MIND MAP

Chemical kinetics

Types of Rate

(i) Average rate = $\frac{\text{Total change in conc.}}{\text{Total time taken}} = \frac{\Delta C}{\Delta t}$

(ii) Instantaneous rate =

$$R_{inst} = \lim_{\Delta t \to 0} \frac{\Delta C}{\Delta t} = \frac{dC}{dt}$$

Rate of Reaction in the form of Stoichiometry of a Chemical Reaction

$$m_1A + m_2B \longrightarrow n_1P + n_2Q + n_3R$$

$$\text{Rate of reaction} = (-)\frac{1}{m_1}\frac{\Delta[A]}{\Delta t}$$

$$= (-)\frac{1}{m_2}\frac{\Delta[B]}{\Delta t} = \frac{1}{n_1}\frac{\Delta[P]}{\Delta t}$$

$$= \frac{1}{n_2}\frac{\Delta[Q]}{\Delta t} = \frac{1}{n_3}\frac{\Delta[R]}{\Delta t}$$

Rate Law

$$xP + yQ \longrightarrow \text{Product}$$

$r = k[P]^x[Q]^y$

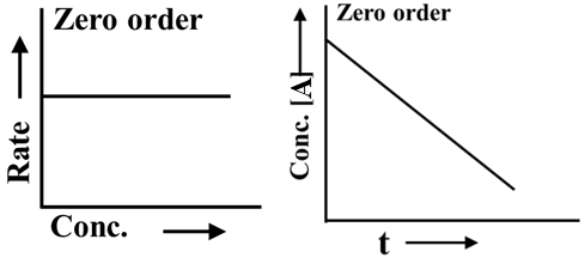
x & y are called order of reaction w.r.t. P & Q respectively and overall order of reaction = x + y. k = rate constant

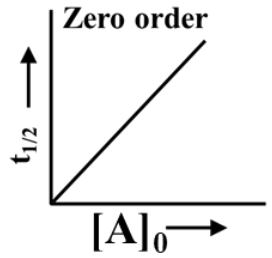
Order is always experimental quantity. Order of reaction may be zero, integer or fractional (+) or (–)ve

Molecularity of Reaction

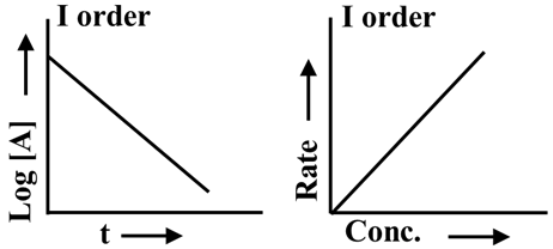
The number of reacting species (atoms, ions, molecules) taking part in an elementary reaction. For an elementary reaction, molecularity represents the number of reactant particles participating in the reaction.

Zero – Order Reaction

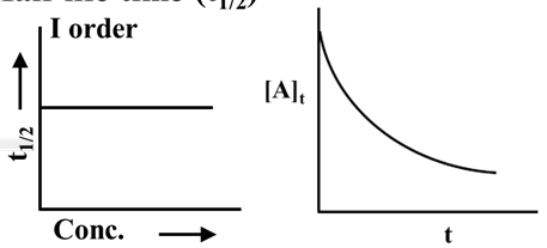




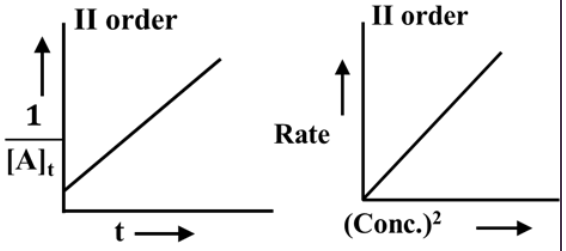
First Order Reaction



Half-life time ($t_{1/2}$)



Second Order Reaction



MIND MAP

Chemical kinetics

	Zero order	First order	Second order	n^{th} order
Differential Rate law	$\frac{-\Delta[A]}{\Delta t} = k[A]^{\circ}$	$-\frac{\Delta[A]}{\Delta t} = k[A]$	$-\frac{\Delta[A]}{\Delta t} = k[A]^2$	$-\frac{\Delta[A]}{\Delta t} = k[A]^n$
(Integrated Rate law)	$[A]_t = [A]_0 - kt$	$\ln[A]_t = -kt + \ln[A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\frac{1}{(A_t)^{n-1}} - \frac{1}{(A_0)^{n-1}} = (n-1)kt$
Linear graph	$[A]_t$ v/s t	$\ln[A]$ v/s t	$\frac{1}{[A]}$ v/s t	$\frac{1}{(A_t)^{n-1}}$ v/s t
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$ depends on $[A]_0$	$t_{1/2} = \frac{0.693}{k}$ independent of $[A]_0$	$t_{1/2} = \frac{1}{k[A]_0}$ depends on $[A]_0$	$t_{1/2} \propto \frac{1}{(A_0)^{n-1}}$

Order	Unit of k
$n = 0$	$= \text{mol } L^{-1}s^{-1}$
$n = 1$	$= s^{-1}$
$n = 2$	$= L\ mol^{-1}\ s^{-1}$
$n = -1$	$= mol^2\ L^{-2}\ s^{-1}$

Volume Measurement

$a \propto V_\infty$ and $x \propto V_t$

$(a - x) \propto V_\infty - V_t$

$$\therefore k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

Optical Rotation Measurement

It is used for optically active sample.

