

Course code :- 1CHMTC0401

Unit :- Chemical Kinetics

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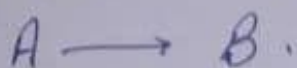
## → ~~The~~ The Concept of Reaction Rates :-

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Rate of Reaction means the speed of reaction with which the reaction takes place.

- The rate of change of concentration of any one of the reactants or products per unit time is k/as Rate of Reaction.

Consider a common hypothetical reaction,



$$\text{Rate of Reaction} = \frac{\text{Decrease in conc. of A}}{\text{Time Interval}}$$

$$= \frac{\text{Increase in conc. of B}}{\text{Time Interval}}$$

Let  $[A]_{t_1}$ ,  $[A]_{t_2}$ ,  $[B]_{t_1}$  and  $[B]_{t_2}$  be the conc. of A + B at time  $t_1$  +  $t_2$  respectively.



$$\begin{aligned} \text{Rate of Consumption of A} &= \frac{[A]_{t_1} - [A]_{t_2}}{t_2 - t_1} \\ &= \frac{[A]_{t_2} - [A]_{t_1}}{t_2 - t_1} \\ &= - \frac{\Delta[A]}{\Delta t} \end{aligned}$$

$$\begin{aligned} \text{Rate of formation of B} &= \frac{[B]_{t_2} - [B]_{t_1}}{t_2 - t_1} \\ &= + \frac{\Delta [B]}{\Delta t} \end{aligned}$$

(-) sign indicates that conc. of reactant is decreasing and (+) sign indicates that conc. of product is increasing.

→ UNIT of the Rate of Reaction: -

moles / litre - seconds

or moles / litre - minute

or moles / litre - hour.

→ FIRST ORDER REACTION: → In this reaction, rate of the reaction is proportional to the first power of the concentration of the reactant. For example;



$$\text{Rate} = -\frac{d[A]}{dt} = k[A]$$

$$+\frac{d[A]}{[A]} = -k dt$$

Integrating both sides..

$$\int_{A_0}^{A_t} \frac{d[A]}{[A]} = -k \int_0^t dt$$

When  $t=0$ ,  $A = [A_0]$ , where  $[A_0]$  is the initial concentration of the reactant.

$$[\ln A]_{A_0}^{A_t} = -k [t]_0^t$$

$$\ln[A_t] - \ln[A_0] = -kt$$

$$\ln[A_0] - \ln[A_t] = kt$$

$$\frac{\ln[A_0]}{[A_t]} = kt$$

$$2.303 \log \frac{[A_0]}{[A_t]} = kt$$

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A_t]}$$

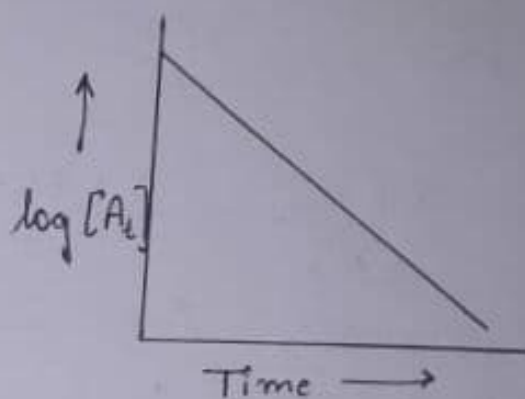


$\log [A_t]$  versus  $t$  :-

$$\log [A_0] - \log [A_t] = \frac{kt}{2.303}$$

$$\log [A_t] = \log [A_0] - \left( \frac{k}{2.303} \right) t$$

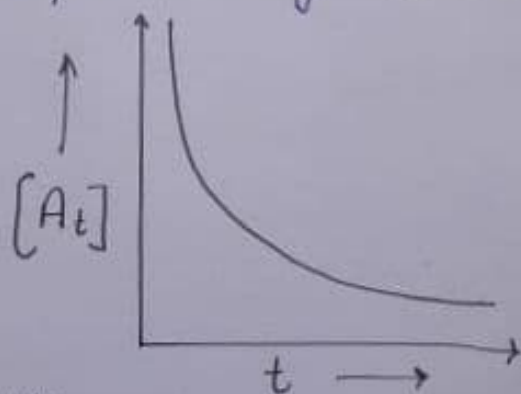
$$\text{Slope} = -\frac{k}{2.303}$$



→ Exponential form of first order reaction :-

$$[A_t] = [A_0] e^{-kt}$$

The concentration of reactant in first order reaction decreases exponentially with time.



→ Half life of first order reaction :-

$$\text{At } t_{1/2}, [A_t] = \frac{[A_0]}{2}$$

$$\therefore k = \frac{2.303}{t_{1/2}} \log \frac{[A_0]}{\frac{[A_0]}{2}}$$

$$k = \frac{2.303}{t_{1/2}} \log 2 = \frac{2.303 \times 0.301}{t_{1/2}}$$



Example ①: A first order reaction has a specific reaction rate of  $10^{-3} \text{ s}^{-1}$ . How much time will it take for  $\log m$  of the reactant to reduce to 2.5 gm?

Solution :-  $k = \frac{2.303}{t} \log \frac{[A_0]}{[A_t]}$

$$t = \frac{2.303}{10^{-3}} \log \frac{10}{2.5}$$

$$t = 2303 \times 0.301 \times 2 = \boxed{1386 \text{ s}}$$

Example ② :- A first order reaction is found to have a rate constant  $k = 7.39 \times 10^{-5} \text{ s}^{-1}$ . Find the half life of this reaction.

Solution :- For first order reaction.

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

For  $t = t_{1/2}$ ,  $x = a/2$

$$t_{1/2} = \frac{2.303}{k} \log \frac{a}{a - \frac{a}{2}}$$

$$= \frac{2.303}{k} \log 2$$

$$= \frac{2.303 \times 0.3010}{7.39 \times 10^{-5}}$$

$$= \boxed{9.38 \times 10^3 \text{ s}}$$

Example ③ :- Half life for a first order reaction is 20 minutes. What is its rate constant?

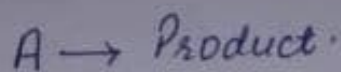
Solution:  $t_{1/2} = 20 \text{ min}$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{20} = \boxed{3.47 \times 10^{-2} \text{ min}^{-1}}$$



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→ RADIOACTIVE DECAY AS A FIRST ORDER PHENOMENON



Let  $N$  be the part of  $A$  at initial conc.

+  $N_0$  be the part of  $A$  at time  $t$

$$\therefore \text{Rate of rxn.} \therefore -\frac{dN}{dt} \propto N$$

$$\text{or } -\frac{dN}{dt} = kN$$

$$\text{or } -\frac{dN}{N} = kdt$$

On Integrating we get,

$$\int_{N_0}^{N} \frac{dN}{N} = \int_{t=0}^{t} kdt$$

$$[-\ln N] = kt + I \quad \text{--- (1)}$$

(Where  $I$  is the integration constant)

If time  $t=0$  +  $N=N_0$ ,

Then eqn. (1) becomes,

$$-\ln N_0 = I$$

Putting the value of  $I$  in eqn. (1), we get.

