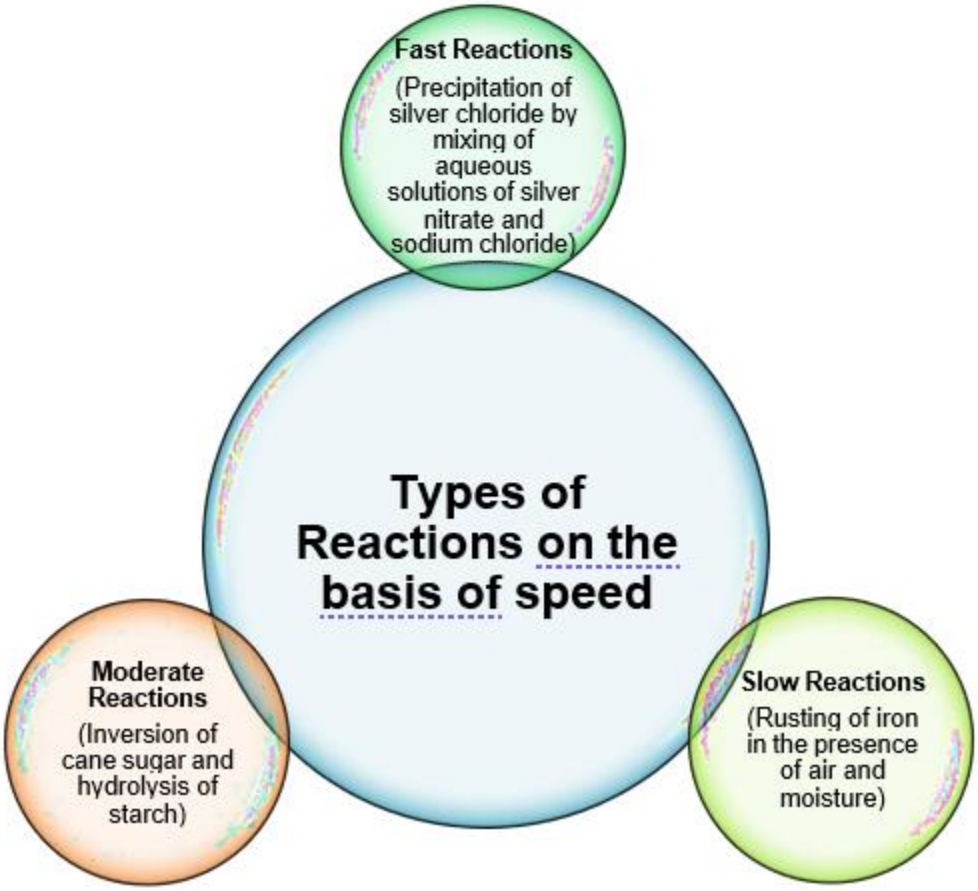
CHEMICAL KINETICS

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

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

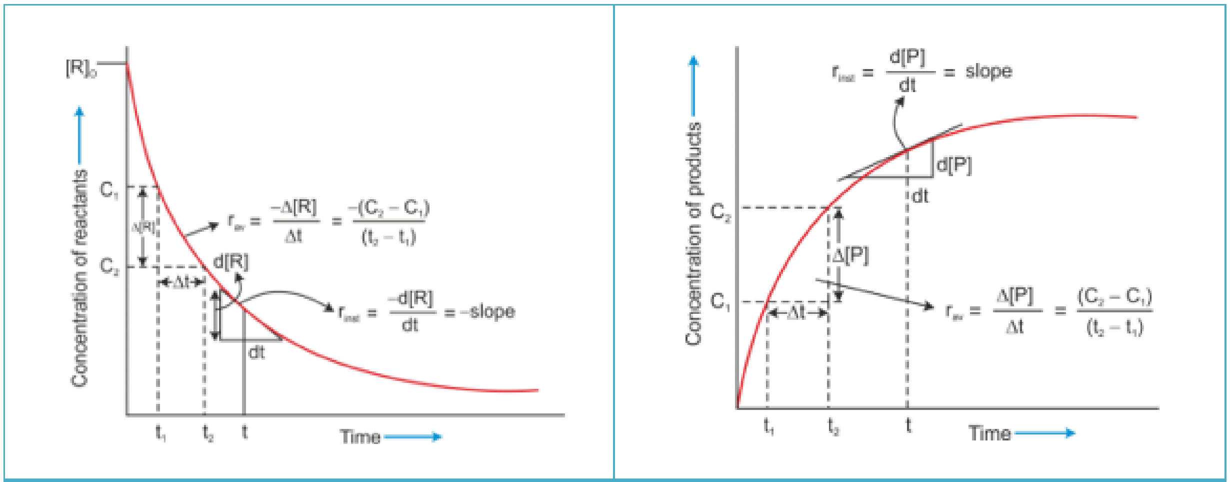
The square brackets in the above expressions are used to express molar concentration.

