* Effect of temperature on rate of reaction:

- Generally it is found that for every rise in temperature by 10°C, rate of reaction becomes two or three times.
- Before explanation of temperatures effect on rate of reaction we need to understand what it is.

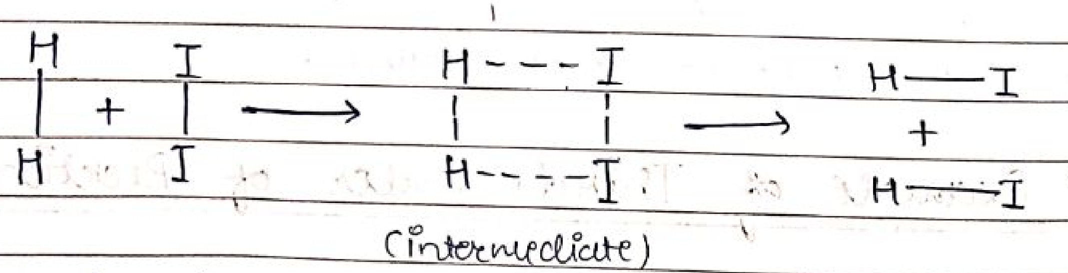
(1.) Temperature coefficient (μ):

- ratio of rate constant of reaction at two different temperatures which will be differ by 10°C.
- for most of the reaction, temperature coefficient lies between 2 and 3.

$$\mu = \frac{K_{T+10}}{K_T} \quad \text{and} \quad \frac{r_2}{r_1} = \frac{K_2}{K_1} = \mu^{\Delta T/10}$$

(2.) Activated complex:

- it is an unstable intermediate formed b/w reacting molecules.
- since it is highly unstable and it readily changes into product.



(intermediate)

reactant molecules — [activated complex] — product molecules.

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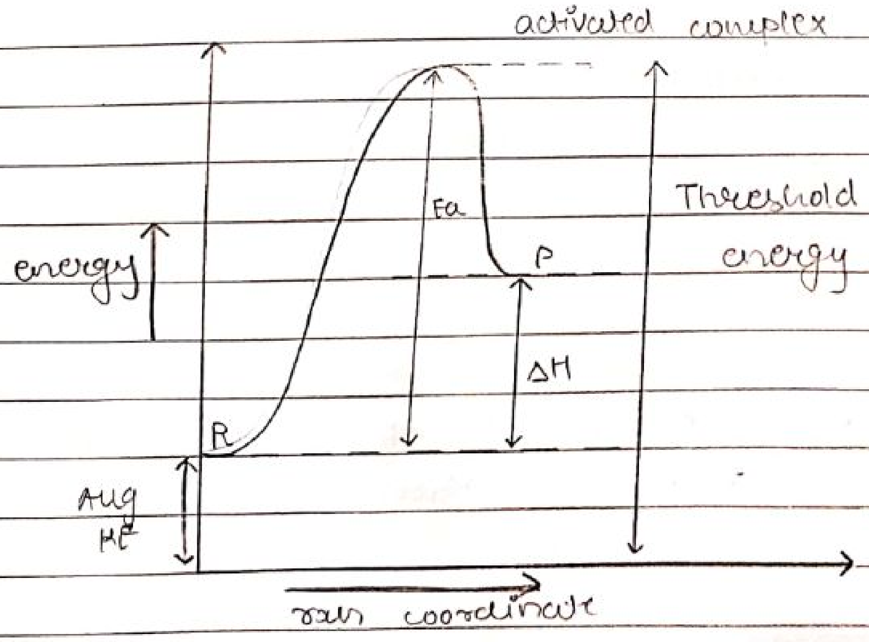
(3.) Threshold Energy:
- minimum energy that reacting molecules must possess in order to undergo effective collision to form the product.

(4.) Activation Energy (Ea):
- it is extra energy which must be possessed by reactant molecules so that collision b/w reactant molecules is effective and leads to formation of product molecules.

- for fast reaction activation energies are low while for slow reactions activation energies are high.

Activation energy (Ea) = Threshold energy − Average energy possessed by reacting molecule.

Reactant —Ea→ Activated complex —energy→ Product



*** NOTE:**

$$\Delta H = (Ea)_f - (Ea)_b$$

here,

ΔH = change in enthalpy.