$$-\ln N = kt + (-\ln N_0)$$

$$\text{or } kt = \frac{-\ln N_0}{-\ln N}$$

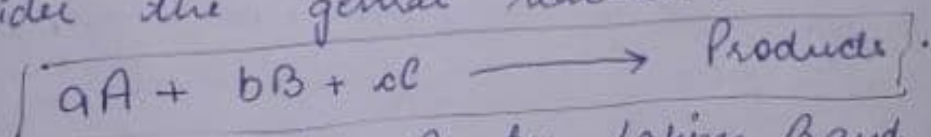
$$\text{or } k = \frac{1}{t} \ln \frac{N_0}{N}$$

$$\boxed{k = \frac{2.303}{t} \log \frac{N_0}{N}} \quad \#$$



## → General methods for determination of order of reaction: - Page: -08

1. **Astwald's Isolation method** :- This method was introduced by Ostwald in 1902 and is used to find the order of a reaction with respect to one reactant at a time. The total order of the reaction is then equal to the sum of the orders of reaction for individual reactants. This method is based on the principle that if <sup>the</sup> concentration of all but one reactant are taken in excess, then during the course of the reaction, the concentration of those reactants taken in excess will remain almost constant and hence variation in rate will correspond to the concentration of that reactant whose concentration is small. This process is repeated with other reactants one by one and order with respect to each reactant is determined. The overall order will be the sum of all these orders. For example, consider the general reaction :-

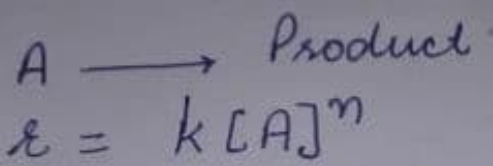


Suppose we isolate A by taking B and C in large excess and get order of reaction with respect to A (say p). Similarly, we isolate B by taking A and C in excess and get order with respect to B (say q) and C (say r) respectively.

Overall order of reaction :-

$$n = p + q + r$$

2) Differential Method:- (Van't Hoff) Page:- 09.



$$r = k[A]^n$$

$$-\frac{dx}{dt} = k(x)^n$$

$$\log\left(-\frac{dx}{dt}\right) = \log k(x)^n$$
$$= \log k + \log(x)^n$$

$$\log\left(-\frac{dx}{dt}\right) = \log k + n \log x \quad \text{--- (1)}$$

$$-\frac{dy}{dt} = k(y)^n$$

$$\log\left(-\frac{dy}{dt}\right) = \log k + n \log y \quad \text{--- (2)}$$

Subtracting eqn (2) from (1)

$$\log\left(-\frac{dy}{dt}\right) - \log\left(-\frac{dx}{dt}\right) = n \log y - n \log x$$
$$= n (\log y - \log x)$$

$$\Rightarrow \boxed{n = \frac{\log\left(-\frac{dy}{dt}\right) - \log\left(-\frac{dx}{dt}\right)}{\log y - \log x}}$$



→ 3) Integration Method: - In this method is also known as method of trial and error. The kinetic data is fitted to different integrated rate equation. Whenever the data fit with the eqn. for correct order of rxn., it will give constant value of rate constant of all data points (concent diff times).

\* Alternatively, graphical method can be

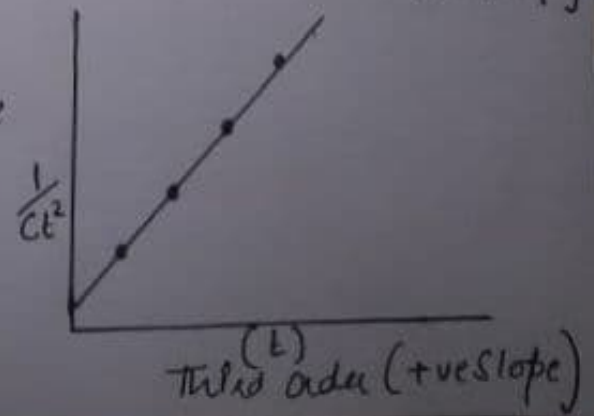
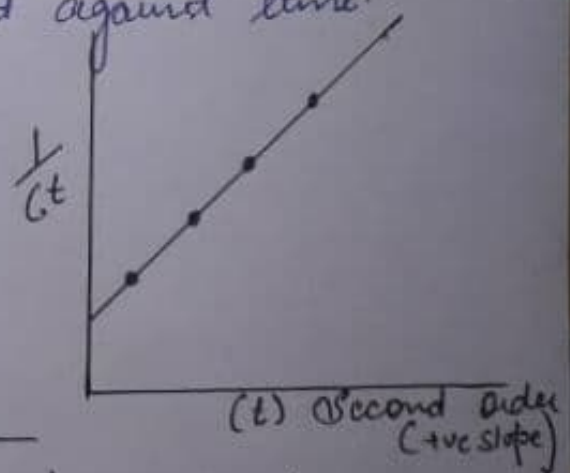
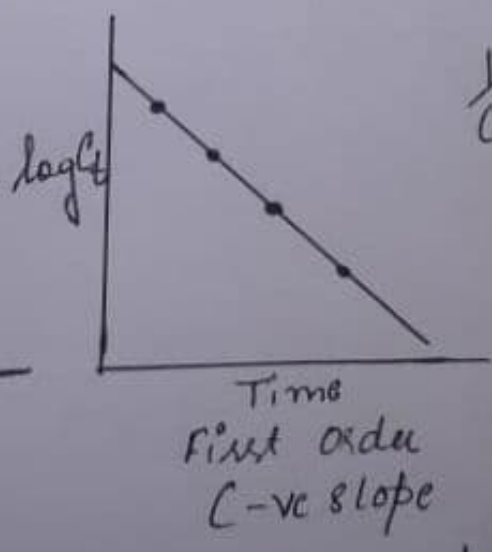
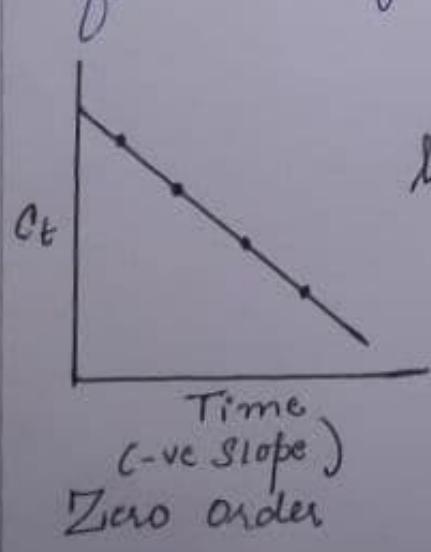
Zero order :-  $k = \frac{1}{t} [A_0 - A] \rightarrow k = \frac{1}{t} [C_0 - C_t]$ .

First order :-  $k = \frac{2.303}{t} \log \frac{A_0}{A} = \frac{2.303}{t} \log \frac{C_0}{C_t}$ .

For Second order :-  $k = \frac{1}{t} \left[ \frac{1}{A} - \frac{1}{A_0} \right] = \frac{1}{t} \left[ \frac{1}{C_t} - \frac{1}{C_0} \right]$ .

For Third order :-  $= \frac{1}{2t} \left[ \frac{1}{C_t} - \frac{1}{C_0} \right]$ .

\* Alternatively, graphical method can also be applied for integrated rate eqn. In this method, appropriate function of conc. is plotted against time.



4) **Half life Method**:- This method is based on the principle that if the reaction is of the  $n^{\text{th}}$  order in a reactant, then half life is inversely proportional to  $(n-1)^{\text{th}}$  power of its initial concentration.

**For eg:-** If initial conc. of a reactant is  $C_1$  & half life period is  $(t_{1/2})_1$ ; if initial conc. of a reactant is  $C_2$  & half life period is  $(t_{1/2})_2$ .

then.

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left[ \frac{C_2}{C_1} \right]^{n-1}$$

$$\text{or } \log (t_{1/2})_1 / \log (t_{1/2})_2 = (n-1) \log C_2 / C_1$$

$$\text{or } n = 1 + \frac{\log (t_{1/2})_1 / \log (t_{1/2})_2}{\log C_2 / C_1}$$

From this,  $n$  can be calculated.



**Half life, Period** ~~Matrix~~:- Half life period of a reaction is defined as the time during which the concentration of a reactant is reduced to half of its initial concentration.

