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## CLASS 12th

## Chemical Kinetics



## Chemical Kinetics

## 01. Types of Reactions

On the basis of reaction rates, the chemical reactions have been classified into the following three groups

## Very fast or instantaneous reactions :

These reactions occur at a very fast rate. Generally these reactions involve ionic species and known as ionic reaction.
These reactions take about $10^{-14}$ seconds for completion.
Example
(i) $\mathrm{AgNO}_{3}+\mathrm{NaCl} \rightarrow \underset{\text { (ppt.) }}{\mathrm{AgCl}}+\mathrm{NaNO}_{3} \quad$ (Precipitation reaction)
(ii) $\mathrm{HCl}+\mathrm{NaOH} \rightarrow \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O} \quad$ (Neutralization reaction)

## Moderate reaction :

These type of reactions proceed with a measurable rates at normal temperature. In this a large number of bonds have to be broken in reactants molecules and a large number of new bonds have to be formed in product molecules. Mostly these reactions are molecular in nature.

## Example (i) Decomposition of $\mathrm{H}_{2} \mathrm{O}_{2}: 2 \mathrm{H}_{2} \mathrm{O}_{2} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}+\mathrm{O}_{2}$

(ii) Decomposition of $\mathrm{N}_{2} \mathrm{O}_{5}: 2 \mathrm{~N}_{2} \mathrm{O}_{5} \rightarrow 2 \mathrm{~N}_{2} \mathrm{O}_{4}+\mathrm{O}_{2}$
(iii) Hydrolysis of ester: $\mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}+\mathrm{NaOH} \rightarrow \mathrm{CH}_{3} \mathrm{COONa}+\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{OH}$

## Very slow reactions :

These reactions are extremely slow and take months together to show any measurable change. The rate of such type of reactions are very slow. So, it is also very difficult to determine the rate of these reactions.

## Example

(i) $\mathrm{Fe}_{2} \mathrm{O}_{3}+\mathrm{xH}_{2} \mathrm{O} \rightarrow \mathrm{Fe}_{2} \mathrm{O}_{3} \cdot \mathrm{xH}_{2} \mathrm{O}$

Hydrated ferric oxide (Rust)
(ii) Reaction between $\mathrm{H}_{2}$ and $\mathrm{O}_{2}$ to form $\mathrm{H}_{2} \mathrm{O}$ at ordinary temperature in absence of catalyst.

## 02. Rate of Reaction

The change in concentration of either reactant or product per unit time.

$$
\text { Formula }: \mathrm{r}=\frac{\mathrm{dc}}{\mathrm{dt}}
$$ dc is change in concentration of reactant or product in a small time interval dt .

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Example

$$
\mathrm{N}_{2}+3 \mathrm{H}_{2} \rightarrow 2 \mathrm{NH}_{3}
$$

(i) Rate of formation of ammonia $=+\frac{\mathrm{d}\left[\mathrm{NH}_{3}\right]}{\mathrm{dt}}$
(ii) Rate of disappearance of nitrogen $=-\frac{\mathrm{d}\left[\mathrm{N}_{2}\right]}{\mathrm{dt}}$
(iii) Rate of disappearance of hydrogen $=-\frac{\mathrm{d}\left[\mathrm{H}_{2}\right]}{\mathrm{dt}}$

Rate of reaction $=+\frac{1}{2} \frac{\mathrm{~d}\left[\mathrm{NH}_{3}\right]}{\mathrm{dt}}=-\frac{\mathrm{d}\left[\mathrm{N}_{2}\right]}{\mathrm{dt}}=-\frac{1}{3} \frac{\mathrm{~d}\left[\mathrm{H}_{2}\right]}{\mathrm{dt}}$

## 03. 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 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 or 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 smell change in concentration is dx in the small interval of time dt. Then the rate of reaction at that instant is given by $\mathrm{dx} / \mathrm{dt}$.

## 04. 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

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

Thus the slope of the tangent gives the rate of reaction.

## 05. 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

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

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## 06. Factors Affecting the Rate of Reaction

(i) Concentration :

According to law of mass action greater is the conc. of the reactants, the more repidly the reaction proceeds.
(ii) Pressure (Gaseous reaction) :

On increasing the pressure, volume decreases and conc. increases and hence the rate increases.
(iii) Temperature :

It is generally observed that rise in temperature increases the reaction rate. It has been found that rate is either doubled or tripled for every $10^{\circ} \mathrm{C}$ rise in temperature.
(iv) Nature of the reactants :

The rate depends upon specific bonds involved and hence on the nature of reactants.
(v) Surface area of the reactants :

In heterogeneous reactions, more powered is the form of reactants, more is the rate. [as more active centres are provided]
(vi) Catalyst :

Affects the rate immensely.

## 07. Law of mass action, rate law and rate constant

## Law of mass action :

(Guldberg and Wage 1864) This law relates rete of reaction with active mass or molar concentration of reactants. According to this law, "At a given temperature, the rate of a reaction at a particular instant is proportional to the product of the reactants at that instant raised to powers which are numerically equal to the numbers of their respective molecules in the stoichiometric equation describing the reaction."

Active mass $=$ Molar concentration of the substance

$$
=\frac{\text { Number of gram mole of the substance }}{\text { Volume in litres }}=\frac{\mathrm{W} / \mathrm{M}}{\mathrm{~V}}=\frac{\mathrm{n}}{\mathrm{~V}}
$$

Where $\mathrm{W}=$ mass of the substance, M is the molecular mass in grams, ' n ' is the number of g moles and V is volume in litre.
Consider the following general reaction, $\mathrm{m}_{1} \mathrm{~A}_{1}+\mathrm{m}_{2} \mathrm{~A}_{2}+\mathrm{m}_{3} \mathrm{~A}_{3} \rightarrow$ Products
Rate of reaction $\propto\left[A_{1}\right]^{m_{1}}\left[A_{2}\right]^{m_{2}}\left[A_{3}\right]^{m_{3}}$

