} \text { litre }^{-1} \\
\Delta \mathrm{t} & =10 \text { minutes }
\end{aligned}
$$

Average rate of reaction $=\frac{-\Delta[\mathrm{A}]}{\Delta \mathrm{t}}=\frac{0.50}{10}=0.005 \mathrm{~mol} \mathrm{litr}{ }^{-1} \mathrm{~min}^{-1}$

## Example 2:

Decomposition of $\mathrm{N}_{2} \mathrm{O}_{5}$ is expressed by the equation,

$$
\mathbf{N}_{2} \mathrm{O}_{5} \longrightarrow 2 \mathrm{NO}_{2}+1 / 2 \mathrm{O}_{2}
$$

If in a certaion time interval, rate of decomposition of $\mathrm{N}_{2} \mathrm{O}_{5}$ is $1.8 \times 10^{-3} \mathrm{~mol}$ litre ${ }^{-1}$ min $^{-1}$, what will be the rates of formation of $\mathrm{NO}_{2}$ and $\mathrm{O}_{2}$ during the same interval?

## Solution :

The rate expression for the decomposition of $\mathrm{N}_{2} \mathrm{O}_{5}$ is

$$
-\frac{\Delta\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]}{\Delta \mathrm{t}}=\frac{1}{2} \frac{\Delta\left[\mathrm{NO}_{2}\right]}{\Delta \mathrm{t}}=2 \times \frac{\Delta\left[\mathrm{O}_{2}\right]}{\Delta \mathrm{t}}
$$

So $\quad \frac{\Delta\left[\mathrm{NO}_{2}\right]}{\Delta \mathrm{t}}=2 \frac{\Delta\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right]}{\Delta \mathrm{t}}=2 \times 1.8 \times 10^{-3}$

$$
=3.6 \times 10^{-3} \mathrm{~mol} \mathrm{litre}^{-1} \mathrm{~min}^{-1}
$$

and

$$
\begin{aligned}
\frac{\Delta\left[\mathrm{O}_{2}\right]}{\Delta \mathrm{t}} & =\frac{1}{2} \frac{\Delta\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right]}{\Delta \mathrm{t}}=\frac{1}{2} \times 1.8 \times 10^{-3} \\
& =0.9 \times 10^{-3} \mathrm{~mol} \mathrm{litre}{ }^{-1} \mathrm{~min}^{-1}
\end{aligned}
$$

[Rate is always positive and hence $=\frac{\Delta\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]}{\Delta \mathrm{t}}$ is taken positive.

## Example 3:

If the decomposition of nitrogen ( $V$ ) oxide $2 \mathrm{~N}_{2} \mathrm{O}_{5} \longrightarrow 4 \mathrm{NO}_{2}+\mathrm{O}_{2}$, following a first order kinetics.
(i) Calculate the rate constant for a 0.04 M solution, if the instantaneous rate is $1.4 \times 10^{-6} \mathrm{~mol} \mathrm{~L} \mathrm{~s}{ }^{-1}$.
(ii) Also calculate the rate of reaction when the concentration of $\mathrm{N}_{2} \mathrm{O}_{5}$ is 1.20 M .
(iii) What concentration of $\mathrm{N}_{2} \mathrm{O}_{5}$ would give a rate of $2.45 \times 10^{5} \mathrm{~mol} \mathrm{~L}{ }^{-1} \mathrm{~s}^{-1}$ ?

## Solution :

(i) As the given reaction is of first order, therefore,

$$
\text { Rate }=\mathrm{k}\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right]
$$

$$
\begin{aligned}
\text { or } \quad & \mathrm{k}=\frac{\text { rate }}{\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]}=\frac{1.4 \times 10^{-6}}{0.04} \quad[\mathrm{M}=\text { conc. in mol L} \\
& \left.=3.5 \times 10^{-5}\right]
\end{aligned}
$$

(ii) Now if the concentration of $\mathrm{N}_{2} \mathrm{O}_{5}$ is 1.20 M , then

$$
\text { rate }=\mathrm{k}\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right]
$$

$$
=3.5 \times 10^{-5} \times 1.20=4.2 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}
$$

(iii) To obtain concentration of $\mathrm{N}_{2} \mathrm{O}_{5}$ when the rate is $2.45 \times 10^{-5} \mathrm{~mol}^{-1} \mathrm{~s}^{-1}$, we note that

$$
\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]=\frac{\text { Rate }}{\mathrm{k}}=\frac{2.45 \times 10^{-5}}{3.5 \times 10^{-5}}=0.7 \mathrm{~mol} \mathrm{~L}^{-1} \text { or } 0.7 \mathrm{M}
$$

