T. D C 2nd Semester (Regular).

Theory of reaction rate (collision-theory).

According to collision-theory.

(i) Reactants are made up of molecules.

(ii) Molecules are always in a state of random motion, and hence go on colliding with each other.

The collision frequency Z is the number of inter molecular collision taking place per unit volume per unit time at a given temperature.

$$Z_{AB} = N_A N_B \sigma^2 \left(\frac{8\pi KT}{\mu}\right)^{1/2}$$

Where Z_{AB} is the collision frequency between the molecules A and B.

σ = collision diameter

N_A, N_B are the number of molecules of A and B per unit volum. μ is the reduced mass $\mu = \frac{m_A m_B}{m_A + m_B}$.

(iii) Only those collisions are effective in producing the products in which the relative translational kinetic energy of the colliding molecules (E_{tr}) exceeds the threshold energy (E_{Th}).

(iv) The colliding molecules must be properly oriented.

According to hard sphere collision-theory. the rate of a reaction will be proportional to

(a) The number of collision per unit volume per second. (Collision frequency).

(b) The ~~Effective collision~~. The fraction of effective collision. ~~The effective collision is~~ $e^{-Ea/RT}$ (having proper Orientation and possessing threshold energy) (f)

Fraction of effective collision is $e^{-Ea/RT}$, where Ea is the activation energy.

So the rate is ~~$v = P\sigma^2 N_A N_B \left(\frac{8\pi KT}{}\right.$~~

$v = Z \times f$

$$v = N_A N_B \sigma^2 \left(\frac{8\pi RT}{\mu}\right)^{1/2} e^{-Ea/RT}$$

$$v = P N_A N_B a^2 \left(\frac{8\pi kT}{\mu}\right)^{1/2} e^{-E_a/RT}.$$

To take care of proper orientation of the colliding molecules a factor called steric factor (P) is introduced. Its value ranges from $1 - 10^{-7}$

To convert it to molar unit, it can be multiplied by Avogadro's number N_0

$$v = P a^2 N_0 N_A N_B \left(\frac{8\pi kT}{\mu}\right)^{1/2} e^{-E_a/RT}.$$

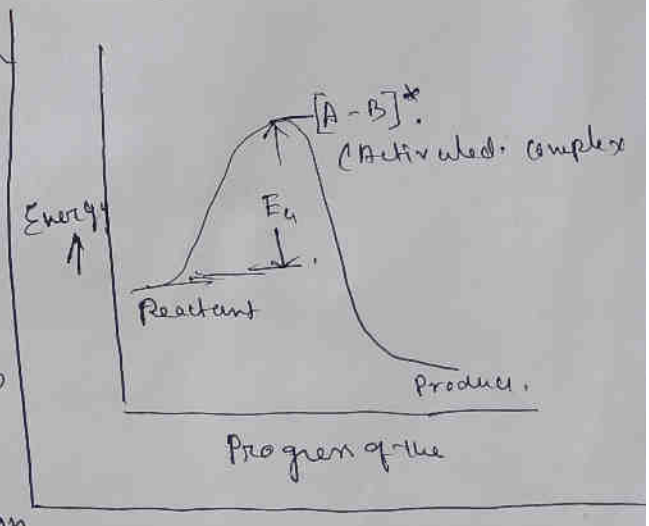
Activated complex Theory (ACT).

The ACT is based on the following postulates :—

(1) Bimolecular reaction between A and B passes through the formation of an activated complex $(AB)^{\#}$. also known as the transition state.

$$A + B \rightleftharpoons (AB)^{\#} \rightarrow \text{Product}$$

The reactants A and B establish an equilibrium with the activated complex, which decompose to give the products. The activated complex has the highest energy in the energy profile diagram.



Considering the bimolecular reaction

$$A + B \rightarrow [A-B]^* \rightarrow \text{Product.}$$

Reactant — transition state

The stability of activated complex is very low due to its high energy.

The rate of the reaction depends (1) On the concentration of activated complex and (b) the rate at which the activated complex breaks up to give the product.

Rate = (Concen^{n} of activated complex) × the frequency at which the activated complex dissociated to product

$$= [A-B]^{\#} \times \nu \quad \rightarrow (1)$$

We know that- $E = \frac{1}{2}KT$ for one molecule.

$E = KT$ for two molecules. (K is the Boltzmann Constant)

We know that $E = h\nu$.

or $KT = h\nu$

$$\nu = \frac{KT}{h}.$$

Putting the value in equ^{n} (1)

$$\text{Rate} = [A-B]^{*} \frac{KT}{h} \quad \rightarrow (2)$$

Since there exist an equilibrium bet^{n} the Reactant and activated complex.

$A + B \rightleftharpoons [A-B]^{\#} \rightarrow$ Product

$$K^{\#} = \frac{[A-B]^{\#}}{[A][B]}.$$

Putting the value in equ^{n} (2)

$$\text{Rate} = K^{\#}[A][B]\frac{KT}{h}$$

$$\text{Rate} = k_2[A][B] \quad \therefore k_2 = K^{*}\left(\frac{KT}{h}\right)$$

Effect of catalyst on reaction rate

A catalyst is a foreign substance that alters the rate of a reaction. The phenomenon of rate alteration (acceleration or retardation) due to the presence of a catalyst is called catalysis. Various types of catalysts are

(a) Positive catalyst → It accelerates the rate of a reaction

(b) Negative catalyst → It retards the rate of a reaction.

