

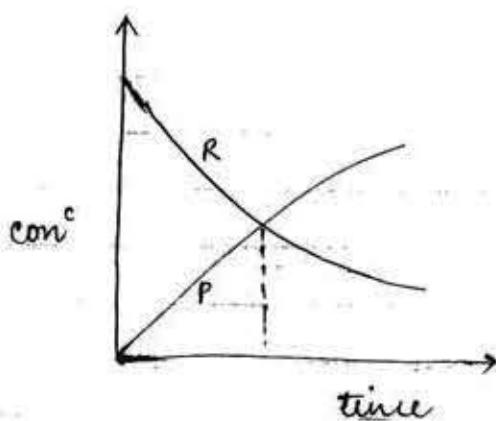
Chemical Kinetics

- * Rate of the reaction
- * Types of rate
- * Order and molecularity of the reaction
- * Factors affecting the rate
- * Integrated rate law for zero order & 1st law
- * Collision theory

Rate of Reaction

Kinetics is the branch of chemistry which deal with the rate of the reaction and factors affecting the rate.

The rate of the reaction is the change in the concentration per unit change in time, with respect to reactant it decreases with time and with respect to product it increases with time.



$$\text{Rate} = \frac{dc}{dt}$$

$$\frac{-d[R]}{dt} = + \frac{d[P]}{dt}$$

unit: $\text{mol L}^{-1} \text{ sec}^{-1}$ (soln)
 atm sec^{-1} (gas)



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

$$-\frac{1}{a} \frac{d[A]}{dt} = +\frac{1}{b} \frac{d[B]}{dt}$$

Q) write the expression of rate of formation of NH_3 with respect to rate of N_2



$$-\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = +\frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

$$\frac{d[\text{NH}_3]}{dt} = -2 \frac{d[\text{N}_2]}{dt}$$

Q) calculate the rate of formation of B if the rate of disappearance of A is 4×10^{-6} mole $\text{L}^{-1}\text{sec}^{-1}$



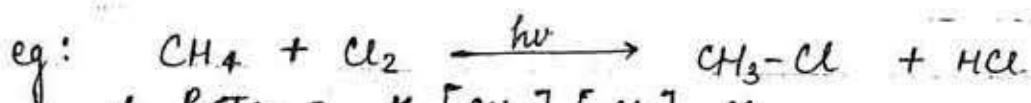
$$-\frac{1}{3} \frac{d[A]}{dt} = +\frac{1}{2} \frac{d[B]}{dt} = \frac{d[C]}{dt}$$

$$\frac{4 \times 10^{-6}}{3} \times 2 = \frac{d[B]}{dt}$$

$$\frac{8 \times 10^{-6}}{3}$$

Factors Affecting the Rate

- i) concentration : If concentration of the reactant increase then Rate of the reaction increases as the rate is proportional to the molar concentration of the reaction
- ii) surface Area : If surface area increases then no. of moles per unit volume increases hence, rate of reaction increases
- Q) Why pulverized coal burns faster than that of wood charcoal.
because of increase in surface area.
- Q) Why powdered sugar dissolves faster than that of sugar crystal.
because of increase in surface area
- iii) Exposure to light : The photochemical reaction starts only in the presence of sunlight. It is independent on the concentration of the reactant with increase in intensity of radiation with increase in intensity of radiation the rate of reaction increases.

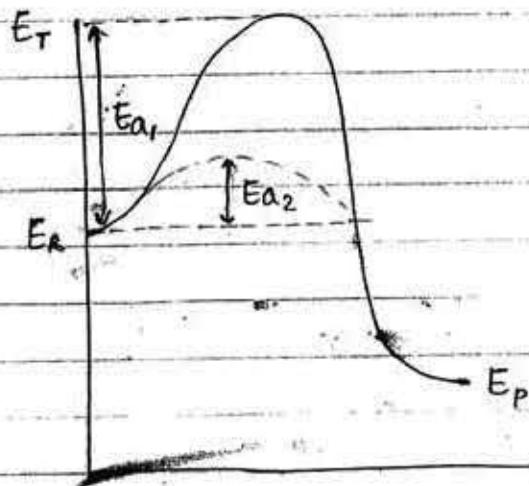


$$\therefore \text{Rate} = K [\text{CH}_4] [\text{Cl}_2] \times$$

but its Rate = $K (\because [\text{CH}_4]^{\circ} [\text{Cl}_2]^{\circ})$

iv) Temperature : On increasing the temperature the kinetic energy of molecules increase hence, the affecting no of collision increases, thereby increasing rate of the reaction.

v) Catalyst : It increases the rate of reaction by decreasing the activation energy and by providing an alternative path by lowering down the activation energy.



$$\therefore E_R + E_a = E_T$$

Q) Why diamond is not converted into its stable form graphite.

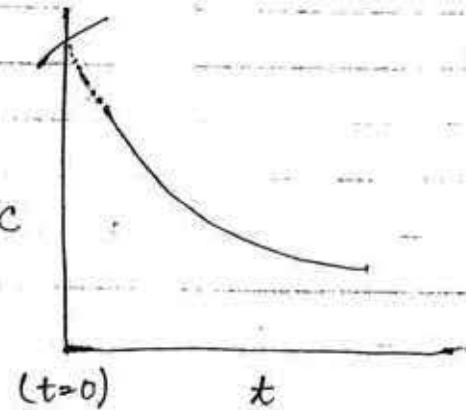
because there is a large activation energy gap between diamond and graphite.

