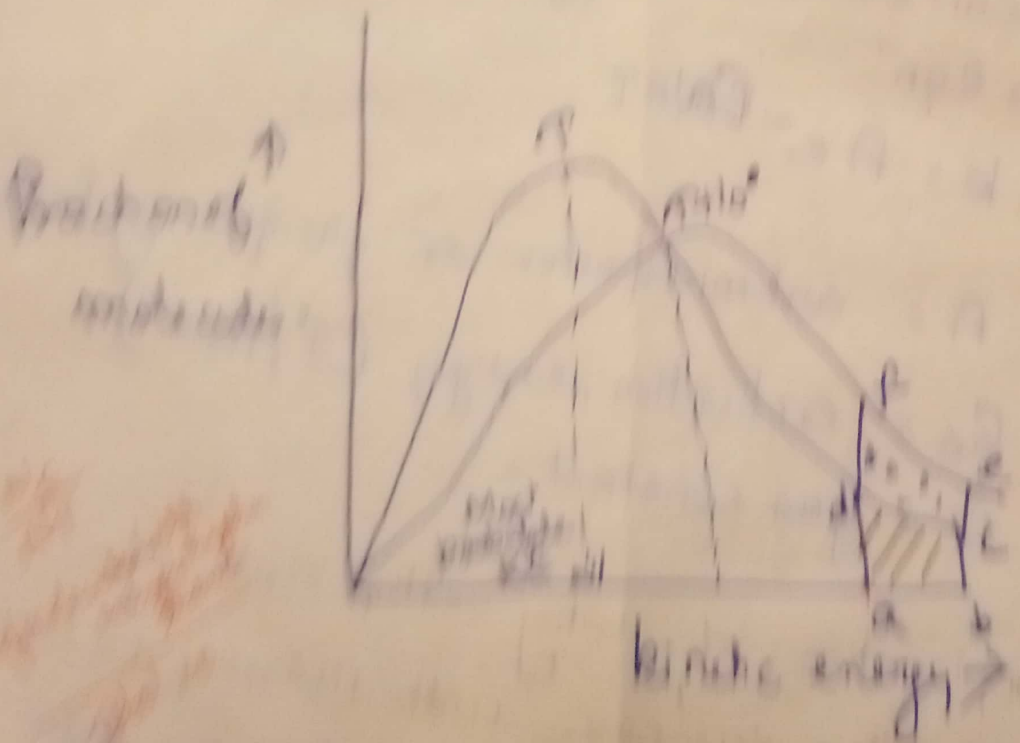


At a particular temp  $T$ , all the reacting molecules do not have the same kinetic energy.

However, fraction of molecules having particular kinetic energy at a particular temp remains constant.

At a particular temp, if fractions of molecules are plotted versus corresponding kinetic energies, a graph is obtained called Maxwell's distribution of energy.

The peak of the curve represents the kinetic energy possessed by the maximum fraction of molecules and is called most probable kinetic energy.



Distribution of energy at temp

If point 'a' represents threshold energy (27) the shaded area abcd represents the fraction of molecules having energy greater than threshold value.

When the temp is increased to  $T_2 > T_1$ , the curve shifts i.e. broadens. Now the fraction of molecules having  $k.e.$  greater than threshold value increases as represented by shaded area abef which is double than abcd. Thus increase in rate of reaction with increase in temp is mainly due to increase in effective collisions.

Quantitatively, the effect of temp on the rate of reaction and hence on ~~the~~ rate constant  $k$ , was proposed by Arrhenius.

$$k = A e^{-E_a/RT}$$

$A$  = frequency factor.

$E_a$  = activation energy.

$T$  = absolute temp.

$R$  = gas constant.

The two quantities 'A' and ' $E_a$ ' are Arrhenius parameters.

The factor  $e^{-E_a/RT}$  gives the fraction of molecules ( $N_E/N_T$ ) having energy equal to or greater than activation energy, where  $N_E$  is the number of molecules with energy  $E$ .

and  $N_T$  represents total no of molecules.

The  $E_a$  is an important quantity as it is the characteristic of the reaction.

