Chapter 9

Chemical Kinetics

FACTORS AFFECTING RATE OF REACTION

(i) **Nature of the reactant :** Different amount of energies are required for breaking of different bonds and different amount of energies are released in the formation of different bonds.

(ii) **Concentration of the reactant :** Greater the concentration of reactants, faster is the reaction.

(iii) **Surface area of the reactant :** Rate of reaction increases with increase in surface area.

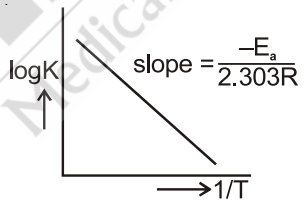
(iv) **Presence of light :** Some reactions do not take place in dark but take place in presence of light. Such reactions are called photochemical reactions.

(v) **Temperature :** The rate of reaction increases with an increase in temperature. For every 10°C rise in temperature the rate of reaction becomes twice or thrice for a homogeneous reaction. The temperature coefficient is defined as the ratio of the specific reaction rates of a reaction at two temperatures differing by 10°C.

Temp. coefficient $= \frac{K_{t+10}}{K_t} =$ between 2 or 3.

The rate constant (K) and temperature are related by **Arrhenius equation** given by

$$\boxed{K \propto e^{-E_a/RT}}$$



Arrhenius equation, $K = Ae^{-\frac{E_a}{RT}}$ *i.e.*, $\ln k = \ln A - \frac{E_a}{RT}$.

$$\log_{10} K = \log_{10} A - \frac{E_a}{2.303\,RT}$$

By plotting graph log K vs $\frac{1}{T}$ activation energy can be determined.

(vi) **Presence of catalyst :** The positive catalyst lowers down the activation energy. The greater the decrease in activation energy higher will be the reaction rate.

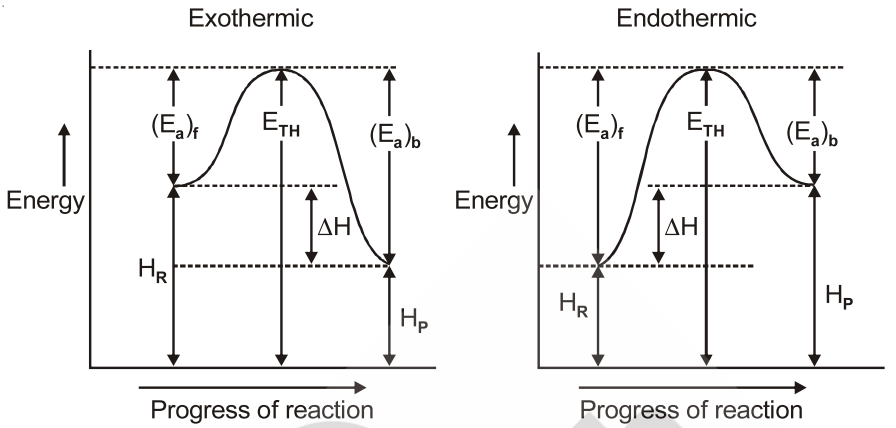
CONCEPT OF ACTIVATION ENERGY

The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy

Activation energy = Threshold energy – average kinetic energy of reacting molecules

Threshold energy = Initial potential energy of reactant molecules + activation energy.

Activation Energy



E_{TH} = Threshold Energy, H_R = Enthalpy or Energy or Potential of reactants.

H_P = Enthalpy or Energy or Potential of product, $(E_a)_f$ = Activation energy for forward reaction.

$(E_a)_b$ = Activation energy for backward reaction.

ORDER OF REACTION

A. Zero order reaction : A reaction is said to be of zero order if the rate of reaction is independent of concentration of the reactant.

Rate Expression :

Let $A \longrightarrow$ Product

[K is a constant called Rate Constant]

$\therefore$ $\boxed{K = \frac{x}{t}}$

Characteristics :

(a) Unit of K = mol L^{-1} $time^{-1}$

(b) Half life period : Time required for the completion of half of the reaction.

Half life for zero order reaction is directly proportional to initial concentration of the reactant

$\boxed{t_{1/2} \propto a}$

(c) The concentration of reactant decreases linearly with time.

B. First Order Reaction :

A first order reaction is one whose rate is determined by the variation of one concentration term only.

All radioactive disintegration reactions are of the first order.

Rate Expression

Let	A	$\longrightarrow$	Product
initially	a		0
after time t	(a – x)		x

$$\Rightarrow \quad \boxed{K = \frac{2.303}{t}\log\frac{a}{(a-x)}}$$

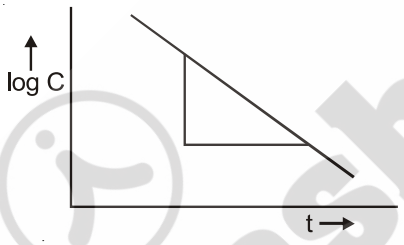
Characteristics

(a) Unit of K = time^{-1}

(b) Half-life period : The half life period is independent of initial concentration of the reactant.

$$\boxed{t_{1/2} = \frac{0.693}{K}}$$

(c) On plotting a graph between log of concentration and time we get



The slope of this line gives the value of $\frac{-K}{2.303}$ from which K can be calculated.

General expression of unit of rate constant K = mole^{1-n} litre^{n-1} time^{-1}, where n is the order of reaction

RATE CONSTANTS FOR DIFFERENT ORDER OF REACTION

Reaction	Order	Rate law eqn.	Rate constant	Half life period
A $\rightarrow$ product	0	Rate = k	$k = \frac{1}{t}([A_0]-[A])$	$t_{1/2} = \frac{[A_0]}{2k}$
A $\rightarrow$ product	1	Rate = k[A]	$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$	$t_{1/2} = \frac{0.693}{k}$
2A $\rightarrow$ product	2	Rate = k[A]^2	$k = \frac{1}{t}\left[\frac{1}{[A]} - \frac{1}{[A_0]}\right]$	$t_{1/2} = \frac{1}{[A_0]k}$

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