It is applicable if there is at least one optically active species involved in chemical reaction.

It is found that $(r_\infty - r_0) \propto a$

$(r_\infty - r_t) \propto (a - x)$

Where r_0, r_t, r_∞ are angle of optical rotation at time $t = 0$, $t = t$ and $t = \infty$.

$$k = \frac{2.303}{t} \log \frac{r_\infty - r_0}{r_\infty - r_t}$$

MIND MAP

Chemical kinetics

Arrhenius Collision Theory

(i) A chemical reaction takes place due to the collisions between the reactant molecules.
Bond cleavage as well as bond formation takes place at the time of collision between the molecules.

(ii) The number of molecular collisions taking place per second per unit volume of the reaction mixture is known as collision frequency (Z_{11} or Z_{12}).

(iii) Under normal conditions, the value of Z_{11} or Z_{12} is about 10^6 mol l^{-1} s^{-1}.

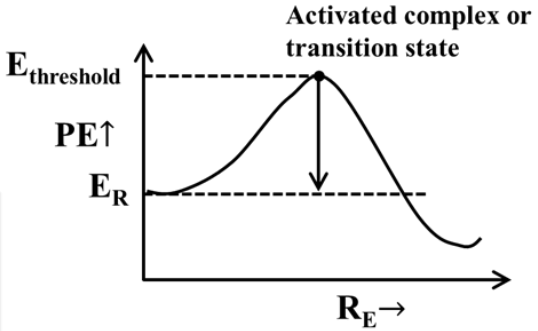
(vi) The collisions that actually produce products are called effective collision.

For a collision to be effective, the following two barriers should be crossed by the molecules.

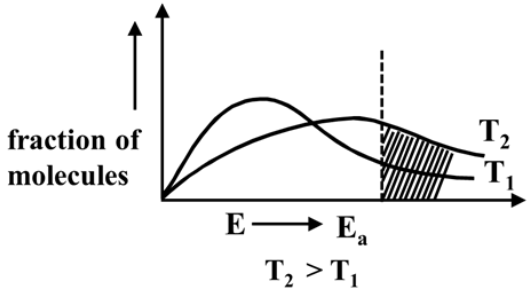
(I) Energy Barrier

The minimum amount of energy, which the colliding molecules must posses in order to make the chemical reaction occur, is known as Threshold energy, E_T.

$E_a = E_{threshold} - E_{reactant}$



The fraction of molecules having energy equal to threshold energy or more is given by the Berthelot's factor, $e^{-E_a/RT}$.



MIND MAP

Chemical kinetics

Rate of rxn = collision frequency x fraction of molecules having sufficient energy x fraction molecules having proper orientation

$r = Z \times e^{\frac{-E_a}{RT}} \times P$ → steric factor or orientation factor

$\therefore k = Ae^{-E_a/RT}$

$k = Ae^{-E_a/RT}$ → Arrhenius eqⁿ.

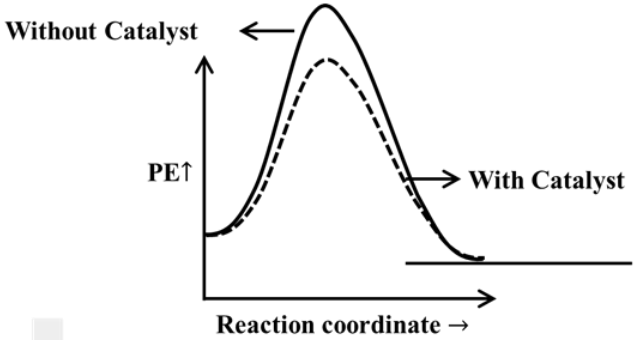
A is called pre-exponential factor.

$\Rightarrow T \uparrow k \uparrow$

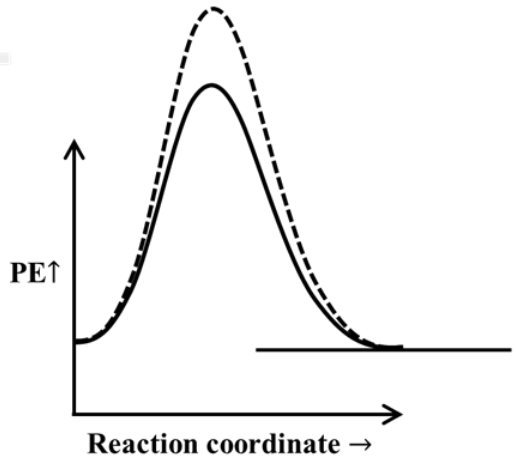
$$\frac{d}{dT}\ln k = \frac{E_a}{RT^2}$$

Catalyst

Catalyst speed up the rate of reaction by providing one alternative path for the reaction of lower E_a .



Inhibiter or -ve catalyst decrease the rate of reaction by providing the path of higher activation energy.



Factors Affecting Rate Of Reaction

Physical State

Gas > Liquid > Solid

Particle Size of Reactant

Reaction rate goes up as particle size decreases due to increase in surface area.

Temperature

$r = k[A]$

$k = Ae^{-E_a/RT}$

On increase in the temperature rate of reaction increases for both endothermic & exothermic reactions.

Generally on increasing the temperature by 10 ° C rate of reaction becomes 2 to 3 times.

⇒ Temperature coefficient of reaction (μ)

$$\mu = \frac{r_{t+10^\circ C}}{r_{t^0 C}} = \frac{k_{t+10^\circ C}}{k_{t^\circ C}}$$