In other words, it may also be stated as the time in which the half of a reaction is completed.

• It is generally denoted as  $t_{1/2}$ .

\* The half life period of a first order reaction may be calculated as given below:-

$$\text{At } t_{1/2}, [A_t] = \frac{[A_0]}{2}$$

$$\therefore k = \frac{2.303}{t_{1/2}} \log \frac{[A_0]}{\frac{[A_0]}{2}}$$

$$k = \frac{2.303}{t_{1/2}} \log 2 = \frac{2.303 \times 0.301}{t_{1/2}} [A_0]$$

$$t_{1/2} = \frac{0.693}{k}$$

Thus, half life period of a first order reaction is independent of the initial conc. of the reactant.

\* The half life period of a zero order reaction may be calculated as:-

For a zero order rxn., rate constant is given by

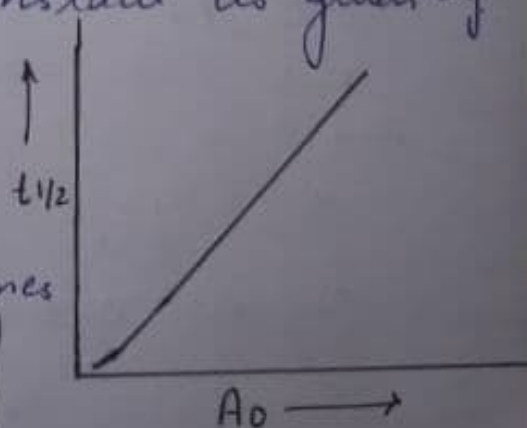
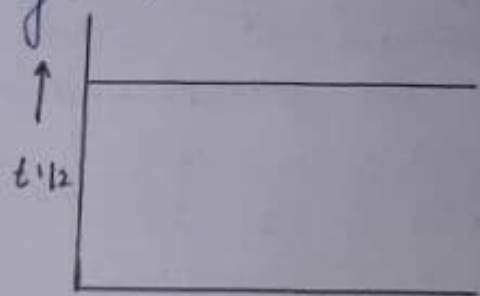
$$k = \frac{[A_0] - [A_t]}{t}$$

$$\text{At } t = t_{1/2}, [A_t] = \frac{1}{2} [A_0]$$

The rate constant at  $t_{1/2}$  becomes

$$k = \frac{[A_0] - \frac{1}{2} [A_0]}{t_{1/2}} \rightarrow t_{1/2} = \frac{[A_0]}{2k}$$

$t_{1/2}$  for a zero order reaction is directly proportional to the initial conc. of the reactant.



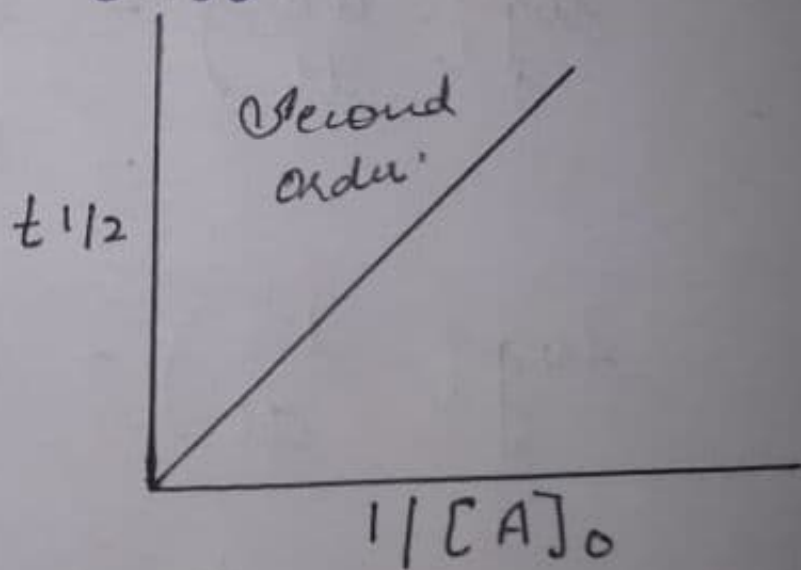
# Similarly, half life period of a second order can be calculated.

$$kt = \frac{1}{[A]} - \frac{1}{[A]_0}$$

For half life period,  $t_{1/2} = [A] = [A]_0/2$

$$\therefore kt_{1/2} = \frac{2}{[A]_0} - \frac{1}{[A]_0} = \frac{1}{[A]_0}$$

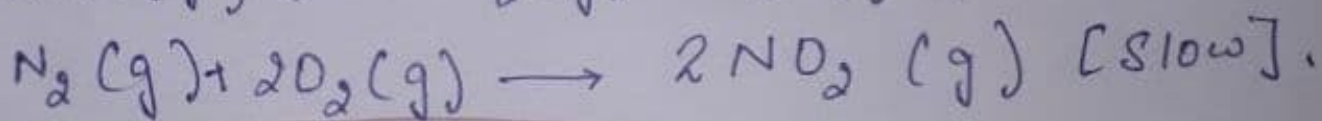
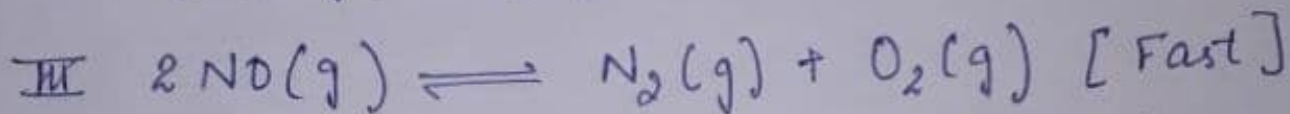
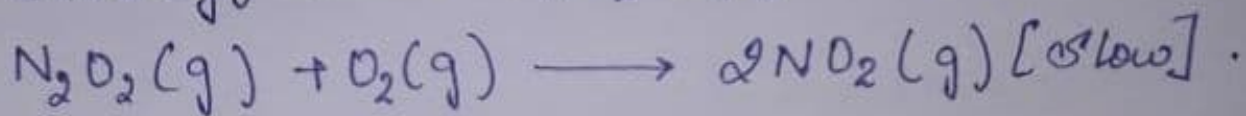
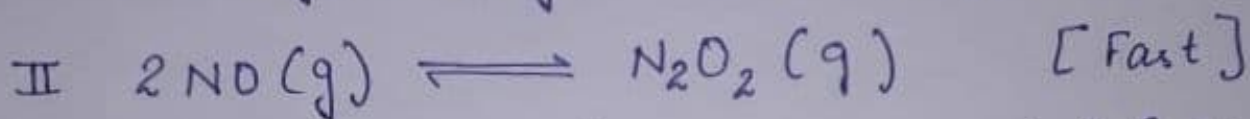
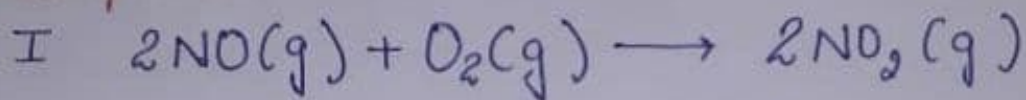
$$\therefore \boxed{t_{1/2} = \frac{1}{k[A]_0}}$$



## → COMPLEX REACTIONS:

Chemical reactions which proceed through more than one steps are termed as complex reactions; and detailed description of various steps of the complex chemical reaction is called mechanism of reaction.