(c) Auto catalysis :- In this case, one of the products itself act as a catalyst.

Characteristics of catalytic reaction :-

Some characteristics are :-

(i) A small amount of the catalyst is sufficient to speed up a chemical reaction.

(ii) The mass and the chemical composition of the catalyst remains unchanged at the end of a reaction.

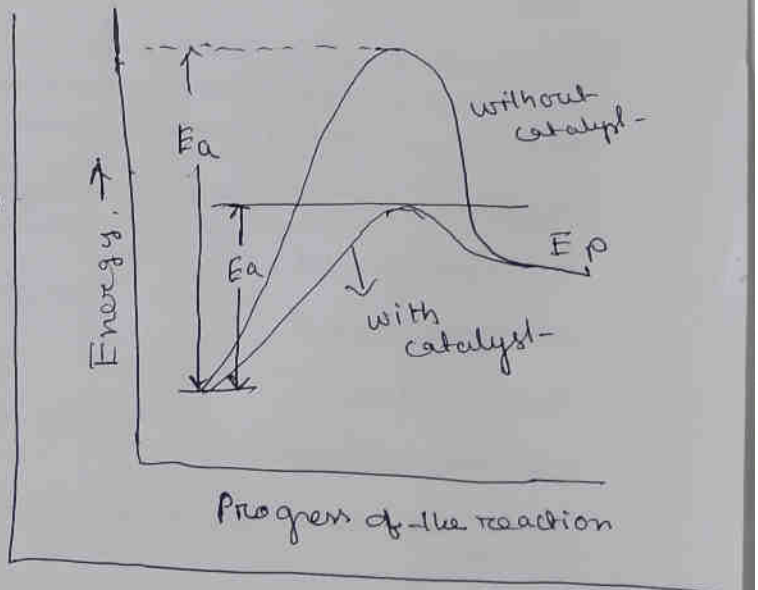
(iii) A catalyst cannot start a reaction, It can only alter the rate of a reaction.

(iv) The presence of catalyst cannot change the state of equilibrium. It can only help to attain the state of equilibrium.

(v) Catalysts are specific in nature.

Effect of catalyst on activation energy :- Although the catalyst remain unchanged, actually it takes part in the reaction. It is consumed in one step and regenerated at the end of the reaction.

A reaction whose activation energy is high will proceed at a slow rate. Catalyst provides a new path to the reaction by lowering the activation energy. In this way, even molecules with lower energies can bring about effective collisions. Hence, rate of the reaction increases.



Photochemical Reactions (Effect of radiation on reaction rate)

The reaction which are initiated by the absorption of radiation are called Photochemical reaction.

Important steps which are involved in such reactions are

(i) The light radiation is absorbed by the reactant molecules

(ii) The frequency of light radiation tells its energy.

(iii) The rate of the reaction depends upon the intensity of the light radiation

(iv) Sometimes, it happens that a reactant molecule A absorbs energy and transfers its extra energy to another molecule B. Then molecule B further reacts. This process is called photosensitisation.

One such photochemical reaction is the combination of H_2 and Cl_2 in sunlight to produce HCl.

$$H_2(g) + Cl_2(g) \xrightarrow{\text{Sunlight}} 2HCl(g) \quad \Delta H = -184.62\,kJ.$$

The above reaction involves the following steps:

1. Initiation step :- Formation of Cl atom, by the dissociation of Cl_2 molecule due to the ~~abso~~ absorption of photons by the molecule. $Cl_2 + h\nu \rightarrow Cl + Cl \rightarrow (1)$

2. Chain propagation step.

$$\left.\begin{aligned} Cl + H_2 &\rightarrow HCl + H \\ H + Cl_2 &\rightarrow HCl + Cl \end{aligned}\right\} \rightarrow (2)$$

3. termination of the chain :-

$$Cl + Cl \rightarrow Cl_2.$$

When almost whole of the reactants are consumed in the formation of HCl, unreacted Cl atom combine among themselves to form Cl_2 molecule.

Photo chemical reaction :—

A photo chemical reaction is a chemical reaction triggered when light energy is absorbed by a reactant molecule. Photosynthesis is a photochemical reaction by which green plants, ~~animals~~ absorb solar energy and utilize it to convert the atmospheric carbon dioxide to carbohydrates in the presence of water.

Difference between photochemical and Thermal reactions

	Photochemical Reaction	Thermal Reaction.
1.	These reactions involves the absorption of Photons ~~light~~ of light.	Thermal reactions are initiated by activation brought about by molecular collision.
2.	Temperature has no significant effect on the rate of photochemical reaction. The rate depends upon intensity of light absorbed.	Temperature has significant effect on the rate of thermal reaction.
3.	In photochemical reactions $\Delta G = +ve$, because a portion of the photon energy is transferred to the product molecules.	4. In thermal reactions ΔG is always negative.