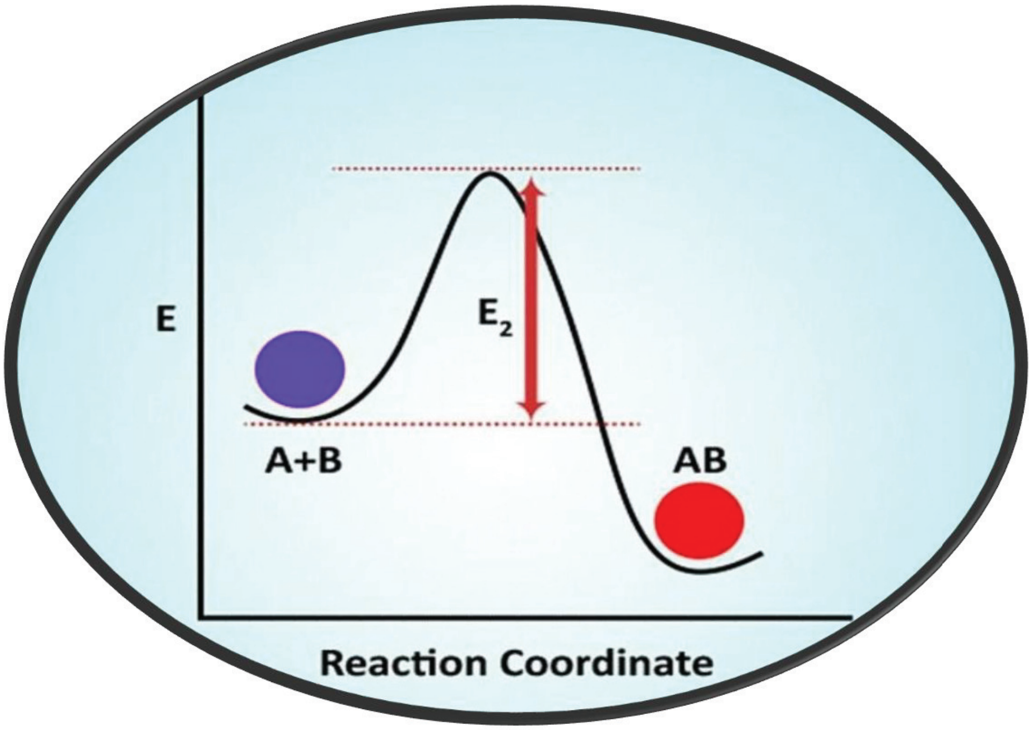
CHEMICAL KINETICS



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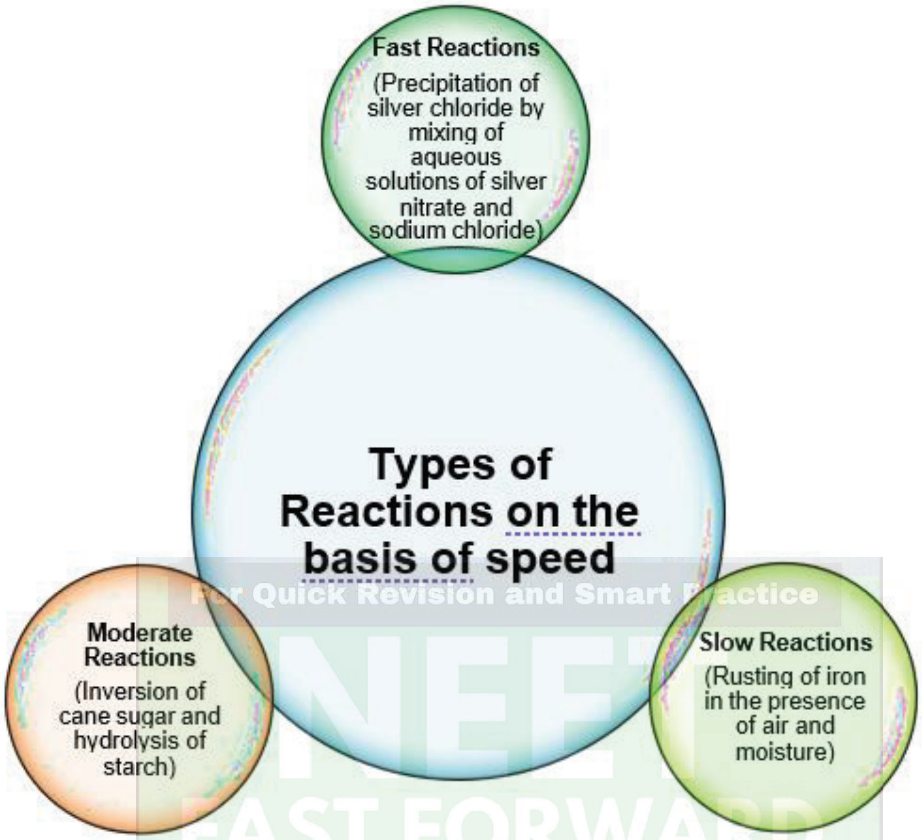
CHEMICAL KINETICS

Rate of Chemical Reaction



Rate of Chemical Reaction

The **rate of reaction** is the change in concentration of a reactant or productin unit time.

- Alternatively, the rate of reaction can also be expressed as

The rate of decrease in concentration of any one of the reactants.

The rate of increase in concentration of any one of the products.

- Consider a hypothetical reaction, assuming that the volume of the system remains constant.

$$R \rightarrow P$$

One mole of the reactant R produces one mole of the product P.