Activation Energy: It is the extra amount of energy given to the reactant to cross the threshold energy barrier.

Threshold Energy: It is the minimum energy required by the reactant to convert into product.

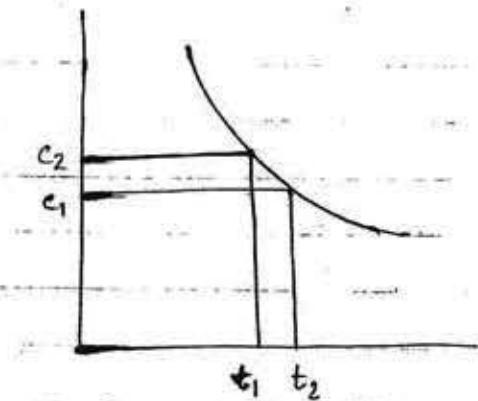
Types of Rate :

- i) Initial Rate: It is the concentration obtained at time $t=0$ only by graphically.



- i) Average Rate: It is the rate measured for a large interval of a time ie.

$$\frac{-\Delta C}{\Delta t} = \frac{-(c_2 - c_1)}{t_2 - t_1}$$



$$\boxed{\text{Q.4.1}} \quad \frac{0.03 - 0.02}{25 - 0} = \frac{0.01}{25} \text{ mol L}^{-1} \text{ sec}^{-1}$$

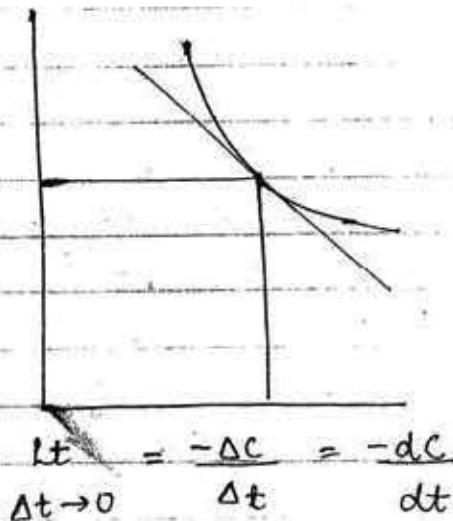
$$-\frac{\Delta C}{\Delta t} = \frac{0.01 \times 60}{25} = \frac{12}{5} \times 0.01 \text{ mol L}^{-1} \text{ min}^{-1}$$

$$\boxed{\text{Q.4.2}} \quad \frac{0.5 - 0.4}{10 - 0} = \left(\frac{0.1}{10} \right) \frac{1}{2} \text{ mol L}^{-1} \text{ sec}^{-1} = -\frac{\Delta C}{\Delta t}$$

$$= \frac{0.1 \times 60}{10 \times 2} = 15 \times 0.1 = 1.5 \text{ mol L}^{-1} \text{ min}^{-1}$$

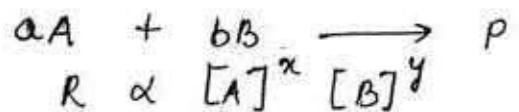
iii) Instantaneous Rate:

It is the rate measured at particular instant of time by drawing the tangent to the curve obtained between concentration and time



iv) Rate law: According to rate law, the rate of the reaction is proportional to the product of the molar concentration of the reactant raised to its power its stoichiometry co-efficient as determined experimentally in slow steps (RDS) rate determining step.

*** Pg 117 Q.4.1(iii)



$$\therefore R = K [A]^x [B]^y$$

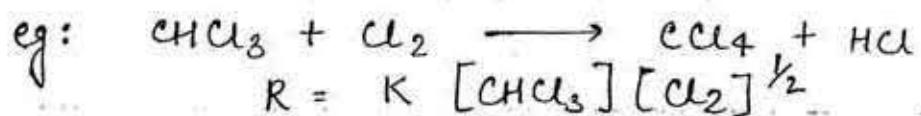
where K is the rate constant, velocity constant or specific ~~rate~~ reaction rate constant

It is equal to the rate of the reaction when molar concentration of the reactant is taken as unity.

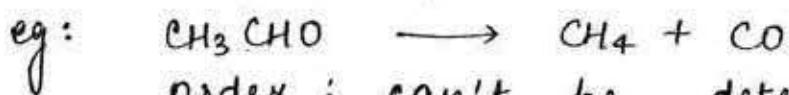
Order of the Reaction :

The sum of the power appeared in the rate law determined experimentally is known as order of the reaction.

It may be zero, fractional and -ve

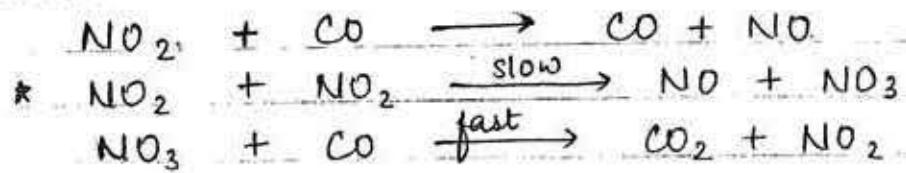


$$\therefore n = 1 + \frac{1}{2} = \frac{3}{2}$$



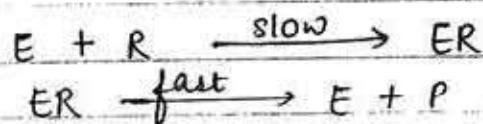
order: can't be determined
 ∵ Rate law is not given.