## Factors Affecting the Reaction Rate :

The rate of any particular reaction depends upon the following factors:
(i) Concentration of the reactants: Greater the concentrations of the reactants, faster is the reaction. Conversely, as the concentrations of the reactants decrease, the rate of reactions also decreases.
(ii) Temperature: The rate of reaction increases with increase of temperature. In most of the cases, the rate of reaction becomes nearly double for 10 K rise of temperature. In some cases, reactions do not take place at room temperature but take place at higher temperature.
(iii) Presence of Catalyst : A catalyst generally increases the speed of a reaction without itself being consumed in the reaction. In case of reversible reactions, a catalyst helps to attain the equilibrium quickly without disturbing the state of equilibrium.
(iv) Surface area of the reactants : For a reaction involving a solid reactant or catalyst, the smaller is the particle size, i.e., greater is the surface area, the faster is the reaction.
(v) Presence of light : Some reactions do not take place in the dark but take place in the presence of light e.g., $\mathrm{H}_{2}+\mathrm{Cl}_{2} \longrightarrow 2 \mathrm{HCl}$. Such reactions are called "photochemical reactions". Now we shall discuss the quantitative effect of concentration and temperature on the rate of reaction. The study of quantitative effect of concentration on the rate of reaction leads to the introduction of a number of new terms such as order of reaction, specific reaction rate (rate constant) and molecularity of reaction. It also leads to the study of mechanism of the reactions. These different aspects are discussed in the following sections.

## 2. Molecularity and Order :

Single step reaction is called elementary reaction while a reaction occurring in two or more steps is called complicated or consecutive reaction. Each step of a complicated reaction is an elementary reaction.
The minimum number of molecules, atoms or ions of reactants required for an elementary reaction to occur is indicated by the sum of the stoichiometric coefficients of the reactant(s) in the chemical equation, is known molecularity of the reaction. Thus for an elementary reaction represented by the general chemical equation .

$$
\mathrm{aA}+\mathrm{bB} \longrightarrow \text { products }
$$

molecularity $=a+b$
Examples:

$$
\begin{aligned}
& \text { Reactions } \\
& \mathrm{PCl}_{5} \rightleftharpoons \text { Molecularity }{ }^{2} \mathrm{PCl}_{3}+\mathrm{Cl}_{2} \\
& \mathrm{H}_{2}+\mathrm{I}_{2} \rightleftharpoons 2 \mathrm{HI}
\end{aligned}
$$

A complicated reaction has no molecularity of its own but molecularity of each of the steps involved in its mechanism.
For example :
The reaction: $2 \mathrm{NO}+2 \mathrm{H}_{2} \rightleftharpoons \mathrm{~N}_{2}+2 \mathrm{H}_{2} \mathrm{O}$, takes place in the sequence of following three steps . I. $\mathrm{NO}+\mathrm{NO} \rightleftharpoons \mathrm{N}_{2} \mathrm{O}_{2} \quad$ (fast and reversible)

$$
\text { II. } \quad \mathrm{N}_{2} \mathrm{O}_{2}+\mathrm{H}_{2} \longrightarrow \mathrm{~N}_{2} \mathrm{O}^{2}+\mathrm{H}_{2} \mathrm{O} \text { (slow) }
$$

$$
\text { III. } \quad \mathrm{N}_{2} \mathrm{O}+\mathrm{H}_{2} \longrightarrow \mathrm{~N}_{2}+\mathrm{H}_{2} \mathrm{O}^{2} \text { (fast) }
$$

The molecularity of each step involved in mechanism is 2 i.e., each step is bimolecular. So as regards the molecularity of the reaction under consideration we simply say that the reaction has mechanism and each step involved in it is bimolecular However, there is another view also , according to which molecularity of a complicated reaction is taken to be equal to the number of molecules, atoms or ions of reactant(s) and/or intermediates coming into contact and colliding simultaneously in the slowest step i.e. the ratedetermining step (RDS) of the reaction.
For example the reaction $\mathrm{ROH}+\mathrm{HCl} \xrightarrow{\mathrm{ZnCl}_{2}} \mathrm{RCl}+\mathrm{H}_{2} \mathrm{O}$, which actually is a nucleophilic substitution reaction

I


II
 (slow)
III

$$
\begin{equation*}
\mathrm{R}^{\oplus}+: \ddot{\mathrm{C}} \dot{\mathrm{l}}:^{-} \longrightarrow \mathrm{R}-\dot{\mathrm{C}} \mathrm{l}: \tag{fast}
\end{equation*}
$$

Here the step II is the slowest step and hence the R.D.S. the molecularity of which is one. Therefore, the mechanism is called unimolecular nucleophilic substitution $\left(\mathrm{S}_{\mathrm{N}} 1\right)$ and the reaction is said to follow $\mathrm{S}_{\mathrm{N}} 1$ mechanism.
The mathematical equation showing the relation of rate of reaction with concentration of reactant(s) is called rate-law of the reaction. For example, the kinetic experiment carried on the reaction.