$(Ea)_f$ = activation energy for forward dir.

$(Ea)_b$ = activation energy for backward dir.

Q:31 $X \longrightarrow Y$ $(Ea)_f$ is 60 KJ/mol ΔH is −20 KJ/mol. $Y \longrightarrow X$ $(Ea)_b$?

→ $\Delta H = (Ea)_f - (Ea)_b$

$-(Ea)_b = \Delta H - (Ea)_f$.

$-x = -20 - 60$

$+x = +80$ ∴ $(Ea)_b = 80$ KJ/mol

Q:32 $(Ea)_f$ is 80 KJ/mol $\Delta H = -40$ KJ/mol. after adding a catalyst $(Ea)_f' = 20$ KJ/mol find ratio of $(Ea)_b$ and $(Ea)_b'$.

→ rxn (I) $-40 = 80 - (Ea)_b$.

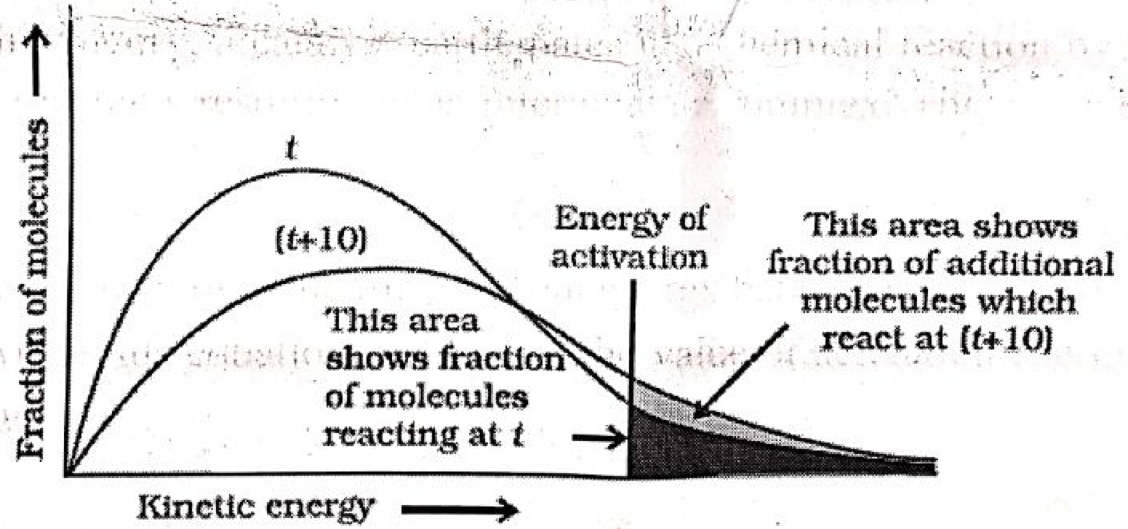
$(Ea)_b = 120$ KJ/mol.

rxn (II) $-40 = 20 - (Ea)_b$.

$(Ea)_b = 60$ KJ/mol.

$k_1 \quad 2.303R \left(\quad T_1T_2 \right)$

(vi) Maxwell and Boltzmann energy distribution curve: Increasing the temperature of a reaction mixture increases the fraction of molecules, which collide with energies greater than Ea. It is clear from the curve that with rise 10°C temperature, the area showing fraction of molecules having energy equal to or greater than activation energy gets double leading to doubling the rate of reaction.



18. Effect of catalyst:

Reactants ⟶ Activated complex $\xrightarrow{\text{Energy.}}$ Products

(v) Arrhenius Equation: It relates rate constant with temperature by following way

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

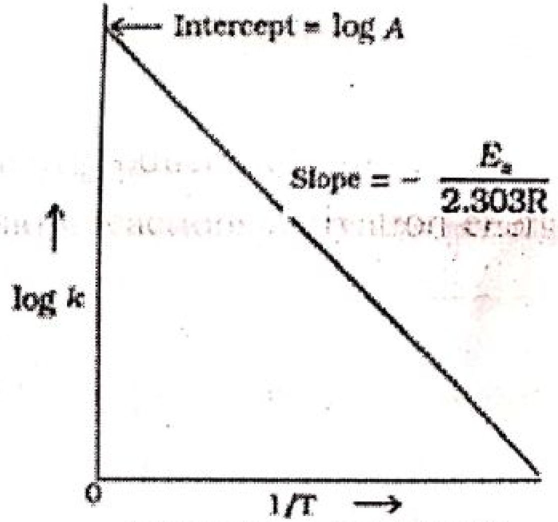
Where, A = Arrhenius factor or the frequency factor. It is also called pre-exponential factor.