Q) Determine the rate law for a complex reaction (the reaction completes in more than 1 step)

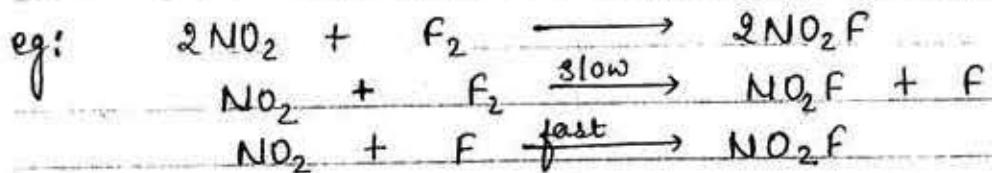


$$\begin{aligned} R &= k [\text{NO}_2]' [\text{NO}_2]' \\ &= k [\text{NO}_2]^2 \end{aligned}$$

eg: $R \longrightarrow P$



$$\therefore R = [E]' [R]'$$



$$\therefore R = k [\text{NO}_2]' [\text{F}_2]'$$

Rate law for n^{th} order :

Q) Calculate the order of the reaction if rate of the reaction increases by 4 times on increasing the concentration by 9 times.

$$4R = K \cdot (9A)^n \quad \text{--- (I)}$$

$$R = KA^n \quad \text{--- (II)}$$

$$\begin{aligned} 4 &= 9^n \\ 2^2 &= 3^{2n} \end{aligned}$$

(∴ bases are different)
 \therefore log are used

taking log ~~to~~ both the sides.

$$\begin{aligned} \log 2 &= \ln \log 3 \\ n &= \frac{\log 2}{\log 3} = \frac{0.3010}{0.48} \end{aligned}$$

- Q) Calculate the order of the reaction if rate increases by 8 times on increasing the concentration by 4 times.

$$\begin{aligned} 8R &= K(4A)^n \\ R &= KA^n \end{aligned}$$

$$\begin{aligned} 8 &= 4^n \\ 2^3 &= 2^{2n} \\ 3 &= 2n \\ \therefore n &= \frac{3}{2} \end{aligned}$$

- Q) Calculate the order of the reaction if rate increases by 9 times on increasing the concentration by 27 times.

$$qR = K(27A)^n \quad \text{--- (I)}$$

$$R = KA^n \quad \text{--- (II)}$$

$$\begin{aligned} q &= 27^n \\ (3)^2 &= (3)^{3n} \end{aligned}$$

$$2 = 3n$$

$$\therefore n = \frac{2}{3}$$

$$\log 2 = 0.30$$

$$\log 3 = 0.48$$

$$\log 5 = 0.70$$

$$\log 7 = 0.85$$

$$\log 10 = 1$$

$$\log 100 = 2$$

$$\log \frac{1}{10} = -1$$

$$\log \frac{1}{100} = -2$$

$$\log 90 = 1$$

$$\log 99.9 = 3$$

$$\log 99 = 2$$

$$\log 99.999 = 5$$

$$\log 50 = 0.7$$

Q) calculate the order w.r.t each reactant
rate law and rate constant.

A

0.1

0.1

0.2

B

0.1

0.2

0.2

initial rate

$$4 \times 10^{-6} = K [0.1]^x [0.1]^y$$

$$16 \times 10^{-6} = K [0.1]^x [0.2]^y$$

$$16 \times 10^{-6} = K [0.2]^x [0.2]^y$$

on $\textcircled{2} \div \textcircled{1}$

$$\textcircled{2}^2 = 4 = \frac{16}{4} = \left(\frac{0.2}{0.1}\right)^y = \textcircled{2}^y$$

$$\therefore \boxed{y = 2}$$

on $\textcircled{3} \div \textcircled{2}$

$$2^0 = 1 = \frac{16}{16} = 2^x$$

$$\therefore \boxed{x = 0}$$

	A	B	initial rate
	0.20	0.30	5.07×10^{-5}
	0.20	0.10	5.07×10^{-5}
	0.40	0.05	1.43×10^{-4}

$$K [0.20]^x [0.30]^y \quad \text{--- } \textcircled{1}$$

$$K [0.20]^x [0.10]^y \quad \text{--- } \textcircled{II}$$

$$K [0.40]^x [0.05]^y \quad \text{--- } \textcircled{III}$$

on $\textcircled{1} \div \textcircled{2}$

$$3^0 = 1 = 3^y$$

$$\therefore \boxed{y = 0}$$

on $\textcircled{3} \div \textcircled{2}$ [on putting value of $y = 0$]

$$\frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = 2^x$$

$$\Rightarrow \frac{1.43 \times 10}{5.07} = 2^x$$

$$\frac{14.3}{5.07} = 2^x$$

$$\log 14.3 - \log 5.07 = x \log 2$$

$$1.1553 - 0.7050 = x \times 0.3010$$

$$\frac{0.4503}{0.3010} = x = \frac{3}{2} = 1.5$$

$$\therefore x = \frac{3}{2} \text{ and } y = 0$$

$$\therefore R = K [A]^{3/2} [B]^0$$

Unit of Rate constant

$$R = K [A]^n \quad \therefore \frac{\text{concn}}{\text{time}} = K [\text{conc}]^n$$

$$\therefore \text{unit of } K = \left(\frac{\text{mole}}{\text{lit}} \right)^{1-n} \text{ sec}^{-1} (\text{sol}^n)$$