$$
2 \mathrm{NO}+2 \mathrm{H}_{2}(\mathrm{~g}) \longrightarrow \mathrm{N}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
$$

has shown that:
(i) rate increases 4 - fold when conc. of NO is doubled keeping the conc. of $\mathrm{H}_{2}$ constant
(ii) rate gets just doubled when conc. of $\mathrm{H}_{2}$ is doubled keeping that of NO constant, and
(iii) rate increases 8 - fold when concentrations of both NO and $\mathrm{H}_{2}$ are doubled simultaneously. These experimental rate data fit into following equation. Rate $\alpha[\mathrm{NO}]^{2}\left[\mathrm{H}_{2}\right]$
This equation is called experimentally observed "Rate law" of the reaction.
Order of reaction is defined as the sum of the powers of the concentration terms appearing in experimentally observed rate law.
Thus for the reaction (reduction of nitric oxide by hydrogen) considered above .
Order w.r.t. $\mathrm{NO}=2 \quad$ Order w.r.t. $\mathrm{H}_{2}=1$
Overall order $=2+1=3$
In general, let a reaction represented by the chemical equation:

$$
\mathrm{aA}+\mathrm{bB} \longrightarrow \text { Products }
$$

obeys the following rate law.

$$
\text { Rate } \alpha[A]^{\mathrm{m}}[\mathrm{~B}]^{\mathrm{n}} \text {, or Rate }=\mathrm{k}[\mathrm{~A}]^{\mathrm{m}}[\mathrm{~B}]^{\mathrm{n}}
$$

Where $\mathrm{k}=$ rate constant of reaction, a constant at constant temp and is actually the rate of reaction when conc. of each reactant is equal to unity $k$ is also called velocity constant or specific reaction rate.
Note that $m$ and $n$ are experimental quantities which may or may not be equal to the respective stoichiometric coefficients.
Also note that if either of $A$ or $B$ is taken in large excess as compared to another, the order w.r.t this reactant will be zero so order $=\mathbf{m}$ (when $B$ is in large excess), and order $=\mathbf{n}$ (when $A$ is large excess), i.e.,

Rate $=k^{\prime}[A]^{m}, k^{\prime}=k[B]^{n}$ another constant, when $B$ is in large excess.
Order w.r.t. $\mathrm{A}=\mathrm{m}$ Order w.r.t. $\mathrm{B}=0$
Rate $=k^{\prime \prime}[B]^{n}, k^{\prime \prime}=k[A]^{m}=$ another constant, when $A$ is in large excess.
Order w.r.t. $\mathrm{A}=0$
Order w.r.t. $\mathrm{B}=\mathrm{n}$
$k^{\prime}$ or $k^{\prime \prime}$ is actually known as pseudo rate constant
Thus, a bimolecular reaction conforms to the first - order when one of the reactants is taken in large excess and the reaction is said to be pseudo unimolecular or pseudo first order.
An example of this is the hydrolysis of ester by dil. acid i.e.

$$
\mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}+\mathrm{H}_{3} \mathrm{O}^{+} \xrightarrow{\mathrm{H}^{+}} \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}
$$

The reaction is originally of second - order obeying the kinetics.

$$
\text { Rate }=\mathrm{k}\left[\mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}\right]\left[\mathrm{H}_{2} \mathrm{O}\right]
$$

But the reaction is usually carried out taking dilute aqueous solution of ester and acid $(\mathrm{HCl})$ such that in the reaction mixture water exists in large excess as compared to ester or better to say, water has almost its maximum concentration of $55.5 \mathrm{~mole}^{-1}$. So there is no appreciable change in the concentration of water and the same remains practically constant.
$\mathrm{k}\left[\mathrm{H}_{2} \mathrm{O}\right]$ becomes another constant $\left(\mathrm{k}^{\prime}\right)$ called pseudo rate constant and reactions obeys the following 1st order kinetics

$$
\text { Rate }=\mathrm{k}^{\prime}\left[\mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}\right]
$$

Thus, the molecularity of the above reaction is 'two' but its order is 'one;.
In the light of the above concept one may define order of reaction as "the number of molecules of the reactant(s) whose concentration alters during the chemical change is the order of reaction".

## Distinction between Molecularity and Order

(i) Molecularity is a theoretical property while order is an experimental property.
(ii) Molecularity concerns to mechanism, order concerns to kinetics
(iii) Molecularity is always a whole number and never zero while order may be any number zero, fractional and integral.
(iv) Molecularity is invariant but order may vary with change in experimental condition. As for example, the isomerisation of cyclo - propane represented by the chemical equation given below is a first order reaction at high cyclo propane pressure and is a second order reaction at low cyclo propane pressure.

(v) Reactions of higher molecularity is rare since the chance of coming into contact and colliding simultaneously decreases as the number of molecules involved in collision increases.