R = Gas constant

Ea = Activation energy measured in joules/mole (J mol –1).

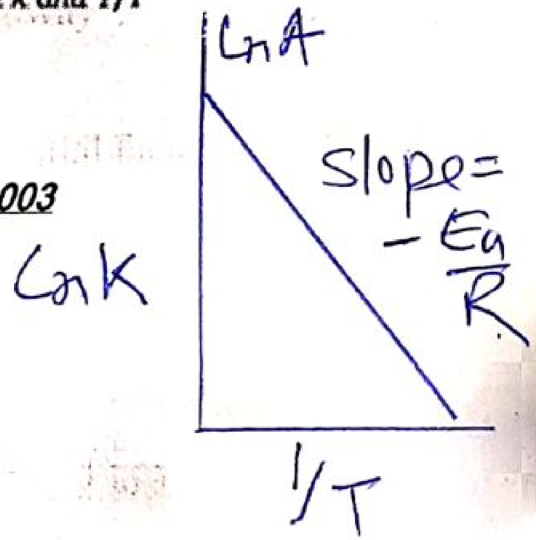
$$\ln k = \ln A - E_a/RT$$

$$\log k = \log A - \frac{E_a}{2.303RT}$$



A plot between ln k and 1/T

The plot of log k vs 1/T gives a straight line with Slope = – Ea /2.303R and intercept = log A. So we can calculate Ea and A by using these values



If k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 then

$\longrightarrow$
$1/T$

Q:27 for FOR $\log K = 15.0 - (10^6/T)$. find value of A and Ea.

$\rightarrow$ $\log K = 15.0 - (10^6/T)$

$\log A = 15$
$A = \log^{-1}(15)$
$A = 10^{15}$

$10^6/T = E_a/2.303 \cdot R \cdot T$
$10^6 \cdot 2.303 \cdot 8.3 = E_a$
$E_a = 1.9 \times 10^4$ kJ

Q:28 Ea in presence of catalyst is 4.15 kJ/mol and in absence of catalyst is 8.3 kJ. Find slope of plot b/w ln K and 1/T in absence of catalyst.

$\longrightarrow$ $E_a = 8.3$ kJ $\longrightarrow$ 8.3×10^3 J.
$R = 8.3$ J.

$\therefore$ Slope $= -\frac{E_a}{R}$

$= -\frac{8.3 \times 10^3}{8.3} \Longrightarrow -1000$

Q:29 Rate constant K_1 & K_2 for 2 diff. rxn are $10^{16} e^{-2000/T}$ & $10^{15} e^{-1000/T}$ respec. Temp at which $K_1 = K_2$?
(cage ka topic)

$\rightarrow$ $K_1 = K_2$ $\longrightarrow$ $10^{16-1} e^{-2000/T} = 10^{15} e^{-1000/T}$ (put $\ln e^{-x} = -x$)

$\ln 10 - 2000/T = -1000/T$.

$2.303 \log 10 = -1000/T$.

$T = \frac{1}{2303}$

⟹ * Arrhenius eqⁿ at different temperature & pressure:

- At temperature T_1, rate constant is K_1 and At temp. is T_2. and Rate constant K_2.

↳ then eqⁿ (2) be written as

$$\log K_1 = \log A - \frac{Ea}{2.303 R} \cdot \frac{1}{T_1} \quad \text{— eq(III)}$$

$$\log K_2 = \log A - \frac{Ea}{2.303R} \cdot \frac{1}{T_2} \quad \text{— eq (IV)}$$

subtracting eqⁿ (III) and (IV)

$$\log K_2 - \log K_1 = -\frac{Ea}{2.303 R}\frac{1}{T_2} - \left(-\frac{Ea}{2.303R}\frac{1}{T_1}\right)$$

$$\log\left(\frac{K_2}{K_1}\right) = \frac{+Ea}{2.303 R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log\left(\frac{K_2}{K_1}\right) = \frac{Ea}{2.303 R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

Q:30 $T_1 = 500K$ $T_2 = 700K$ $K_1 = 0.02\ sec^{-1}$ $K_2 = 0.07\ sec^{-1}$
calculate value A and Ea.

