Derivation for the Rate constant (K) for Second order Reaction.

$$2A \longrightarrow \text{Product}$$

$$a \qquad\qquad 0 \qquad t=0$$

$$(a-x) \qquad\qquad x \qquad t=t$$

$$\frac{dx}{dt} \propto [a-x]^2$$

$$\frac{dx}{dt} = K[a-x]^2$$

$$\frac{dx}{[a-x]^2} = K\,dt$$

on Integration

$$\frac{1}{(a-x)} = Kt + C \quad \text{—— ①}$$

when $t=0$, $x=0$ $\rightarrow$ $C = \frac{1}{a}$

on putting the value of C in eq ①

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

$$\frac{a-(a-x)}{a(a-x)} = Kt$$

$$\boxed{K = \frac{1}{t} \cdot \frac{x}{(a-x)a}}$$

For Half life :-

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

$$K = \frac{1}{T_{1/2}} \cdot \frac{a}{2\left(a-\frac{a}{2}\right)a}$$

$$\boxed{T_{1/2} = \frac{1}{Ka}}$$

Q The decomposition of a gas is of second order. when the initial concn. of the gas is 5×10^{-4} moles/Litre and if it is 40% decompose in 50 minutes. Find the Rate constant

$a = 5\times10^{-4}$

$x = \frac{40 \times 5\times10^{-4}}{100} = 2\times10^{-4}$

$(a-x) = 3\times10^{-4}$

$$K = \frac{1}{50} \times \frac{2\times\cancel{10^{-4}}}{(3\times10^{-4})\,5\times\cancel{10^{-4}}}$$

$$K = \frac{1}{50} \times \frac{2}{15}\times10^{4} = 26.66$$

Q A second order rxn is 20% complete in 500 seconds How long will it take for 60% completion of rxn.

let $a = 100$

$x = \frac{20}{100}\times100 = 20$

$(a-x) = 80$

$$k = \frac{1}{500} \times \frac{\cancel{100}\ 20}{\cancel{80}\,40\times100} = \frac{1}{2}\times10^{-5}$$

For 60% completion

$x = \cancel{100} \times \frac{60}{\cancel{100}} = 60$

$a-x = 100 - 60 = 40$

$k = \frac{1}{t} \frac{x}{(a-x)a} = \frac{1}{2} \times 10^{-5} = \frac{1}{t} \times \frac{\cancel{60}^{3}}{\cancel{40}(10^{?})_{\cancel{20}\,10}}$

$t = 0.3 \times 10^{4}\ sec$

Q In a second order of rxn the initial concn. of reactant is given as 24 mole/L if the rxn is 30% complete in 60 min. Calculate.

i) Rate constant
ii) Half life
iii) Time req to comp. 75% of rxn.

i) $a = 0.24$

$x = 0.24 \times \frac{30}{100} = 0.072$

$a - x = 0.168$

$k = \frac{1}{60} \times \frac{0.072}{0.168 \times 0.24} = 29.8 \times 10^{-2}$

ii) $T_{1/2} = \frac{1}{ka} = \frac{1}{29.8 \times 10^{-2} \times 0.24} = 13.98\ min$

iii) $= \quad x = 0.24 \times \frac{75}{100} = 0.18$

$a - x = 0.24 - 0.18 = 0.06$

$k = 29.8 \times 10^{-2} = \frac{1}{t} \times \frac{0.18}{0.06 \times 0.24}$

$t = 42.8\ min$

Derivation for the Rate constant (K) for second order Rxn:-

Case II :-> When both the Reactants are of Different types.

$$A + B \longrightarrow \text{Product}$$

(a)	(b)	0	t=0
(a-x)	(b-x)	x	t=t

$$\frac{dx}{dt} \propto [a-x]^1 [b-x]^1$$

$$\frac{dx}{dt} = k[a-x].[b-x]$$

$$\frac{dx}{[a-x][b-x]} = k\,dt \quad \text{--- (1)}$$

on spliting it in Partial fraction

$$\frac{1}{(a-b)}\left\{\frac{dx}{b-x} - \frac{dx}{a-x}\right\} = k\,dt$$

on Integration:-

$$\frac{1}{(a-b)}\left\{-\log_e(b-x) + \log_e(a-x)\right) = Kt + C \quad \text{--- (2)}$$

when $t=0$, $x=0$; $C = \frac{1}{a-b} . \ln\frac{a}{b}$

On ~~the~~ putting the value of (c) in eq (2).

$$\frac{1}{a-b}\left\{\ln\left(\frac{a-x}{b-x}\right)\right\} = Kt + \frac{1}{(a.b)} . \ln\frac{a}{b}$$

$$K = \frac{1}{t(a-b)} \left\{ \ln \frac{(a-x)b}{(b-x)a} \right\}$$

$$\boxed{K = \frac{2.303}{t(a-b)} \left\{ \ln \frac{(a-x)}{(b-x)} \cdot \frac{b}{a} \right\}} \rightarrow \text{Second order Rxn.}$$

$$a >>>> b$$

$$K = \frac{2.303}{t(\cancel{a-b})} \left\{ \ln \frac{(\cancel{a-x})^{\to 0}\, b}{(b-x)\, \cancel{a}} \right\}$$

$K\, 0$ (very big)

$$\boxed{K = \frac{2.303}{t} \ln \frac{b}{b-x}} \rightarrow \text{First order rxn}$$

Collision Theory for Reaction Rates:-

This theory is based on Following points.

i) A chemical rxn occurs only as a result of collision b/w the reactant species.

ii) All the reactant molecules that collide do not necessarily results the product formation.