## Unit of rate constant

$\mathrm{nA} \longrightarrow$ Product

$$
\begin{aligned}
& \frac{\mathrm{dx}}{\mathrm{dt}}=\mathrm{k}[\text { conc. }]^{\mathrm{n}} \\
& \frac{[\text { conc. }]}{\mathrm{sec}}=\mathrm{k}[\text { conc. }]^{\mathrm{n}} \\
& \mathbf{k}=[\text { conc. }]^{1-\mathrm{n}} \sec ^{-1} \\
& =[\text { mole/litre }]^{1-\mathrm{n}} \mathrm{sec}^{-1}
\end{aligned}
$$

## Example 4:

State the order w.r.t. each reactant, order of overall reaction and units of rate constant in each of the following reactions
(i) $\mathrm{H}_{2} \mathrm{O}_{2}+3 \mathrm{I}^{-}+2 \mathrm{H}^{+} \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}+\mathrm{I}_{3}^{-}(\mathrm{aq})$

Rate $=k\left[\mathrm{H}_{2} \mathrm{O}_{2}\right]\left[\mathrm{I}^{-}\right]$
(ii) $\mathrm{CO}+\mathrm{Cl}_{2} \longrightarrow \mathrm{COCl}_{2}$

Rate $=\boldsymbol{k}\left[\mathrm{CO}^{2}\left[\mathrm{Cl}_{2}\right]^{1 / 2}\right.$

## Solution :

(i) Rate $=\mathrm{k}\left[\mathrm{H}_{2} \mathrm{O}_{2}\right]\left[\mathrm{I}^{-}\right]$

Order w.r.t. $\mathrm{H}_{2} \mathrm{O}_{2}=1$; Order w.rt. $\mathrm{I}^{-}=1$
Overall order $=2$
Units of $\mathrm{k}=\left(\mathrm{mol} \mathrm{L}^{-1}\right)^{1-2} \mathrm{~s}^{-1}=\mathrm{mol}^{-1} \mathrm{Ls}^{-1}$
(ii) Rate $=\mathrm{k}[\mathrm{CO}]^{2}\left[\mathrm{Cl}_{2}\right]^{1 / 2}$

Order w.r.t. to $\mathrm{CO}=2$; Order w.r.t. $\mathrm{Cl}_{2}=1 / 2$
Overall order $=2.5$

## Example 5 :

For the reaction, $2 \mathrm{NO}+\mathrm{Cl}_{2} \longrightarrow 2 \mathrm{NOCl}$ at 300 K following data are obtained

|  | Initial Concentration |  |  |
| :---: | :---: | :---: | :---: |
|  | $[\mathrm{NO}]$ |  | $\left[\mathrm{Cl}_{2}\right]$ |
|  | Initial rat |  |  |
|  | No. | 0.010 | 0.010 |
| $1.2 \times 10^{-4}$ |  |  |  |
| 2. | 0.010 | 0.020 | $2.4 \times 10^{-4}$ |
| 3. | 0.020 | 0.020 | $9.6 \times 10^{-4}$ |

Write rate law for the reaction. What is the order of the reaction? Also calculate the specific rate constant.

## Solution :

Let the rate law for the reaction be

$$
\begin{equation*}
\text { Rate }=\mathrm{k}[\mathrm{NO}]^{\mathrm{x}}\left[\mathrm{Cl}_{2}\right]^{\mathrm{y}} \tag{i}
\end{equation*}
$$

From Expt. (1), $1.2 \times 10^{-4}=\mathrm{k}[0.010]^{\mathrm{x}}[0.010]^{\mathrm{y}}$
From Expt. (2), $\quad 2.4 \times 10^{-4}=\mathrm{k}[0.010]^{\mathrm{x}}[0.020]^{\mathrm{y}}$
Dividing Eq. (ii) by Eq. (i),

$$
\begin{aligned}
\frac{2.4 \times 10^{-4}}{1.2 \times 10^{-4}} & =\frac{[0.020]^{y}}{[0.100]^{y}} \\
2 & =2^{y} \\
y & =1
\end{aligned}
$$

From Expt. (2), $2.4 \times 10^{-4}=\mathrm{k}[0.010]^{\mathrm{x}}[0.020]^{\mathrm{y}}$
From Expt. (3), $9.6 \times 10^{-4}=\mathrm{k}[0.020]^{\mathrm{x}}[0.020]^{\mathrm{y}}$
Dividing Eq. (iii) by Eq. (ii),

$$
\begin{aligned}
\frac{9.6 \times 10^{-4}}{2.4 \times 10^{-4}} & =\frac{[0.020]^{\mathrm{x}}}{[0.100]^{\mathrm{y}}} \\
4 & =2^{\mathrm{x}} \\
x & =2
\end{aligned}
$$

Order of reaction $=x+y=2+1=3$
Rate law for the reation is, $\quad$ Rate $=\mathrm{k}[\mathrm{NO}]^{2}\left[\mathrm{Cl}_{2}\right]$
Considering Eq. (i) (again), $1.2 \times 10^{-4}=\mathrm{k}[0.010]^{2}[0.010]$

$$
\mathrm{k}=\frac{1.2 \times 10^{-4}}{[0.010]^{3}}=1.2 \times 10^{2} \mathrm{~mol}^{-2} \mathrm{litre}^{2} \mathrm{sec}^{-1}
$$