→ $$\log\left(\frac{K_2}{K_1}\right) = \frac{Ea}{(2.303)(R)}\left[\frac{700-500}{(700)(500)}\right]$$

8.314 × 2.303 = 19.14...

$$\log\left(\frac{0.07}{0.02}\right) = \frac{Ea}{1.91 \times 10^{-4}}\left[\frac{~~200~~}{~~350000~~}\right]$$

1750

$$(\log 7 - \log 2) = \frac{Ea}{~~1.91 \times 10^{-4}~~ -3} \cdot ~~5.7171 \times 10^{-4}~~ \; 290$$

$(0.846 - 0.301) = Ea \cdot 2.9 \times 10^{3}$

$(0.545) = Ea \cdot 2.9 \times 10^{3}$

$Ea = \frac{545 \times 10^{-3}}{2.9 \times 10^{-3}} \longrightarrow \underline{187.93 \times 10^{6}} J.$

∴ activation (A) → T_1 & K_1.

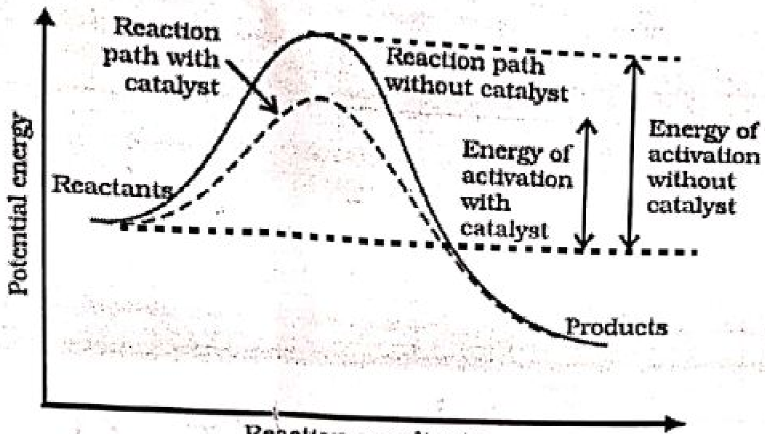
$K = Ae^{-Ea/RT}$

$0.02 = A \cdot e^{-187.93 / 8.314 \times 500} \rightarrow 4157$.

$0.02 = A \cdot e^{-0.044}$

18. Effect of catalyst:

- A catalyst is a substance which increases the rate of a reaction without itself undergoing any permanent chemical change.
- The action of the 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 products and the catalyst.
- The catalyst provides an alternate pathway by reducing the activation energy b/w reactants and products and hence lowering the potential energy barrier which shown in figure.
- According to Arrhenius equation that lowers the value of activation energy faster will be the rate of a reaction.



Effect of catalyst on activation energy

19. Collision theory of chemical reactions: This theory was developed by Max Trautz and William Lewis. It is based on kinetic theory of gases. According to this theory,

- For a reaction to occur there must be collision in b/w reacting molecules.
- The number of collision per second per unit volume of the reaction mixture is known as ***Collision frequency (Z).***
- All collisions do not lead to the formation of products. Only effective collision brings about a chemical reaction.
- Collisions which lead to the formation of product molecules are called ***Effective collisions.***
- For effective collision reacting molecules must possess a minimum amount of kinetic energy (threshold energy) and proper orientation of collision
- For effective collisions, another factor *P*, called the probability or steric factor is also introduced. It takes into account the fact that in a collision, molecules must be properly oriented i.e.,

$$Rate = PZ_{AB}.e^{\frac{-E_a}{RT}}$$

Where, Z_{AB} represents the collision frequency of reactants, A and B and $e^{-Ea/RT}$ represents the fraction of molecules with energies equal to or greater than *E*a. And P is called the probability or steric factor.