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

- $\Delta[R]$ 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.

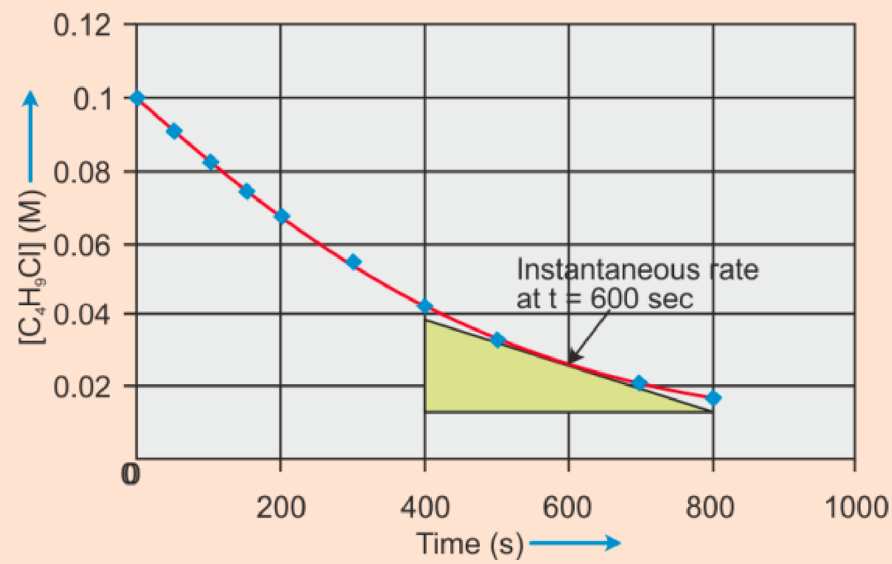
Time (s^{-1})	0	50	100	150	200	300	400	700	800
Concentration (mol L^{-1})	0.100	0.0905	0.0820	0.0741	0.0671	0.0549	0.0439	0.0210	0.017

- 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)

- By drawing the tangent at time t on either of the curves for the concentration of R versus time t orconcentration of P versus time t and calculating the slope of the curve, we can determine the instantaneous rate of reaction.
- Hence, in this example, r_{inst} at 600 s is calculated by plotting the graph of the concentration of butylchloride as against time t.
- A tangent is drawn on the curve at a point t = 600 s.

$$\therefore r_{inst} \text{ at } 600s = \left[\frac{0.0165-0.037}{(800-400)}\right] molL^{-1} = 5.12\times10^{-5}\, molL^{-1}s^{-1}$$

$$\text{At } t=250s \qquad r_{inst} = 1.22\times10^{-4}\, molL^{-1}s^{-1}$$
$$t=350s \qquad r_{inst} = 1.0\times10^{-4}\, molL^{-1}s^{-1}$$
$$t=450s \qquad r_{inst} = 6.4\times10^{-5}\, molL^{-1}s^{-1}$$

- Now consider a reaction,

$$Hg(l) + Cl_2(g) \rightarrow HgCl_2(s)$$

Here, the stoichiometric coefficients of the reactants and products are the same; hence, the rate of reaction is given as

$$\text{Rate of reaction} = -\frac{\Delta[Hg]}{\Delta t} = -\frac{\Delta[Cl_2]}{\Delta t} = \frac{\Delta[HgCl_2]}{\Delta t}$$

Therefore, we can say that from the above equation that the rate of disappearance of any of the reactants is the same as the rate of appearance of the products.

- Consider another reaction,

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

In this reaction, two moles of HI decompose to produce one mole each of H2 and I2, i.e. the stoichiometric coefficients of reactants or products are not equal to one; hence, we need to divide the rate of disappearance of any of the reactants or the rate of appearance of products by their respective stoichiometric coefficients.