## Example 6 :

For the hypothetical reaction , $2 A+B \longrightarrow$ products
The following data are obtained :

| Expt No. | Initial conc. of (A) (mol L ${ }^{-1}$ ) | $\begin{aligned} & \text { initial conc. of (B) } \\ & \left(\text { mol } L^{-1}\right) \end{aligned}$ | initial rate (mol L L ${ }^{-1} \mathbf{s}^{-1}$ ) |
| :---: | :---: | :---: | :---: |
| 1. | 0.10 | 0.20 | $3 \times 10^{2}$ |
| 2. | 0.30 | 0.40 | $3.6 \times 10^{3}$ |
| 3. | 0.30 | 0.80 | $1.44 \times 10^{4}$ |
| 4. | 0.10 | 0.40 | ........ |
| 5. | 0.20 | 0.60 | $\ldots$ |
| 6. | 0.30 | 1.20 | ....... |

Find out how the rate of the reaction depends upon the concentration of $A$ and $B$ and fill in the blanks.

## Solution :

From Expt (2) and (3), it is clear that when concentration of A is kept constant and that of B is doubled, the rate increases four times. This show that the reaction is of second order with respect to $B$.
Similarly, from Expt. (1) and (2), it is observed that when concentration of A is increased three times and that of B two times, the rate becomes twelve times. Hence, the reaction is first order with respect to A .
Thus the rate law for the reaction is :

$$
\text { Rate }=\mathrm{k}[\mathrm{~A}][\mathrm{B}]^{2}
$$

Fill in the blanks : Substituting the values of Expt. (1) in the rate equation,

$$
3 \times 10^{2}=\mathrm{k}[0.10][0.20]^{2}
$$

or

$$
\mathrm{k}=\frac{3 \times 10^{2}}{[0.10][0.20]^{2}}=7.5 \times 10^{4} \mathrm{~L}^{2} \mathrm{~mol}^{-2} \mathrm{~s}^{-1}
$$

Expt.(4): Rate $=\mathrm{k}[0.10][0.40]^{2}$

$$
=7.5 \times 10^{4} \times 0.10 \times 0.40 \times 0.40
$$

$$
=1.2 \times 10^{3} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}
$$

$\operatorname{Expt}(5):$ Rate $=\mathrm{k}[0.20][.60]^{2}$

$$
=7.5 \times 10^{4} \times 0.20 \times 0.60 \times 0.60
$$

$$
=5.4 \times 10^{3} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}
$$

$\operatorname{Expt}(6):$ Rate $=\mathrm{k}[0.30][1.20]^{2}$

$$
\begin{aligned}
& =7.5 \times 10^{4} \times 0.30 \times 1.20 \times 1.20 \\
& =3.24 \times 10^{4} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}
\end{aligned}
$$

## 3. Rate Law and Mechanism :

As already mentioned in the reaction:

$$
2 \mathrm{NO}+2 \mathrm{H}_{2} \longrightarrow \mathrm{~N}_{2}+2 \mathrm{H}_{2} \mathrm{O}
$$

Obeys the following third order kinetics
Rate $\alpha[\mathrm{NO}]^{2}\left[\mathrm{H}_{2}\right]$
The kinetics is not in tune with chemical equation. As the law of mass action suggests each concentration term should be raised to power 2. Neither experimental facts nor those coming from Law of mass action can be unacceptable to us. Under this condition we are led to believe that the reaction does not occur according to the chemical equation as written. That is the reaction is not elementary but is complicated. In order to explain the observed rate law following mechanism has been proposed.

III

$$
\begin{aligned}
& \mathrm{N}_{2} \mathrm{O}_{2}+\mathrm{H}_{2} \longrightarrow \mathrm{~N}_{2} \mathrm{O}+\mathrm{H}_{2} \mathrm{O} \text { (slow) } \\
& \mathrm{N}_{2} \mathrm{O}+\mathrm{H}_{2} \longrightarrow \mathrm{~N}_{2}+\mathrm{H}_{2} \mathrm{O} \text { (fast) }
\end{aligned}
$$

The step II being the slowest i.e., the rate - determining step (R.D.S.). Note that the rate of formation of $\mathrm{N}_{2}$ cannot be faster than the rate of formation of $\mathrm{N}_{2} \mathrm{O}$. So, the rate of overall reaction or rate of formation of $\mathrm{N}_{2}$ will be equal to the rate of step II which according to law of mass action may be given as.

Rate of overall reaction = Rate of step II $=\mathrm{k}\left[\mathrm{N}_{2} \mathrm{O}_{2}\right]\left[\mathrm{H}_{2}\right]$
Where $\mathrm{k}=$ rate constant of step II
The conc. of the intermediate $\left(\mathrm{N}_{2} \mathrm{O}_{2}\right)$ may be evaluated by applying law of mass action upon the equilibrium existing in step I as mentioned below.

$$
\mathrm{K}_{\mathrm{c}}=\frac{\left[\mathrm{N}_{2} \mathrm{O}_{2}\right]}{[\mathrm{NO}]^{2}} \text { or }\left[\mathrm{N}_{2} \mathrm{O}_{2}\right]=\mathrm{K}_{\mathrm{c}}[\mathrm{NO}]^{2}
$$

Putting this in the rate expression, we get

$$
\text { Rate }=\mathrm{k} \cdot \mathrm{k}_{\mathrm{c}}[\mathrm{NO}]^{2}\left[\mathrm{H}_{2}\right]=\mathrm{k}_{\text {obs }}[\mathrm{NO}]^{2}\left[\mathrm{H}_{2}\right]
$$

Where $\mathrm{k}_{\mathrm{obs}}=\mathrm{k} . \mathrm{k}_{\mathrm{c}}=$ observed rate constant of the reaction

$$
\text { Rate } \alpha[\mathrm{NO}]^{2}\left[\mathrm{H}_{2}\right]
$$

This is the same rate - law as observed experimentally.