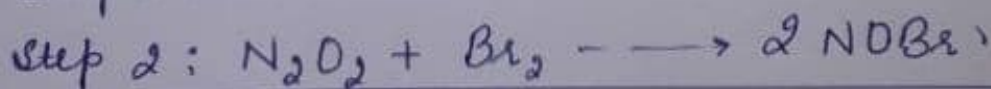
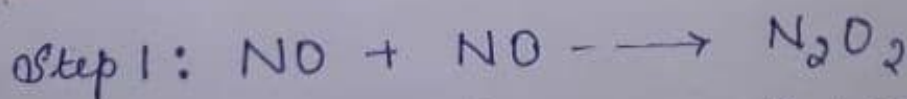
Example. ①



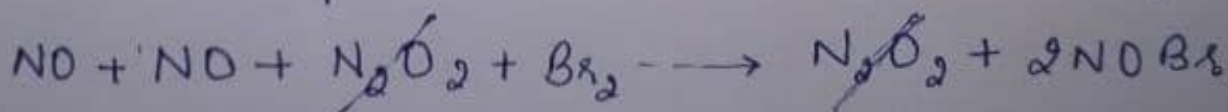
$$\text{Rate} = k[\text{NO}]^2[\text{O}_2]$$

All the above steps proceed at diff. rates and slowest step of mechanism is called rate determining step, and rate law is written for slowest step.

Mechanism:-



Now, we add up the terms on both the sides of rxn.



Reaction :-





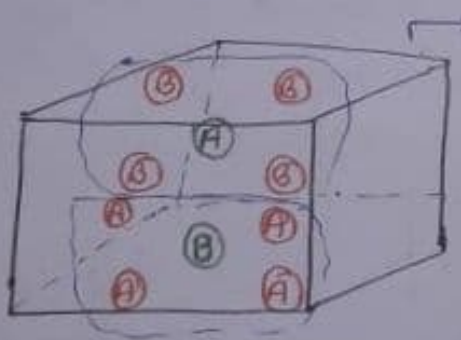
# → COLLISION THEORY:-

This theory is based upon the kinetic theory of gases according to which the molecules of a gas are continuously moving and hence colliding with each other. Hence, for a collision to take place, atleast 2 molecules must be involved. Then it is called as bimolecular reactions.

\* The basic idea of this theory is that, chemical reaction occurs only as a result of collisions b/w the reacting molecules. During this collision atoms get rearranged.

→ Acc. to classical collision theory, molecules must collide to react and rate of chemical rxn  $\propto$  No. of reacting molecules

It accounts for the dependence of the rate on the product of concentration terms.



A is surrounded by 4 molecules of B.

B is surrounded by 4 molecules of A.

Then how many ways collision b/w A + B occur?

One A molecule can collide with any of 4(B) molecules hence, it has 4 opportunities for collisions. The same is true for each of 4 A molecules, making 16 possible collision on all. Therefore, assuming the reaction rate is proportional to the no. of collisions. i.e. collision/sec.

Thus rate of reaction  $\propto$  product of concentration  
rate  $\propto [A][B]$



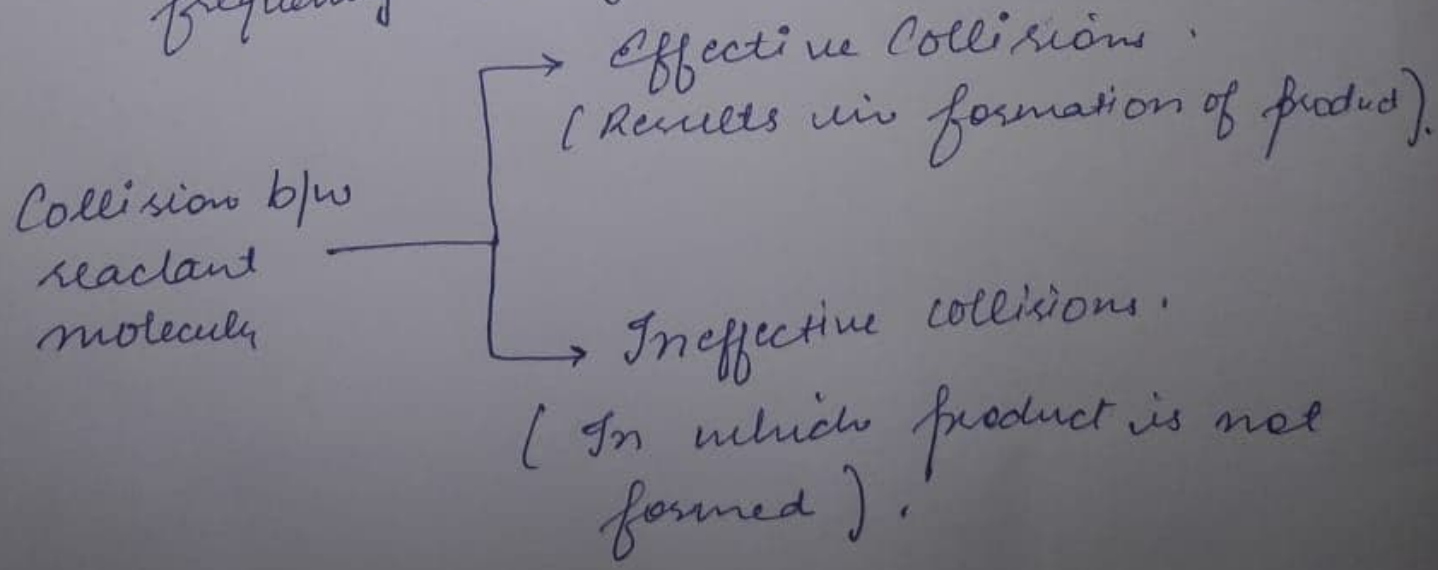
→ Postulates of Collision Theory:-

I Collisions between reactant molecules are responsible for the formation of product molecules. This means 2 molecules must collide with each other.

II All the collisions do not lead to product formation i.e every collision does not bring a chemical change. The collisions that actually produce the products are effective collisions. These effective collisions which bring chemical change are few in comparison to total no. of collisions. The collisions that do not form a product are termed as ineffective elastic collision. i.e molecules just collide and disperse in different direction with different velocities. Rate of reaction is governed by collision frequency. (Z).

[Z = No. of collisions per sec. per unit vol. of reaction molecules].

→ If collisions are supposed to be effective. [Actually it is not possible]. i.e every collision result in formation of product then rate of reaction must be very high and equal to collision frequency.



$K = Z \times f$  If  $f = 1$ , then  $K = Z$

Thus, rate of reaction is governed by effective collisions.

Relation b/w rate of reaction  $(-\frac{dx}{dt})$  & collision frequency  $(Z)$

Now, according to KT of gases, the fraction of molecules in a gas possessing energy greater than a particular value  $E$ . i.e.  $E_a$ .

So,  $f = \frac{\Delta N}{N} = e^{-E_a/RT}$   
 $\Delta N =$  No. of molecules possessing energy greater than  $E$ .  
 $N =$  Total no. of molecules.  
*Boltzmann factor*

Putting these values,  $K = Z \times f$

$K = Z \times e^{-E_a/RT}$

III) Two factors decide whether collision will be effective or not and these are:-

- i) Energy factor      ii) Orientation factor

1) ENERGY factor :- For an effective collision the colliding molecules must possess a certain minimum value of energy called threshold energy.