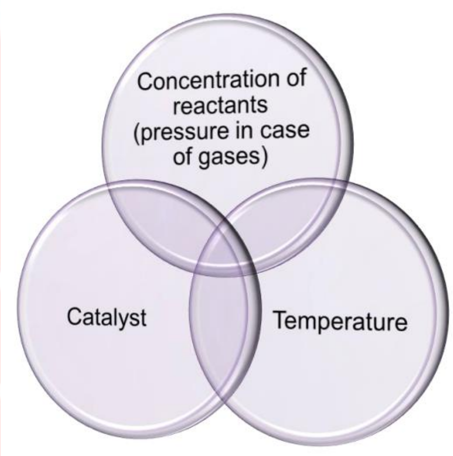
Because the rate of consumption of HI is twice the rate of formation of H2 or I2, to make them equal, the term Δ[HI] is divided by 2.

The rate of this reaction is given by

$$\text{Rate of reaction} = -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

- For a gaseous reaction at constant temperature, concentration is directly proportional to the partial pressure of a species, and hence, the rate can be expressed as the rate of change in partial pressure of the reactant or the product.

Instantaneous Rate of Reaction



MIND MAP : LEARNING MADE SIMPLE

CHAPTER - 4

Chemical Kinetics

Rate Of Chemical Reaction
Change in concentration of reactants or products in unit time; Unit : mol $L^{-1}s^{-1}$ or atm s^{-1}

- **Average Rate:** Appearance of products or disappearance of reactants over a long time interval.
  $r_{av} = \frac{d[P]}{dt}$ = slope
  $r_{av} = \frac{-d[R]}{dt}$ = –slope
- **Instantaneous Rate:** Rate of change in concentration of reactant/product at a particular time
  $r_{inst} = \frac{-d[R]}{dt} = \frac{+d[P]}{dt}$
- **R → P**
  - Rate of disappearance of R $= \frac{\text{Decease in concentration of R}}{\text{Time taken}} = \frac{-\Delta[R]}{\Delta t}$
  - Rate of appearance of P $= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = \frac{+\Delta[P]}{\Delta t}$
- **Factors Influencing:**
  - **Concentration :** Higher the concentration of reactants, faster is the rate of reaction
  - **Temperature :** Increases with increase in temperature. becomes almost double with 10°C rise.
  - **Presence of Catalyst :** Increases with a catalyst.
  - **Surface Area :** Greater is the surface area, faster is the rate of reaction.
  - **Activation Energy :** Lower the activation energy, faster is the reaction.
- **Rate Law:** Expression in which reaction rate in given in terms of molar concentration of reactants with each term raised to power which may or may not be same as stoichiometric coefficient of reactants in a balanced chemical equation. $aA + bB \longrightarrow cC + dD$
  Rate $= K[A]^x[B]^y = \frac{d[R]}{dt}$

Rate Constant: Rate of a reaction when concentration of each of the reactant in unity.

Order	Unit
0	$molL^{-1}s^{-1}$
1	s^{-1}
2	$mol^{-1}Ls^{-1}$

Order Of A Reaction
Sum of powers of concentration of the reactants in the rate law.

Molecularity Of A Reaction
Number of reacting species taking part in an elementary reaction colliding to bring out a reaction.

Half-life Of A Reaction
Time in which the concentration of a reactant is reduced to one half of its initial concentration

- 1st Order: $t_{1/2} = \frac{0.693}{K}$
- 0 Order: $t_{1/2} = \frac{[R]_0}{2K}$

Pseudo First Order Reaction
- Are not truly of first order but under certain conditions behave as first order reaction
- Acid hydrolysis of ethyl acetate
- Inversion of sugar

Integrated Rate Equation
Integration of differential rate equation to give a relation between concentrations at different times and rate constant.

Order	Integrated Rate Law	Straight Plot	Units (K)
0	$kt = [R]_0 - [R]$	[R] vs t	mol $L^{-1}s^{-1}$
1	$kt = \ln\{[R]_0/[R]\}$	In[R] vs t	s^{-1}

Arrhenius Equation
$K = Ae^{-Ea/RT}$

$\log k = \log A - \frac{E_a}{2.303RT}$

$\log = \frac{k2}{k1} = \frac{E_a}{2.303RT}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

Activation Energy, E_a
: Energy required to form an intermediate called activated complex (c)
E_a = Threshold energy - Average Kinetic energy of reacting molecules

Collision Theory: Rate of reaction depends on the collision frequency and effective collisions.

- **Collision Frequency:** Number of collisions per unit volume of reaction mixture
  Rate $= Z_{AB}e^{-Ea/RT}$
- **Effective Collision:** Collision in which molecules collide with sufficient kinetic energy and proper orientation for breaking of bonds and formation of new bonds.
  - Rate $= PZ_{AB}e^{-Ea/RT}$
    P is Steric or Probability factor
  - E_a and proper orientation of the molecules determine the criteria for an effective collision.