$$= (\text{atm})^{1-n} \text{ sec}^{-1} (\text{gas})$$

Q) calculate the order for the given rate constant :

$$(i) K = 2.3 \times 10^{-5} \text{ mol}^{-1} \text{ sec}^{-1}$$

$$\therefore 1-n = -1$$

$$\therefore n = 2$$

$$(ii) K = 5.6 \times 10^{-4} \text{ mol}^{-2/3} \text{ lit}^{2/3} \text{ sec}^{-1}$$

$$1-n = \frac{-2}{3}$$

$$\therefore n = \frac{5}{3}$$

$$\text{iii) } K = \text{sec}^{-1} \text{ mol}^0$$

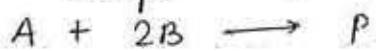
$$1-n=0$$

$$n=1$$

Q) For a given rate equation,

$$R = K [A]^1 [B]^2$$

i) slow step.



ii) $A \times 2, B \times 2 \therefore R = ?$

$$R' = K [2A]^1 [2B]^2$$

$$= K 2[A]^1 4[B]^2$$

$$= 8R$$

iii) $B \times 3, \therefore R = ?$

$$R' = K [A]^1 [3B]^2$$

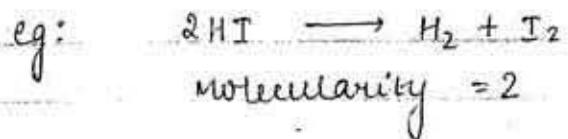
$$= 9R$$

Elementary reaction: The reaction which completes in one step i.e. slow step while the reaction which completes in multisteps is known as complex reaction.

Molecularity of the Reaction:

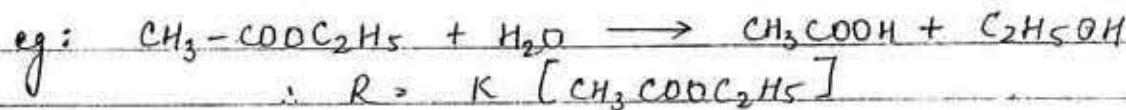
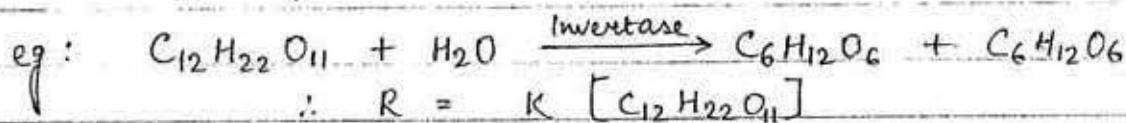
It is the no. of reacting molecule participate in elementary step which collides with each other to give desired product.

- It is applicable only for elementary reactions.
- It never becomes 0, -ve and fractional.
- It is determined theoretically.



Pseudo unimolecular Reaction: The reaction in which more than one molecule participate in its elementary step but rate depends upon concentration of only one molecule because conc of another molecule is in excess.

eg: Inversion of cane sugar and hydrolysis of ester.



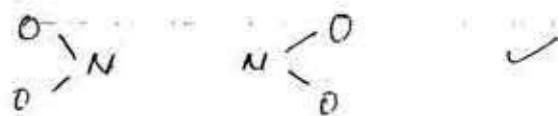
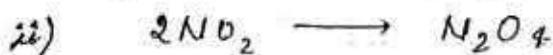
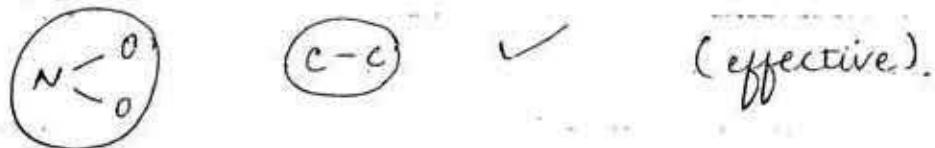
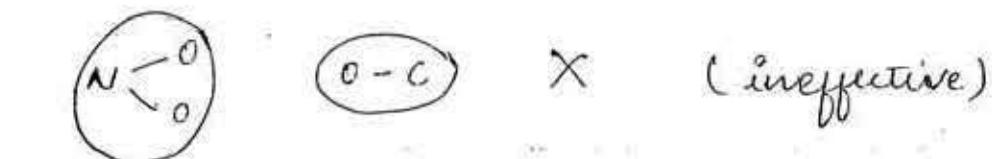
Collision Theory:

According to this theory, the reactant converts into product only when it makes effective collision.