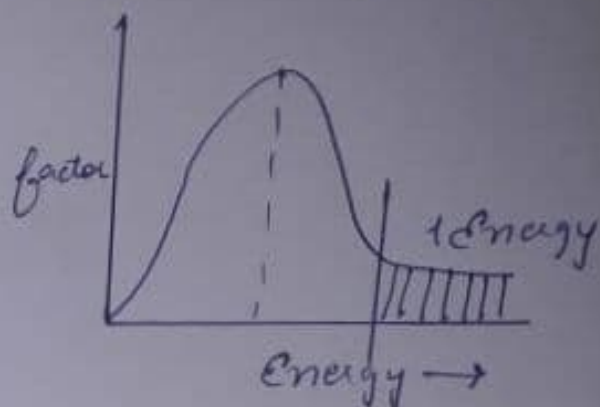
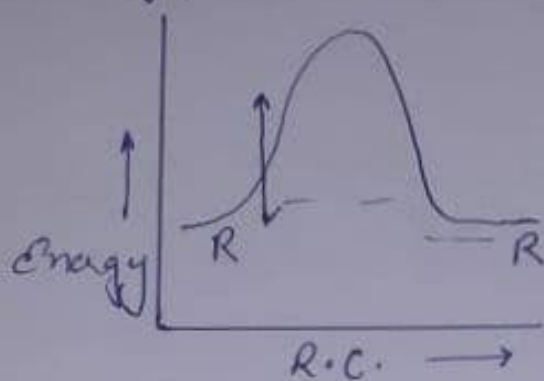
\* The molecules which possess this min. value of energy are called Active molecules.

\* While others are called passive molecules. These molecules are made active by supplying them a definite amount of energy which is equal to the activation energy.

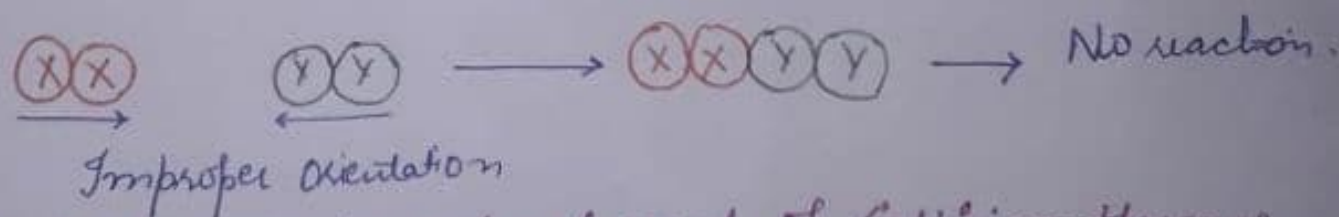
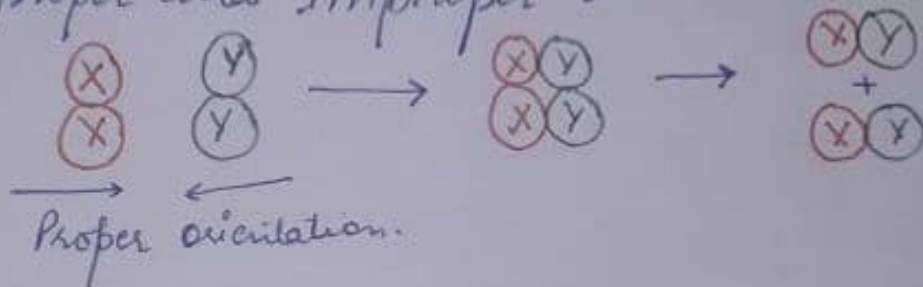


Passive molecules  $\xrightarrow{+E_a}$  Active molecules. Page: - 18

$E_a = T \cdot \text{Energy} - \text{Energy of reactant molecules}$ .  
 At a given temp.  $T$  :- The fraction of molecules possessing energy  $\geq E_a$ ; is given by Boltzmann factor.



2) Orientatation factors :- The reacting molecules must collide in a proper orientation so that the old bonds break + new bonds are formed. The proper and improper orientations are shown below.



→ Mathematical treatment of Collision theory :-

$$\text{Rate of Reaction} : \frac{dn}{dt} = Z_{AB} e^{-E_a/RT} \quad \text{--- (1)}$$

$Z_{AB}$  = No. of binary collision/sec. between 2 molecules A & B in 1 ml of gas.

$E_a$  = Activation energy.

From K.T of gases, reaction velocity

$$\frac{dx}{dt} \propto n^2$$

$$\text{So, } \frac{dx}{dt} = k [n]^2 \text{ --- (2)}$$

k = specific reaction rate.

n = Concentration of reactant.

From eqn. (1) + (2), we get:

$$k = \frac{Z_{AB}}{n^2} e^{-E_a/RT} \text{ --- (3)}$$

$$\text{or } k = Z_{AB} e^{-E_a/RT} \text{ --- (4)}$$

$Z_{AB}$  = Collision frequency.

From the simple K.T of gases, the value of  $Z_{AB}$  is given by:-

$$Z_{AB} = 4n^2 \sigma^2 \left[ \frac{\pi RT}{M_{AB}} \right]^{1/2} \text{ --- (5)}$$

$\sigma$  = Collision diameter.

Substituting the value of eq. (5) in eq. (4), we get.

$$k = \frac{4n^2 \sigma^2 \left( \frac{\pi RT}{M_{AB}} \right)^{1/2} e^{-E_a/RT}}{n^2}$$

$$k = 4\sigma^2 \left( \frac{\pi RT}{M_{AB}} \right)^{1/2} e^{-E_a/RT} \text{ --- (6)}$$

$$k = Z e^{-E_a/RT} \text{ --- (7)}$$

$Z = 4\sigma^2 \left( \frac{\pi RT}{M_{AB}} \right)^{1/2}$   
↓  
Collision frequency



Taking log of eq. (6) we get,

$$\log k = \log \left[ 4\sigma^2 \left( \frac{\pi RT}{M_{AB}} \right)^{\frac{1}{2}} \right] - \frac{E_a}{RT}$$

Differentiating temperature we get.

$$\frac{d(\log k)}{dt} = \frac{1}{2T} + \frac{E_a}{RT^2} \quad \left( \text{The expression } \frac{1}{2T} \text{ can be ignored in comparison with } \frac{E_a}{RT^2} \right)$$

Then this eqn. can become as.

$$\frac{d(\log k)}{dt} = \frac{E_a}{RT^2} \quad \left[ \text{Identical to Arrhenius eqn.} \right]$$

Since, if the reaction involves 2 different molecules, then the value of collision frequency ( $Z$ ).

$$Z = \sigma^2 \left[ \frac{8KT}{\pi M_{AB}} \right]^{\frac{1}{2}} \pi$$

Thus,

$$\text{Rate} = \left( \frac{8KT}{\pi M_{AB}} \right)^{\frac{1}{2}} \pi \sigma^2 \cdot e^{-E_a/RT}$$

$M_{AB}$  or  $(M)$

$(M)$  = Reduced mass of A + B.

$$M_{AB} = \frac{M_A \times M_B}{M_A + M_B}$$

$M_A + M_B$  are molecular masses of A + B.

There are several reactions where calculated & experimental values of  $k$  differ widely. In order to account for the deviations a factor ' $P$ ' was introduced.

$$k = P \cdot Z_{AB} \times e^{-E_a/RT}$$

$P$  = steric factor

→ Second Order Reaction: - It is a type of chemical reaction that depends on the concentrations of one-second order reactant or two first-order reactants. This reaction proceeds at a rate proportional to the square of the concentration of one reactant, or the product of the concentrations of two reactants.