## Example 7:

The possible mechanism for the reaction

$$
\begin{array}{lll} 
& 2 \mathrm{NO}+\mathrm{Br}_{2} \longrightarrow 2 \mathrm{NOBr} \\
\text { is } & \mathrm{NO}+\mathrm{Br}_{2} \longrightarrow \mathrm{NOBr}_{2} & \text { (fast) } \\
& \mathrm{NOBr} \mathrm{O}_{2}+\mathrm{NO} \longrightarrow 2 \mathrm{NOBr} & \text { (slow). }
\end{array}
$$

Establish the rate law.

## Solution :

As the slowest step is the rate determining step, therefore the rate law is
$\mathrm{R}=\mathrm{k}\left[\mathrm{NOBr}_{2}\right][\mathrm{NO}]$
Now since $\mathrm{NOBr}_{2}$ is an intermediate its concentration can be calculated from step 1 as follows:

$$
\mathrm{K}=\frac{\left[\mathrm{NOBr}_{2}\right]}{[\mathrm{NO}]\left[\mathrm{Br}_{2}\right]} \quad[\mathrm{K}=\text { eq. constant }]
$$

or $\quad\left[\mathrm{NOBr}_{2}\right]=\mathrm{K}[\mathrm{NO}]\left[\mathrm{Br}_{2}\right]$
Substituting this value in above equation

$$
\begin{array}{ll} 
& \mathrm{r}=\mathrm{k} . \mathrm{K}[\mathrm{NO}]^{2}\left[\mathrm{Br}_{2}\right] \\
\text { or } & \text { rate }=\mathrm{k}^{\prime}[\mathrm{NO}]^{2}\left[\mathrm{Br}_{2}\right] \\
\therefore & \text { Rate }=\mathrm{k}^{\prime}[\mathrm{NO}]^{2}\left[\mathrm{Br}_{2}\right]
\end{array} \quad\left[\mathrm{Q} \mathrm{k} \cdot \mathrm{~K}=\text { constant } \mathrm{k}^{\prime}\right]
$$

## Example 8 :

Rate law for ozone layer depletion is

$$
\frac{d\left[\mathrm{O}_{3}\right]}{d t}=\frac{\mathrm{K}^{2}\left[\mathrm{O}_{3}\right]^{2}}{\left[\mathrm{O}_{2}\right]}
$$

Give the probable mechanism of reaction?
Solution : $\mathrm{O}_{3} \rightleftharpoons \mathrm{O}_{2}+\mathrm{O}$ (fast reaction)

$$
\begin{align*}
& \mathrm{O}_{3}+\mathrm{O} \longrightarrow 2 \mathrm{O}_{2} \quad \text { (slow reaction, rate constant k) } \\
& \text { Rate }=\mathrm{k}\left[\mathrm{O}_{3}\right][\mathrm{O}] \tag{1}
\end{align*}
$$

$\mathrm{K}_{\mathrm{c}}=\frac{\left[\mathrm{O}_{2}\right][\mathrm{O}]}{\left[\mathrm{O}_{3}\right]}$ or $[\mathrm{O}]=\mathrm{K}_{\mathrm{c}} \frac{\left[\mathrm{O}_{3}\right]}{\left[\mathrm{O}_{2}\right]}, \quad$ (equilibrium constant $\mathrm{K}_{\mathrm{c}}$ )
putting the value in (1)
From (1) Rate $=k \cdot\left[\mathrm{O}_{3}\right] \cdot \mathrm{kc} \frac{\left[\mathrm{O}_{3}\right]}{\left[\mathrm{O}_{2}\right]}=\mathrm{k} \cdot \mathrm{K}_{\mathrm{c}} \cdot \frac{\left[\mathrm{O}_{3}\right]^{2}}{\left[\mathrm{O}_{2}\right]}=\mathrm{K} \cdot \frac{\left[\mathrm{O}_{3}\right]^{2}}{\left[\mathrm{O}_{2}\right]}$ $\mathrm{k}=\mathrm{k} \times \mathrm{K}_{\mathrm{c}}$.