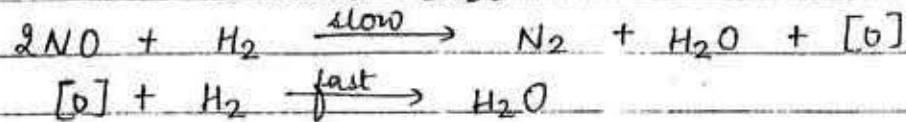
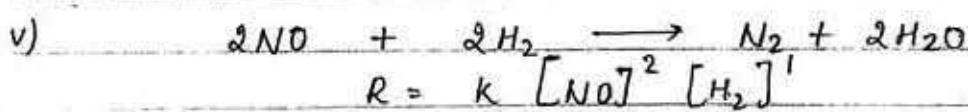
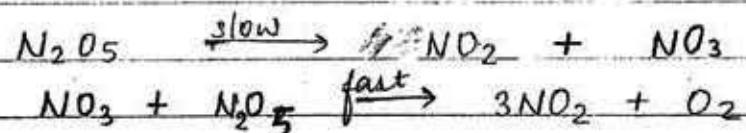
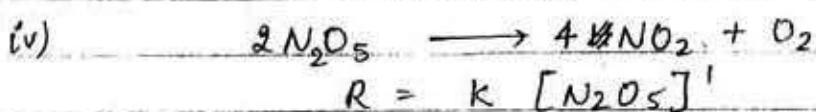
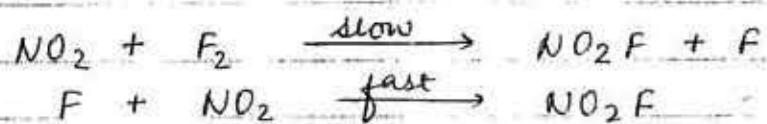
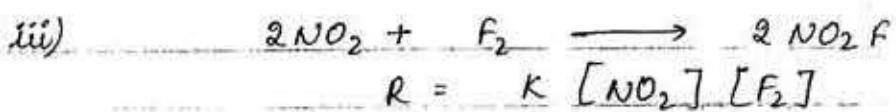
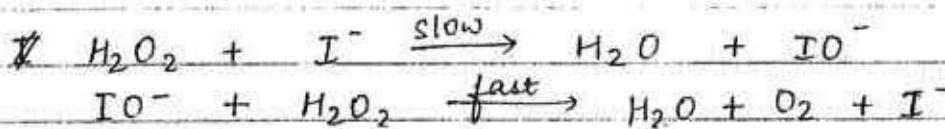
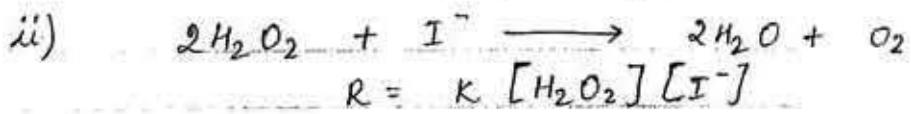
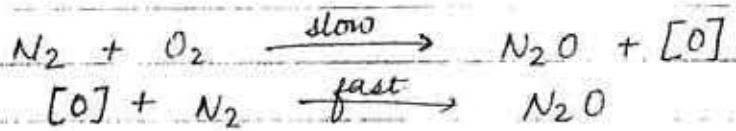
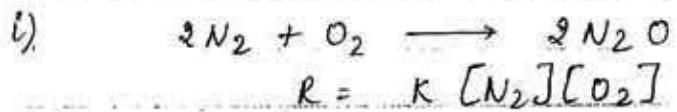
In order to make effective collision, it has to cross two energy barrier.

- a) Threshold energy barrier : The reactant molecule should possess energy greater than equal to (\geq) threshold energy.
- b) Orientation Barrier : The reactant molecule should have proper facing in order to make effective collision.

e.g.: To convert NO_2 into NO by reacting with CO , it should have proper orientation.

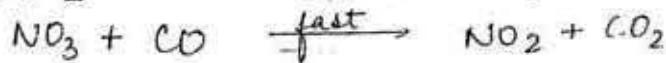
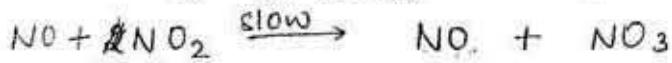


Reaction Mechanism :

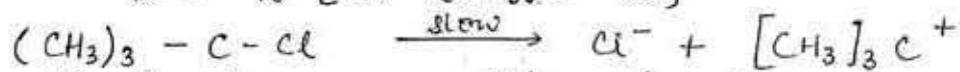




$$R = k [NO_2]^2$$



$$R = k [(\text{CH}_3)_3\text{C}-\text{Cl}]$$



Integrated rate law for a) 0 order rxn
b) 1st order rxn



$$\text{Rate} = -\frac{d[A]}{dt} \quad \text{--- (I)}$$

$$R = k[A]^n \quad \text{--- (II)}$$

From eq(I) and (II)

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

$$-\frac{d[A]}{dt} = k[A]^0$$

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

$$-[A] = kt + C$$

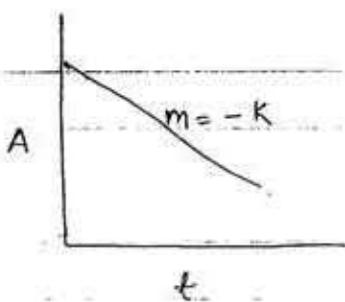
when $t = 0$, $A = A_0$

$$-A_0 = 0 + C$$

$$-[A] = kt - A_0$$

$$[A] = -kt + A_0$$

$$y = mx + c$$



$$\therefore \boxed{\frac{A_0 - A}{t} = K}$$

conc decreases with time

* when conc increases with time.