Using the above equation its value can be calculated:-

Taking logarithm of both sides of eqn:-

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

If the value of rate constant at temp  $T_1$  and  $T_2$  are  $k_1$  and  $k_2$  respectively, then we have:-

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

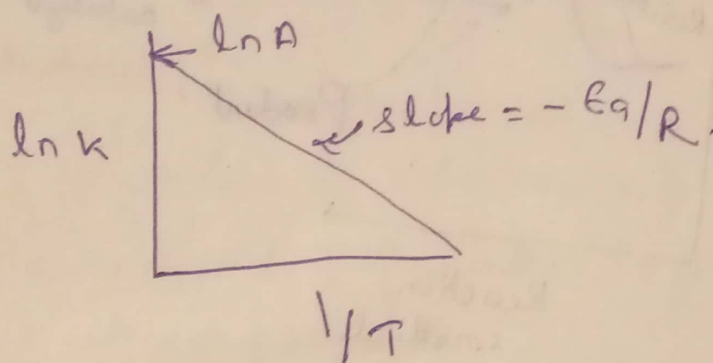
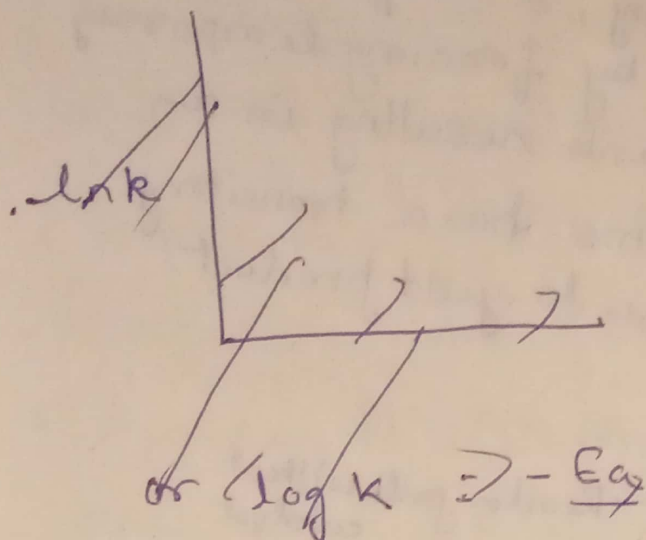
Subtracting equation (iii) from 4 -

$$\ln k_2 - \ln k_1 = -\frac{E_a}{RT_2} - \left(-\frac{E_a}{RT_1}\right)$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

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

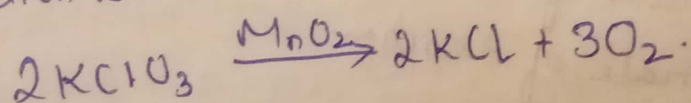
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \frac{[T_2 - T_1]}{T_1 T_2}$$



Effect of catalyst:-

A catalyst is a substance which alters the rate of a reaction without itself undergoing any permanent chemical change.

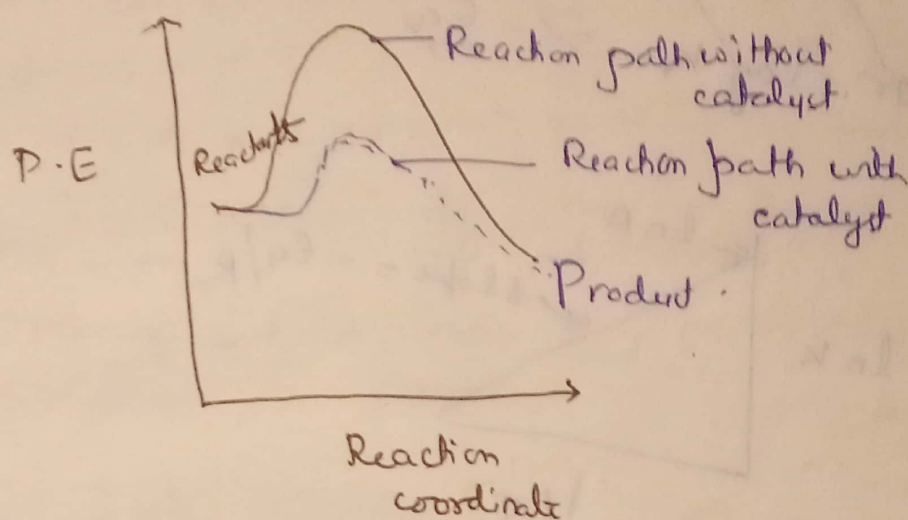
For example,  $\text{MnO}_2$  catalyses the following reaction so as to increase its rate considerably.



The substance which decreases the rate of reaction is an inhibitor.

The action of catalyst can be explained by intermediate complex theory

According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield product and catalyst



Catalyst reduces the activation energy thereby providing an alternative pathway and consequently increasing the rate of reaction.

It is clear from Arrhenius equation that lower the value of activation energy faster will be the rate of reaction.