Example 9:
In hypothetical reaciton $A_{2}+B_{2} \longrightarrow 2 A B$ follows the mechanism as given below:

$$
\begin{aligned}
& A_{2} \rightleftharpoons A+A \text { (fast reaction) } \\
& A+B_{2} \longrightarrow A B+B \text { (slow reaction) } \\
& A+B \longrightarrow A B \text { (fast reaction) }
\end{aligned}
$$

Give the rate law and order of reaction.

## Soluton :

Slowest step is rate determining.

$$
\begin{equation*}
\text { Rate }=\mathrm{k}[\mathrm{~A}]\left[\mathrm{B}_{2}\right] \tag{1}
\end{equation*}
$$

Here [A] should be eleminated.

$$
\mathrm{K}_{\mathrm{c}}=\frac{[\mathrm{A}][\mathrm{A}]}{\left[\mathrm{A}_{2}\right]}=\frac{[\mathrm{A}]^{2}}{\left[\mathrm{~A}_{2}\right]}
$$

$$
[\mathrm{A}]=\mathrm{K}_{\mathrm{c}}^{1 / 2}\left[\mathrm{~A}_{2}\right]^{1 / 2}
$$

From (1). Rate $=\mathrm{kK}_{\mathrm{c}}^{1 / 2}\left[\mathrm{~A}_{2}\right]^{1 / 2}\left[\mathrm{~B}_{2}\right]$

$$
\begin{aligned}
& =\mathrm{K}\left[\mathrm{~A}_{2}\right]^{1 / 2}\left[\mathrm{~B}^{2}\right] ; \quad\left[\mathrm{K}=\mathrm{k} \cdot \mathrm{~K}_{\mathrm{c}}\right] \\
\text { Order }= & 1+1 / 2=3 / 2
\end{aligned}
$$

## Example 10 :

For the formation of phosgene from $\operatorname{CO}(g)$ and chlorine,

$$
\mathrm{CO}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g}) \longrightarrow \mathrm{COCl}_{2}(\mathrm{~g})
$$

The experimentally determined rate equation is,

$$
\frac{d\left[\mathrm{COCl}_{2}\right]}{d t}=k\left[\mathrm{CO}_{[ }\left[\mathrm{Cl}_{2}\right]^{3 / 2}\right.
$$

Is the following mechanism consistent with the rate equation?
(i) $\mathrm{Cl}_{2} \rightleftharpoons 2 \mathrm{Cl}$
(fast)
(ii) $\mathrm{Cl}+\mathrm{CO} \rightleftharpoons \mathrm{COCl}$
(iii) $\mathrm{COCl}+\mathrm{Cl}_{2} \rightleftharpoons \mathrm{COCl}_{2}+\mathrm{Cl}$

## Solution :

Multiplying equation (ii) by 2 and adding (i), we get:

$$
\mathrm{Cl}_{2}+2 \mathrm{CO} \rightleftharpoons 2 \mathrm{COCl}
$$

$$
\mathrm{K}=\frac{[\mathrm{COCl}]^{2}}{\left[\mathrm{Cl}_{2}\right][\mathrm{CO}]^{2}}
$$

$$
\begin{equation*}
[\mathrm{COCl}]=(\mathrm{K})^{1 / 2}\left[\mathrm{Cl}_{2}\right]^{1 / 2}[\mathrm{CO}] \tag{1}
\end{equation*}
$$

Slowest step is rate determining, hence

$$
\begin{equation*}
\text { Rate }=\mathrm{k}[\mathrm{COCl}]\left[\mathrm{Cl}_{2}\right] \tag{2}
\end{equation*}
$$

From (1) and (2), we get

$$
\begin{aligned}
& \text { Rate }=\mathrm{kK}^{1 / 2}\left[\mathrm{Cl}_{2}\right]^{1 / 2}\left[\mathrm{Cl}_{2}\right][\mathrm{CO}] \\
& \text { Rate }=\mathrm{k}^{\prime}\left[\mathrm{Cl}_{2}\right]^{3 / 2}[\mathrm{CO}] \quad\left[\mathrm{k}^{\prime}=\mathrm{k} \cdot \mathrm{k}^{1 / 2}\right]
\end{aligned}
$$

Thus, rate law is in accordance with the mecahnism.

## EXERCISE-I

## RATE OF REACTION AND STOICHIOMETRIC COEFFICIENT

Q. 1 In a catalytic experiment involving the Haber process, $\mathrm{N}_{2}+3 \mathrm{H}_{2} \longrightarrow 2 \mathrm{NH}_{3}$, the rate of reaction was measured as

$$
\text { Rate }=\frac{\Delta\left[\mathrm{NH}_{3}\right]}{\Delta \mathrm{t}}=2 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}
$$