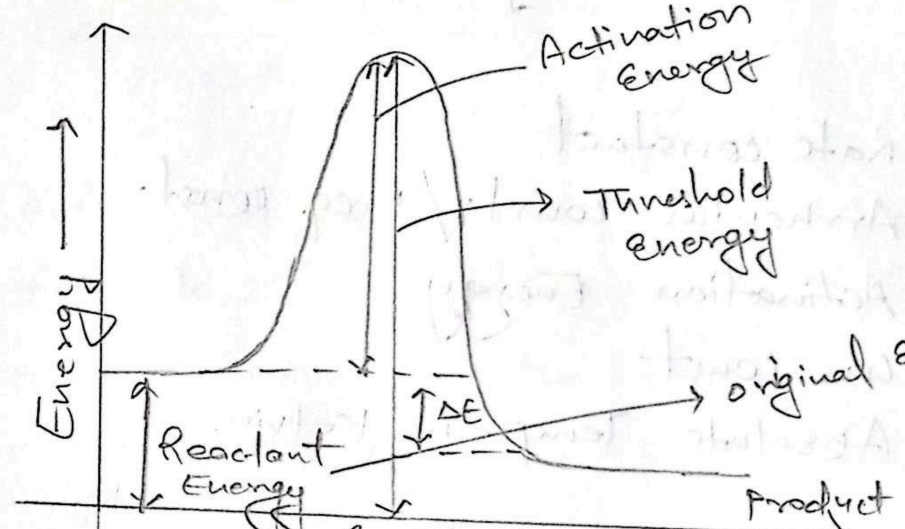
iii) Only those reactant molecules that brings the product formation, their collisions are termed as effective collision.

iv) The total no. of collisions which occurs among the reacting species/second per unit volume is called as collision frequency (Z).

Two types of ~~Energy~~ barriers are considered imp. for a rxn to occur:-

i) Energy barrier
ii) Orientation barrier

i) <u>Energy Barrier</u> :- For any reactant molecule to take part in a chemical rxn it must posses a minimum amount of Energy to cross the Energy Barrier and changes to product. This min. amt of energy required to cross the Energy Barrier is called <u>Threshold energy</u>. And the Extra Energy which the reactant molecules aqquire or gain during the collision to ~~cross~~ reach the level of min. required energy is called <u>Activation Energy</u>



The original Energy which the reactant molecules posses in the form of K.E is called reactant energy

<u>Orientation Barrier</u>

Besides the energy requirement it is also imp. for a reactant molecule that it must collide with

a proper orientation.
A reactant molecules having energy higher than the req. energy, but if it does not collide with proper orientation it will not cross the energy barrier and will bounce back

Arrhenius eqn and Activation Energy concept

Arrhenius give a mathematical relation b/w the rate constant and temperature. This temp. dependent rate const eqn. ~~as~~ can be expressed as:-

$$\left[K = Ae^{-Ea/RT}\right] \quad -(1)$$

where,

K = Rate constant
A = Arrhenius const / Freq. const.
Ea = Activation Energy
R = Gas const
T = Absolute Temp. in Kelvin.

Taking log in eq (1)

$$\left[\log K = \log A - \frac{Ea}{2.303R} \cdot \frac{1}{T}\right]$$

From the above eqn it is clear that as the value of Ea increase Rate constant / R.O.R decreases and similarly for if the Temp incr. Rate constant Increase.

we can easily calculate the value of Activation Energy for a particular rxn by determining the rate constant values of that rxn at 2 diff Temp.

If k_1 and k_2 are the 2 rate constant for a rxn at 2 diff temp. of T_1 and T_2

$$\log k_1 = \log A - \frac{E_a}{2.303R} \cdot \frac{1}{T_1} \quad \text{--- (1)}$$

$$\log k_2 = \log A - \frac{E_a}{2.303R} \cdot \frac{1}{T_2} \quad \text{--- (2)}$$

on substracting eq (1) and eq (2)

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

Q The R.O.R. Tripples on increasing the Temp. from 17°C to 57°C. Calculate the Activation Energy of the rxn if the value of Gas const is 8.314 J/kmol.

$$\log\left(\frac{3\cancel{k}}{\cancel{k}}\right) = \frac{E_a}{2.303(8.314)} \times \left(\frac{1}{17} - \frac{1}{57}\right)$$

$$0.477 = \frac{E_a}{19.147}\left(\frac{40}{969}\right)$$

$$E_a = 221.24 \text{ cal}$$