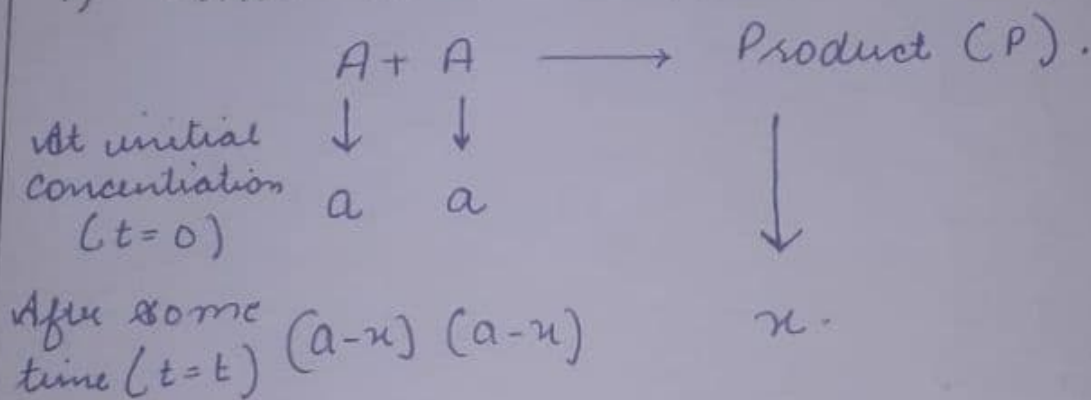
eg:- Decomposition of nitrogen peroxide.



$$\text{Rate} = k [\text{NO}_2]^2.$$

→ Integrated Rate Equation: -

i) When both the reactants are same.



$$\begin{aligned} \text{Rate } \frac{dx}{dt} &= k [A][A] \\ &= k (a-x)(a-x) \end{aligned}$$

$$\frac{dx}{dt} = k (a-x)^2.$$

$$\text{or } \frac{dx}{(a-x)^2} = k dt.$$

Integrating b/s within limits, we get.

$$\int_{x=0}^{x=x} \frac{dx}{(a-x)^2} = k \int_{t=0}^{t=t} dt.$$

$$\int (a-x)^{-2} dx = k \cdot t + C.$$

$$\frac{-(a-x)^{-2+1}}{-2+1} = k \cdot t + C.$$

$$\frac{(a-x)^{-1}}{-1} = k \cdot t + C.$$

$$\boxed{\frac{1}{a-x} = k \cdot t + C} \text{ --- (i)}$$

Now, value of  $C$ ; at  $t=0$  &  $x=0$

$$\boxed{\frac{1}{a} = C}$$

Now, putting the value of  $C$  in eqn. (i), we get,

$$\frac{1}{(a-x)} = k \cdot t + \frac{1}{a}.$$

$$\frac{1}{(a-x)} - \frac{1}{a} = k \cdot t.$$

$$\frac{a - (a-x)}{a \cdot (a-x)} = k \cdot t.$$

$$\frac{x}{a \cdot (a-x)} = k \cdot t.$$

$$\boxed{\frac{x}{a \cdot (a-x)} = k \cdot t} \text{ --- (ii).}$$



Equation (ii) is known as rate constant for second order reaction in terms of same reactant concentration.

In eq. (ii) if the initial concentration i.e.  $a = A_0$  and concentration after time 't'  $x = (A_0 - A_t)$  then the above equation becomes :-

$$\left[ \frac{A_0 - A_t}{A_0 [A_0 - (A_0 - A_t)]} \right] = kt.$$

$$\frac{A_0 - A_t}{A_0 (A_0 - A_0 + A_t)} = kt$$

$$\therefore \left( \frac{A_0 - A_t}{A_0 \cdot A_t} \right) = kt$$

$$\therefore \left[ k = \frac{1}{t} \left[ \frac{1}{A_t} - \frac{1}{A_0} \right] \right] \text{ --- (iii)}$$

Eqn. (iii) represents another form of equation (ii)

Hence Proved

# Second Order Reaction

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When both the reactants are diff.

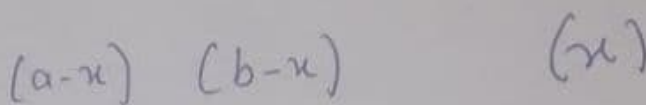
Consider a general reaction



At initial  
conc.  $t=0$



After some  
time  $t=t$



$$\text{Rate} = \frac{dx}{dt} \times (a-x)(b-x)$$
$$\text{or } \frac{dx}{dt} = k(a-x)(b-x)$$

Where  $k$  is rate constant

$$\frac{dx}{(a-x)(b-x)} = k \cdot dt \quad \text{--- (i)}$$

By using partial fraction in eqn (i), we get

$$\frac{1}{(a-x)(b-x)} = \frac{A}{a-x} + \frac{B}{b-x} \quad \text{--- (ii)}$$

$$1 = \frac{A(a-x)(b-x)}{(a-x)} + \frac{B(a-x)(b-x)}{(b-x)}$$

$$1 = A(b-x) + B(a-x)$$

$$\text{At } x=a \quad 1 = A(b-a) + B(0)$$

$$1 = A(b-a)$$

$$\boxed{A = \frac{1}{b-a}}$$

$$\text{At } x=b$$

$$1 = A \times 0 + B(a-b)$$

$$1 = B(a-b)$$

$$\boxed{B = \frac{1}{a-b}}$$

Now, putting the values of A+B Page: - 25  
in eqn. (ii), we get.

$$\frac{1}{(a-x)(b-x)} = \frac{1}{(b-a)(a-x)} + \frac{1}{(a-b)(b-x)}$$

$$= \frac{-1}{(a-b)(a-x)} + \frac{1}{(a-b)(b-x)}$$

$$\frac{1}{(a-b)} \left[ \frac{1}{(b-x)} - \frac{1}{(a-x)} \right] dx = k \cdot dt.$$

$$\frac{1}{(a-b)} \left[ \frac{dx}{(b-x)} - \frac{dx}{(a-x)} \right] = k \cdot dt. \quad \text{--- (iii)}$$

Integrating eqn. (iii), we get.

$$\frac{1}{(a-b)} [-\ln(b-x) + \ln(a-x)] = kt + I.$$

Where  $I$  is integration constant.

$$\frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} = kt + I. \quad \text{--- (iv)}$$

Putting the values of  $t=0$ ,  $x=0$  in eqn. (iv),  
we get.

$$\frac{1}{(a-b)} \ln \frac{(a-0)}{(b-0)} = k \times 0 + I.$$

$$\text{or } \boxed{\frac{1}{(a-b)} \ln \frac{a}{b} = I.}$$

Substituting the values of  $I$  in eqn. (iv),  
we get.



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$$\frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} = kt + \frac{1}{(a-b)} \ln \frac{a}{b}$$

$$\text{or } \frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} - \frac{1}{(a-b)} \ln \frac{a}{b} = kt$$

$$\text{or } \frac{1}{(a-b)} \left[ \ln \frac{(a-x)}{(b-x)} - \ln \frac{a}{b} \right] = kt$$

$$\text{or } \frac{1}{(a-b)} \ln \frac{b(a-x)}{a(b-x)} = kt$$

$$\text{or } k = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

$$\text{or } \boxed{k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}}$$

Hence, proved

## → Activated Complex Theory :-

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The excess energy (over and above the average energy of the reactants) which must be supplied to the reactants to undergo chemical reaction is called activation energy,  $E_a$ . It is equal to the difference b/w the threshold energy needed for the reaction and the average kinetic energy of all the reacting molecules. That is;

$$\left\{ \begin{aligned} \text{Activation Energy} &= \text{Threshold energy} - \text{Average kinetic energy} \\ &\text{of the reacting molecules} \\ \text{or } E_a &= E(\text{threshold}) - E(\text{reactants}). \end{aligned} \right.$$

Each reaction has definite value of  $E_a$  and this decides the fraction of total collisions which are effective. If the activation energy for a reaction is low, larger number of molecules can have this energy and the fraction of effective collisions,  $f$ , will be large. This rxn will proceed at high rate. On the other hand, if the activation energy is high, then fraction of effective collisions will be small and the reaction may be quite slow. Thus.