$$\frac{A - A_0}{t} = K$$

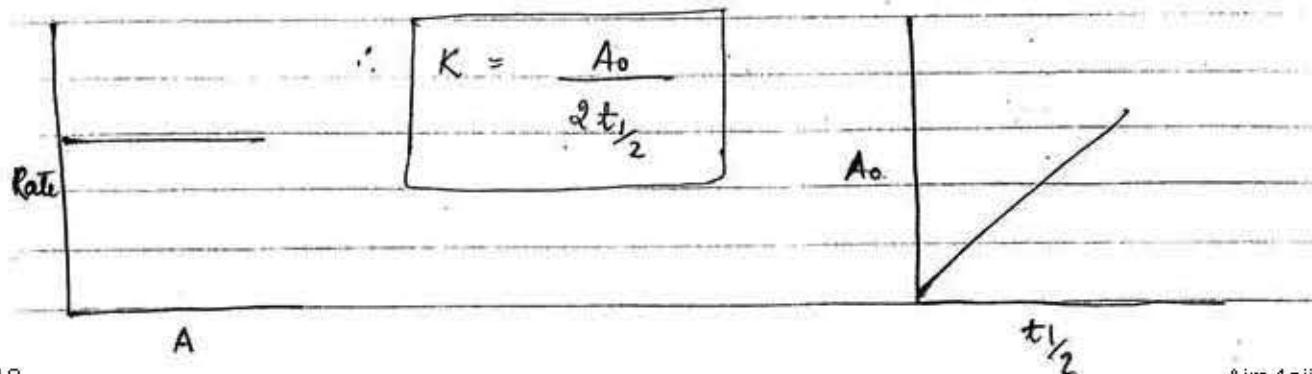
e.g. Population growth.

half life of the reaction : It is the time in which final concentration becomes half of the initial concentration.

$$\therefore K = \frac{A_0 - A}{t}$$

$$\therefore A = \frac{A_0}{2}$$

$$\therefore K' = \frac{A_0 - \frac{A_0}{2}}{\frac{t_1}{2}} = \frac{A_0}{\frac{2t_1}{2}}$$



Q) Derive the relationship b/w rate constant and half life for a zero order reaction.

Ans) last page (derivation).

e.g. of zero order reaction:

→ decomposition of ammonia on the surface of platinum.

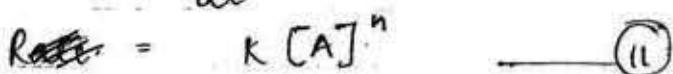
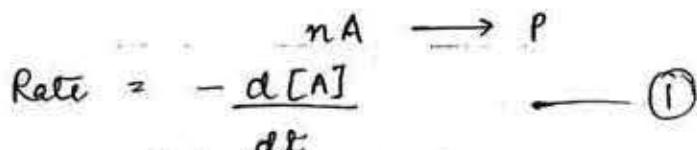
→ decomposition of HI on the surface
of gold [Au]

→ Halogenation of alkane in the presence of sunlight

Note

* All photochemical reaction and the reaction takes place in the presence of catalyst comes in the category of zero order reaction.

Integrated Rate law for 1st order reaction



From eq ① and ⑪

$$-\frac{d[A]}{dt} = \cdot K [A]^n$$

$$\boxed{n=1}$$

$$-\frac{d[A]}{dt} = K [A]^1$$

$$= -\int \frac{d[A]}{[A]} = \int K dt$$

$$= -\ln[A] = kt + c \quad [\because \int kx = \ln x]$$

when $t=0, A=A_0$

$$-\ln[A_0] = 0 + c$$

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

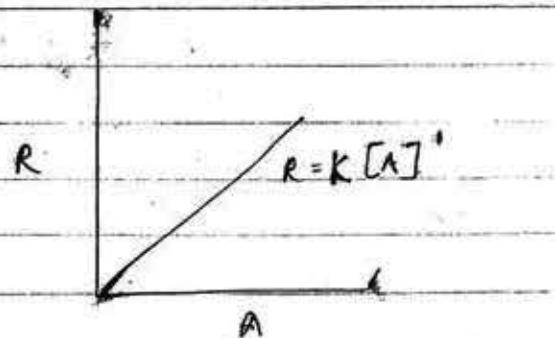
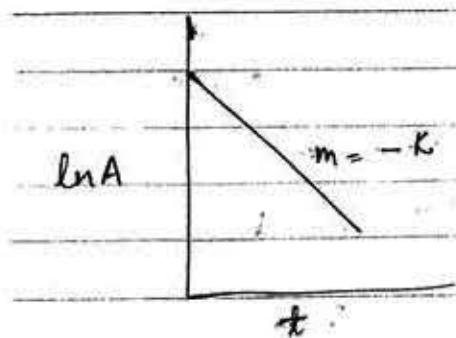
$$\ln A_0 - \ln A = kt$$

$$\frac{\ln A_0}{A} = kt$$

$$\frac{2.303}{t} \log \frac{A_0}{A} = K$$

$$[\therefore \ln = \log_e = 2.303 \log_{10}]$$

$$\ln[A] = -kt + \ln A_0$$



half life of the reaction.

$$(t = t_{1/2}) \quad (A = \frac{A_0}{2})$$

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

$$k = \frac{2.303}{t_{1/2}} \log 2 = \boxed{\frac{0.693}{t_{1/2}}}$$

eg of 1st order reaction.