- If $[R]_1$ and $[P]_1$ are the concentrations of R and P at time t_1 and $[R]_2$ and $[P]_2$ are theirconcentrations at time t_2, then

$$\Delta t = t_2 - t_1$$
$$\Delta[R] = [R]_2 - [R]_1$$
$$\Delta[P] = [P]_2 - [P]_1$$

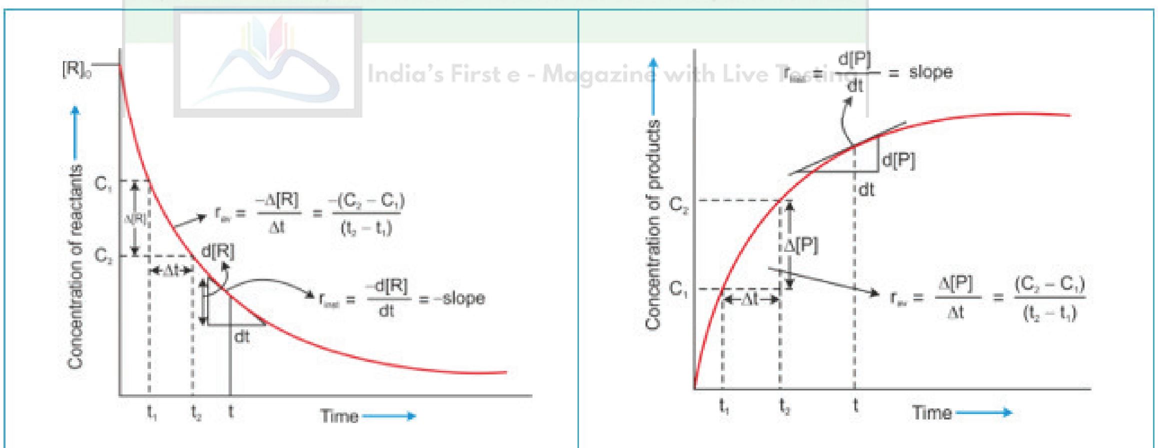
The square brackets in the above expressions are used to express molar concentration.

$$\text{Rate of disappearance of R} = \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = -\frac{\Delta[R]}{\Delta t} \quad \text{\_\_\_\_\_(1)}$$

- $\Delta[R]$ is a negative quantity because the concentration of reactants is decreasing.

$$\text{Rate of appearance of P} = \frac{\text{Increase in concentration of P}}{\text{Time taken}} = +\frac{\Delta[P]}{\Delta t} \quad \text{\_\_\_\_\_(2)}$$

- Equations 1 and 2 represent the average rate of a reaction, r_{av}.
This average rate depends on the change in concentration of reactants or products and the timetaken for that change to occur.



Instantaneous and average rate of a reaction

Units of Rate of a Reaction

- From Equations 1 and 2, it is clear that the units of rate are concentration time^{-1}.

- For example, if concentration is in mol L^{-1} and time is in seconds, then the units are mol $L^{-1}s^{-1}$.
- In gaseous reactions, the concentration of gases is expressed in terms of their partial pressures;hence, the units of the rate equation will be atm s^{-1}.

Instantaneous Rate of Reaction

- Consider the hydrolysis of butyl chloride (C_4H_9Cl).

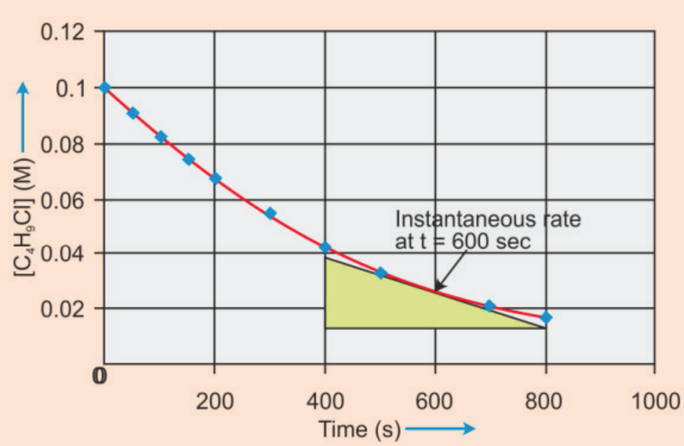
$$C_4H_9Cl + H_2O \rightarrow C_4H_9OH + HCl$$

- We have provided the concentrations over different intervals of time below.

Time (s^{-1})	0	50	100	150	200	300	400	700	800
Concentration (mol L^{-1})	0.100	0.0905	0.0820	0.0741	0.0671	0.0549	0.0439	0.0210	0.017

- We can determine the difference in concentration over different intervals of time, and thus, wedetermine the average rate by dividing Δ[R] by Δt.
- It can be seen from experimental data that the average rate falls from 1.90 × 10^{-4} mol $L^{-1}s^{-1}$ to 0.4 × 10^{-4} mol $L^{-1}s^{-1}$.
- However, the average rate cannot be used to predict the rate of reaction at a particular instant as itwould be constant for the time interval for which it is calculated.
- Hence, to express the rate at a particular moment of time, we determine the instantaneous rate.
- It is obtained when we consider the average rate at the smallest time interval, say dt, when Δt approaches zero.
  Therefore, for an infinitesimally small dt, the instantaneous rate is given by

$$r_{inst} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$



Instantaneous rate of hydrolysis of butyl chloride(C_4H_9Cl)