Low activation energies : Fast reactions

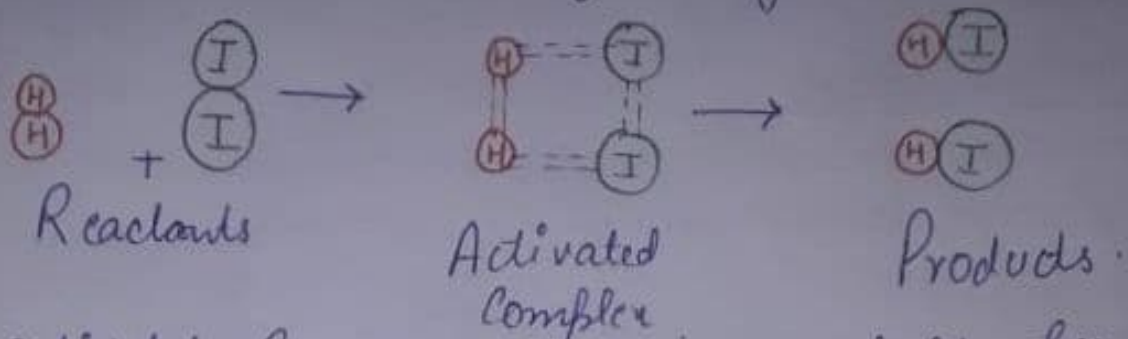
High activation energies : Slow reactions.

\* Activated Complex State :- When the colliding molecules possess the K.E equal to  $E_a$ , the atomic configuration of species formed at this stage is different from the reactants as well as the products. This stage is called the activated state or transition state. and specific configuration of this state is called activated complex or intermediate.

For example :- In the rxn. b/w  $H_2(g)$  and  $I_2(g)$ ,



activated complex has configuration Page No:-28  
 in which H-H and I-I bonds are breaking  
 and H-I bonds are forming as shown;

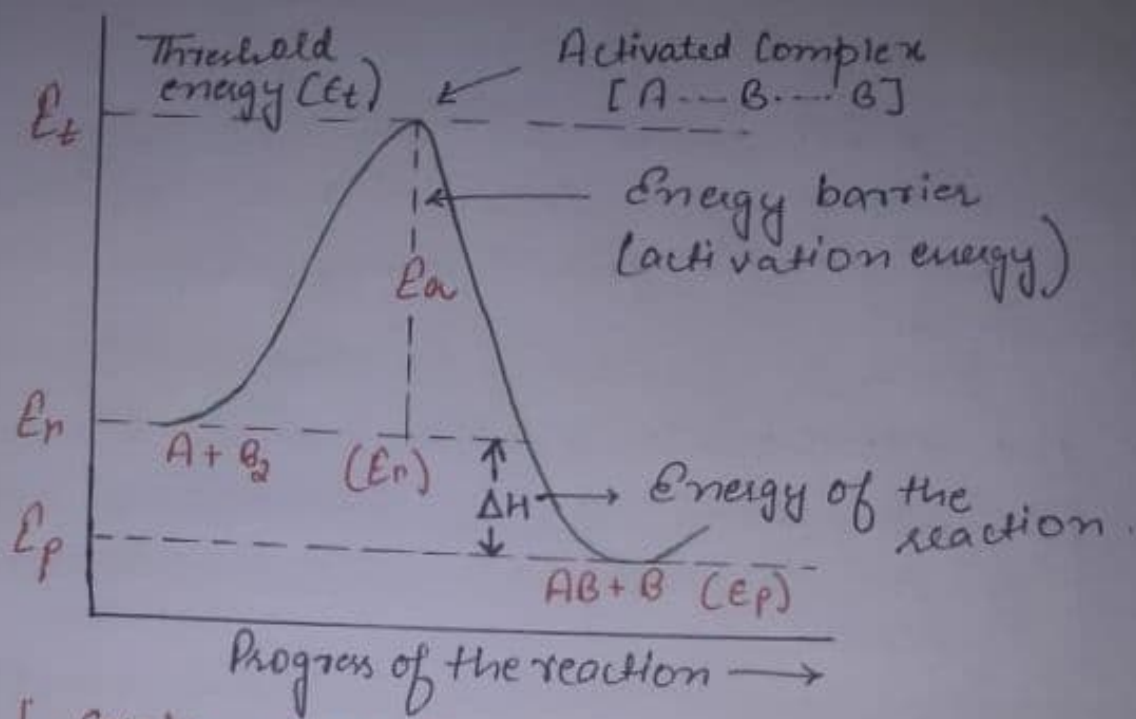


\* This activated complex state is unstable transition state of the reacting system which is mid-way b/w the reactants and the products. It has a very short life span (being highly unstable) and splits into the products to acquire stable state of lower energy.

\* Progress of a Reaction:- Acc. to the concept of activation energy, the reactants don't change directly into the products. The reactants first absorb energy equal to activation energy and thereby form activated complex. At this state, the molecules have energy atleast equal to threshold energy. This means that the reaction involves some energy barrier which must be overcome before products are formed. The energy barrier is known as Activation energy barrier. In graphical representation of the reaction, the energy barrier is shown as an energy hump which has to be crossed before reactants go to the products.

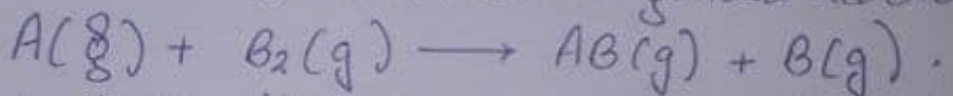
(Graph No:-01)





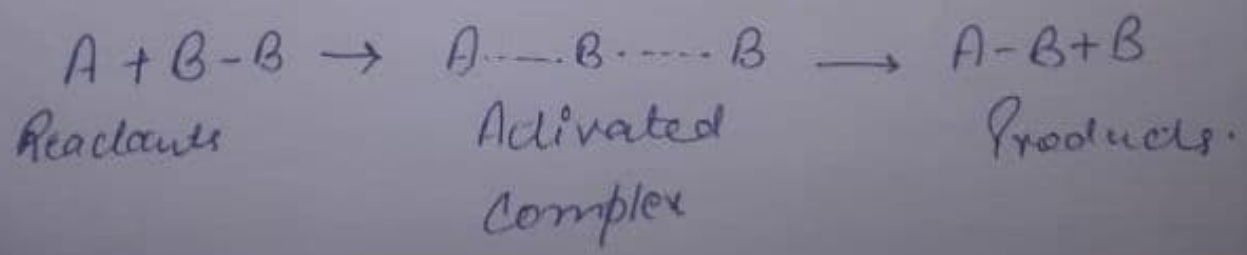
[ Graph no: - 01 ]

As an illustration, consider the general reaction,

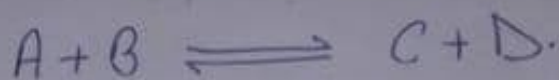


The reactants have the average energy,  $E_r$  and the products have the energy  $E_p$ . The reaction involves the approach of an atom  $A$  to a molecule  $B_2$ . The reaction cannot occur until the colliding reactants  $A + B_2$  possess sufficient energy to reach the top of the energy barrier and form activated complex. The energy required to form activated complex is called

activation energy. The activated complex formed  $[A \dots B]$  has a very short life span and splits into the products. This may be shown as:-



reactions.  
Consider a reversible reaction:-



Mathematically,  $E_a$  (forward) and  $E_a$  (backward) are related to the overall energy change,  $\Delta H$  in the process as:-

$$\Delta H = E_a (\text{forward}) - E_a (\text{backward}).$$

For the exothermic reaction.