If there were no sides reactions, what was the rate of reaction expressed in terms of (a) $\mathrm{N}_{2}$, (b) $\mathrm{H}_{2}$ ?
Q. 2 For the reaction $3 \mathrm{BrO}^{-} \rightarrow \mathrm{BrO}_{3}^{-}+2 \mathrm{Br}^{-}$in an alkaline aquesous solution, the value of the second order (in $\left.\mathrm{BrO}^{-}\right)$rate constant at $80^{\circ} \mathrm{C}$ in the rate law for $-\frac{\Delta\left[\mathrm{BrO}^{-}\right]}{\Delta \mathrm{t}}$ was found to be $0.056 \mathrm{~L} \mathrm{~mol}^{-1} \mathrm{~s}^{-1}$.
What is the rate of constant when the rate law is written for (a) $\frac{\Delta\left[\mathrm{BrO}_{3}^{-}\right]}{\Delta \mathrm{t}}$, (b) $\frac{\Delta\left[\mathrm{Br}^{-}\right]}{\Delta \mathrm{t}}$ ?
Q. 3 Dinitropentaoxide decomposes as follows:

$$
\mathrm{N}_{2} \mathrm{O}_{5}(\mathrm{~g}) \longrightarrow 2 \mathrm{NO}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{O}_{2}(\mathrm{~g})
$$

Given that

$$
\begin{aligned}
& -\mathrm{d}\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right] / \mathrm{dt}=\mathrm{k}_{1}\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right] \\
& \mathrm{d}\left[\mathrm{NO}_{2}\right] / \mathrm{dt}=\mathrm{k}_{2}\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right] \\
& \mathrm{d}\left[\mathrm{O}_{2}\right] / \mathrm{dt}=\mathrm{k}_{3}\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right]
\end{aligned}
$$

What is the relation between $\mathrm{k}_{1}, \mathrm{k}_{2}$ and $\mathrm{k}_{3}$ ?
Q. 4 The reaction $2 \mathrm{~A}+\mathrm{B}+\mathrm{C} \rightarrow \mathrm{D}+\mathrm{E}$ is found to be first order in A second order in B and zero order in C .
(i) Give the rate law for the reaction in the form of differential equation.
(ii) What is the effect in rate of increasing concentrations of $\mathrm{A}, \mathrm{B}$, and C two times?
Q. 5 For the elementary reaction $2 \mathrm{~A}+\mathrm{B}_{2} \longrightarrow 2 \mathrm{AB}$. Calculate how much the rate of reaction will change if the volume of the vessel is reduced to one third of its original volume?
Q. 6 Ammonia and oxygen reacts at higher temperatures as
$4 \mathrm{NH}_{3}(\mathrm{~g})+5 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 4 \mathrm{NO}(\mathrm{g})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$
In an experiment, the concentration of NO increases by $1.08 \times 10^{-2} \mathrm{~mol}_{\text {litre }}{ }^{-1}$ in 3 seconds. Calculate.
(i) rate of reaction.
(ii) rate of disappearance of ammonia
(iii) rate of formation of water
Q. 7 In the following reaction $2 \mathrm{H}_{2} \mathrm{O}_{2} \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}+\mathrm{O}_{2}$ rate of formation of $\mathrm{O}_{2}$ is $3.6 \mathrm{M} \mathrm{min}^{-1}$.
(a) What is rate of formation of $\mathrm{H}_{2} \mathrm{O}$ ?
(b) What is rate of disappearance of $\mathrm{H}_{2} \mathrm{O}_{2}$ ?
Q. $8 \quad$ The reaction $\mathrm{A}(\mathrm{g})+2 \mathrm{~B}(\mathrm{~g}) \longrightarrow \mathrm{C}(\mathrm{g})+\mathrm{D}(\mathrm{g})$ is an elementary process. In an experiment, the initial partial pressure of $A B B$ are $P_{A}=0.6$ and $P_{B}=0.8 \mathrm{~atm}$, if $\mathrm{P}_{\mathrm{C}}=0.2 \mathrm{~atm}$ then calculate the ratio of rate of reaction relative to initial rate.

## Answer Key

Q. 1 (a) $1 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}$, (b) $3 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}$
Q. 2 (a) $0.019 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}$, (b) $0.037 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}$
Q. $3 \quad 2 \mathrm{k}_{1}=\mathrm{k}_{2}=4 \mathrm{k}_{3}$ Q. 4 (i) $\frac{\mathrm{dx}}{\mathrm{dt}}=\mathrm{k}[\mathrm{A}][\mathrm{B}]^{2}$, (ii) rate increases by 8 times
Q. 5 rate increase by 27 times
Q. $6 \quad$ (i) $\mathrm{r}=\frac{1}{4} \frac{\mathrm{~d}[\mathrm{NO}]}{\mathrm{dt}}=9 \times 10^{-4} \mathrm{~mol} \mathrm{litr} \mathrm{e}^{-1} \mathrm{sec}^{-1}$, (ii) $36 \times 10^{-4} \mathrm{~mol} \mathrm{litre}^{-1} \mathrm{sec}^{-1}$, (iii) $54 \times 10^{-4} \mathrm{~mol} \mathrm{litre}{ }^{-}$ ${ }^{1} \sec ^{-1}$

## Q. 7

(i) 7.2 mol litre $^{-1} \mathrm{~min}^{-1}$, (ii) 7.2 mol litre $^{-1} \mathrm{~min}^{-1}$
Q. $8 \quad 1 / 6$