→ decomposition of N_2O_5 into N_2O and ammonium nitrate (NH_4NO_3)

*** All radioactive decay

Q) Calculate the half life of the reaction if 75% of the reaction completes in 32 minutes

$$\begin{bmatrix} t_{75} & OR \\ t_{75} & = 32 \text{ min} \\ t_{50} & = ? \end{bmatrix}$$

$$\begin{bmatrix} t_{3/4} & OR \\ t_{3/4} & = 32 \text{ min} \\ t_{1/2} & = ? \end{bmatrix}$$

$$\therefore K = \frac{2.303}{t} \log \frac{A_0}{A}$$

$$\therefore K = \frac{2.303}{32} \log \frac{100}{25} \quad \text{--- (i)}$$

$$K = \frac{2.303}{t_{50}} \log \frac{100}{50} \quad \text{--- (ii)}$$

From (i) and (ii)

$$\frac{2.303}{32} \log 4 = \frac{2.303}{t_{50}} \log 2$$

$$\frac{\log 2^2}{32} = \frac{\log 2}{t_{50}} \quad * t_{75} = 2$$

$$\frac{2 \log 2}{32} = \frac{\log 2}{t_{50}} \quad * t_{75} = 2^3$$

$$\therefore t_{50} = 16 \text{ min} \quad * t_{12.5} = 2^4$$

Q) calculate the half life of the sample if initial conc reduces (to) 20% in 30 sec.

$$\frac{2.303}{30} \log \frac{100}{20} = \frac{2.303}{t_{50}} \log \frac{100}{50}$$

$$\frac{\log 5}{30} = \frac{\log 2}{t_{50}}$$

$$\frac{0.70}{30} = \frac{0.30}{t_{50}}$$

$$\therefore t_{50} = \frac{0.30}{0.70 \times 0.70} \rightarrow \frac{3}{140} \frac{1}{70}$$

Q) Calculate the half life of the rxn if 99.9% completes in 10 sec

$$\frac{2.303}{10} \log \frac{1000}{0.1} = \frac{2.303}{t_{50}} \log \frac{100}{50}$$

$$\frac{\log 1000}{10} = \frac{\log 2}{t_{50}}$$

$$\frac{3}{10} = \frac{0.3}{t_{50}}$$

$$\therefore t_{50} = \frac{3}{0.3} = 1 \text{ sec}$$

Pg 119

Q. 4.14

$$\frac{2.303}{5730} \log \frac{100}{50} = \frac{2.303}{t_{50}} \log \frac{100}{80}$$

$$\frac{\log 2}{5730} = \frac{\log \left(\frac{5}{4}\right)}{t_{50}}$$

$$\frac{\log 2}{5730} = \left(\log \frac{5}{4} - \log 4 \right) \frac{1}{t_{50}}$$

$$\frac{0.3}{5730} = \frac{0.1}{t_{50}}$$

$$\therefore t_{50} = \frac{0.1 \times 5730}{0.3} = 1910 \text{ years.}$$

Pg 119

Q 4.18

$$\frac{2.303}{t_{99}} \log \frac{100}{1} > \frac{2.303}{t_{90}} \log \frac{100}{10}$$

$$\frac{\log 100}{t_{99}} = \frac{\log 10}{t_{90}}$$

$$t_{90} = \frac{\log 10}{\log 100} \times t_{99}$$

$$t_{90} = \frac{1}{2} t_{99}$$

$$\therefore t_{99} = 2 t_{90}$$

Pg 119 / Q. 4.19

$$\frac{2.303}{40} \log \frac{100}{10} = \frac{2.303}{t_{50}} \log \frac{100}{50}$$

$$\frac{\log(10)}{40} = \frac{\log 2}{t_{50}}$$

$$\frac{\log 10 - \log 7}{40} = \frac{\log 2}{t_{50}}$$

$$\frac{1 - 0.8}{40} = \frac{0.3}{t_{50}}$$

$$\therefore t_{50} = \frac{0.3 \times 40}{0.2} = 0.6$$

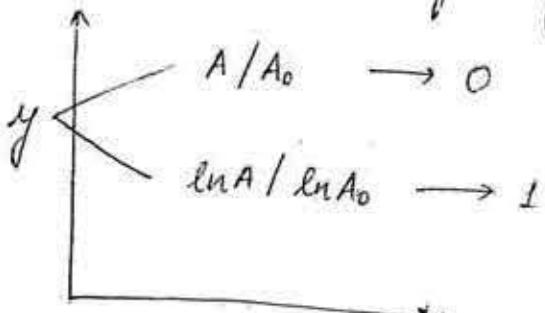
- (Q) calculate the population of India in 2010 if population of India in 2000 is 800 million and the population growth is ~~is~~ 25 per thousand people per year and it follows the 1st order kinetics.

$$\textcircled{+} \frac{dA}{dt} = kA' \quad \cancel{\frac{25}{1000}} = \frac{2.303}{10} \frac{\log \frac{A}{A_0}}{t}$$

$$\therefore \frac{2.303}{t} \log \frac{A}{A_0} (\text{final}) = \frac{2.303}{t_{50}} \log \frac{100}{50}$$

$$\therefore \frac{\log \frac{A}{A_0}}{10} = \frac{800}{800}$$

Short tricks for graph :

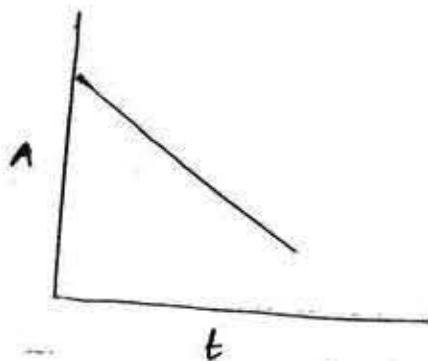


$$\text{time / Temperature } m = \frac{E_a}{R}$$

$$m = \pm K$$

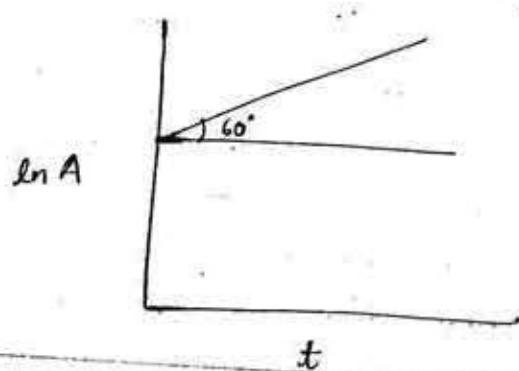
$$\text{when } y = \log \quad \text{then} \quad m = \frac{-K}{2,303}$$

e.g.