$$\left[ \begin{array}{l} \text{Activation energy} \\ \text{for the forward} \\ \text{reaction} \end{array} \right] < \left[ \begin{array}{l} \text{Activation energy} \\ \text{for the backward} \\ \text{reaction} \end{array} \right].$$

$$E_a (\text{forward}) < E_a (\text{backward}).$$

$$\text{Thus, } \Delta H = E_a (\text{forward}) - E_a (\text{backward}) = \boxed{-ve}.$$

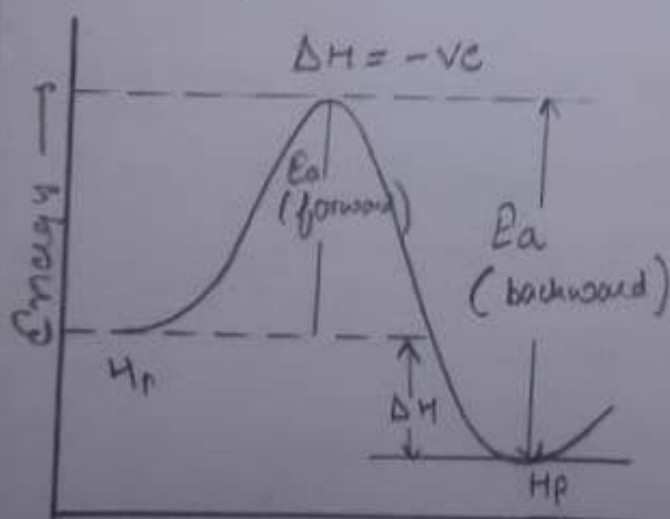
On the other hand, for endothermic reaction

$$\left[ \begin{array}{l} \text{Activation energy for} \\ \text{the forward reaction} \end{array} \right] > \left[ \begin{array}{l} \text{Activation energy for} \\ \text{the backward reaction} \end{array} \right].$$

$$E_a (\text{forward}) > E_a (\text{backward}).$$

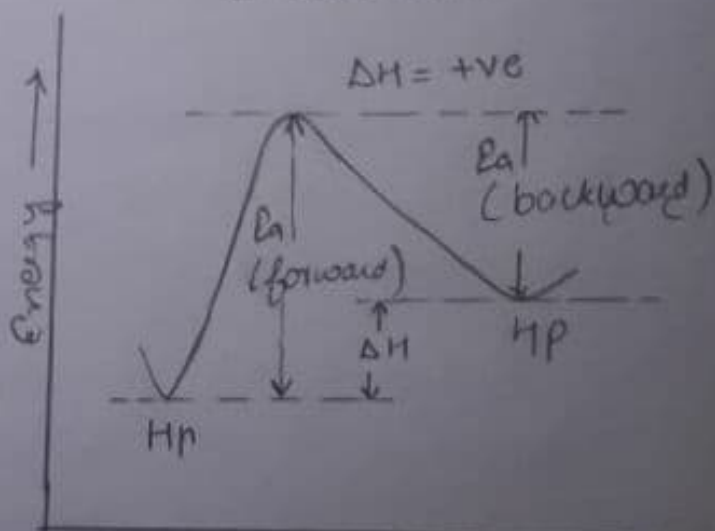
$$\text{Thus, } \Delta H = E_a (\text{forward}) - E_a (\text{backward}) = \boxed{+ve}$$

Exothermic Run.



Progress of Reaction  $\rightarrow$   
(a)

Endothermic Run



Progress of reaction  $\rightarrow$   
(b)

## → Numerical problems :-

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Example 1 :- The rate constant  $k$  for the first order gas phase decomposition of ethyl iodide,  $C_2H_5I \rightarrow C_2H_4 + HI$  is  $1.60 \times 10^{-5} s^{-1}$  at 600K and  $6.36 \times 10^{-3} s^{-1}$  at 700K. Calculate the energy of activation for this reaction.

Soln :- We are given.

$$k_1 = 1.60 \times 10^{-5} s^{-1}; T_1 = 600K$$

$$k_2 = 6.36 \times 10^{-3} s^{-1}; T_2 = 700K.$$

We know that  $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$

Substituting the values of  $k_1, k_2$  &  $R (= 8.314 JK^{-1} mol^{-1})$ ,

We get.

$$\log \frac{6.36 \times 10^{-3}}{1.60 \times 10^{-5}} = \frac{E_a}{2.303 \times 8.314} \left[ \frac{1}{600} - \frac{1}{700} \right]$$

$$\log (3.98 \times 10^2) = \frac{E_a}{(19.15) \times (4200)}$$

$$\therefore E_a = 2.6 \times 19.15 \times 4200 J mol^{-1} = 2.09 \times 10^5 J mol^{-1} \\ = 209 kJ mol^{-1}$$

Example 2 :- What would be the energy of activation for a reaction when a change of temperature from 20°C to 30°C exactly triples the reaction rate constant?

Solution :- We are given,

$$T_1 = 273 + 20 = 293K; \quad k_1 = k \text{ (say)}$$

$$T_2 = 273 + 30 = 303K; \quad k_2 = 3k$$

Substituting these values in eqn: -

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right] \text{ We get,}$$



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$$\log \frac{3K}{K} = \frac{E_a}{2.303 \times 8.314} \cdot \left[ \frac{303 - 293}{303 + 293} \right]$$

$$\text{or } \log 3 = \frac{E_a}{2.303 \times 8.314} \times \left[ \frac{303 - 293}{303 + 293} \right]$$

$$\text{or } E_a = 81100 \text{ joules mol}^{-1} \text{ or } 81.100 \text{ kJ mol}^{-1}$$

Example 3  $\Rightarrow$  Half life of a first order chemical reaction is 69 hr at 300K. Also, rate of this reaction is doubled as temperature is increased from 300K to 310K. Determine activation energy and pre-exponential factor for this reaction.

Solution  $\Rightarrow \frac{k_{310}}{k_{300}} = 2$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log 2 = \frac{E_a}{2.303R} \left[ \frac{310 - 300}{310 \times 300} \right] = \frac{10E_a}{300 \times 310 \times 2.303}$$

$$E_a = 53.60 \text{ kJ mol}^{-1}$$

At 300K :-

$$t_{1/2} = 69 \text{ hr.}$$

$$k = \frac{0.693}{69} = 0.01 \text{ hr}^{-1}$$

Now applying the Arrhenius equation

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln(0.01) = \ln A - \frac{53600}{8.314 \times 300}$$

$$A = 2.15 \times 10^7 \text{ hr}^{-1}$$

Example 4: If the rate of a reaction gets doubled as the temperature is increased from  $27^\circ\text{C}$  to  $37^\circ\text{C}$ . Find the activation energy of reaction?

Solution:  $\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$

$$\ln 2 = \frac{E_a}{R} \left[ \frac{10}{300 \times 310} \right]$$

$$E_a = 9300 R \ln 2 = 53.4 \text{ kJ mol}^{-1}$$

Example 5: Rate constant  $k$  of a reaction varies with temperature according to the eqn.

$$\log k = \text{constant} - \frac{E_a}{2.303R} \left( \frac{1}{T} \right)$$

Where  $E_a$  is the energy of activation for the reaction. When a graph is plotted for  $\log k$  versus  $\frac{1}{T}$ , a straight line with a slope  $-6670 \text{ K}$  is obtained. Calculate the energy of activation for this reaction.

Solution: Slope of the line =  $\frac{-E_a}{2.303R} = -6670 \text{ K}$

$$E_a = 2.303 \times 8.314 \times 6670$$

$$= 127.7114 \text{ kJ mol}^{-1}$$

Question 6: Why reactions having high molecularity are less observed?

Answer: A reaction takes place because the molecules collide. The chances of a large number of molecules or ions to collide simultaneously are less. Hence, the reactions of higher molecularity are less observed.