Order = 0

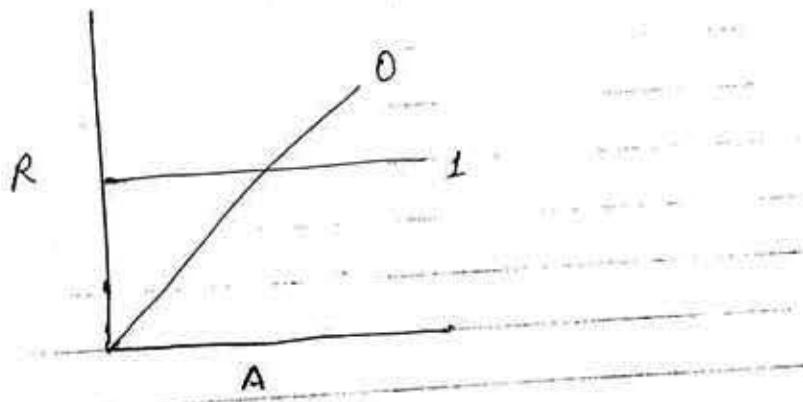
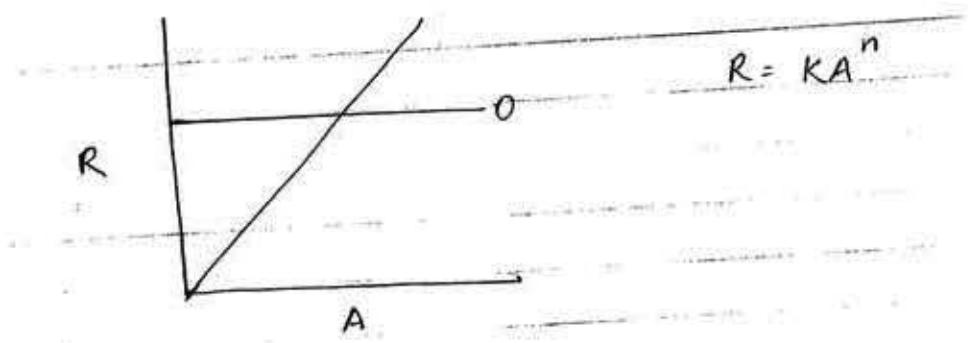
unit of $K = \left(\frac{\text{mole}}{\text{Lit}} \right)^1 \text{ sec}^{-1}$



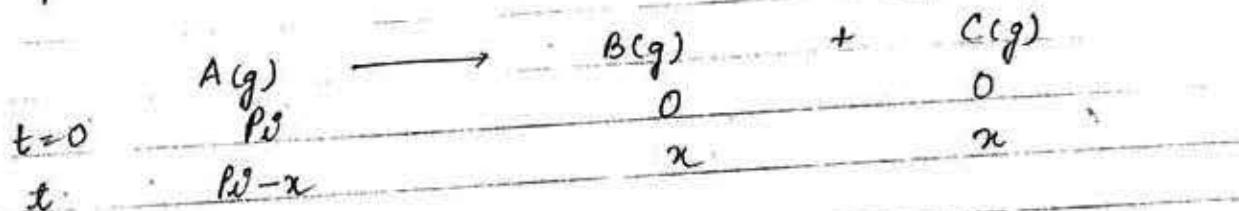
Order = 1

$$K = m = \tan 60^\circ = \sqrt{3}$$

$$t_{\frac{1}{2}} = \frac{0.693}{\sqrt{3}}$$



1st order kinetics for gaseous reactant and product:



$$\therefore p_t = p_i - x + x + x$$

$$p_t = p_i + x$$

$$\therefore x = p_t - p_i$$

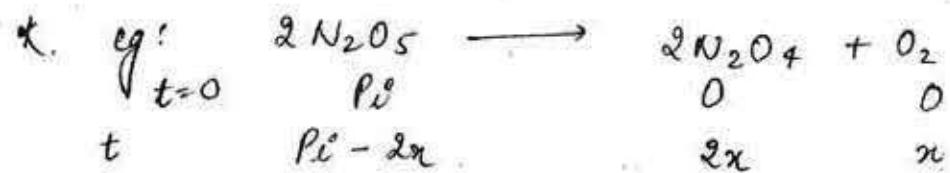
$$K = \frac{2.303}{t} \log \frac{p_i}{p_i - x}$$

$$= \frac{2.303}{t} \log \frac{p_i}{p_i - (p_t - p_i)}$$

$$\therefore K = \frac{2.303}{t} \log \frac{P_i}{2P_i - P_t}$$

eg: $\boxed{4.2 \times 1}$ $\boxed{P_g 119}$

$$\begin{aligned} K &= \frac{2.303}{t} \log \frac{P_i}{2P_i - P_t} \\ &= \frac{2.303}{100} \log \frac{0.5}{2 \times 0.5 - 0.6} \\ &= \frac{2.303}{100} \log \frac{0.5}{0.4} \\ &= \frac{2.303}{100} \log 0.1 \end{aligned}$$

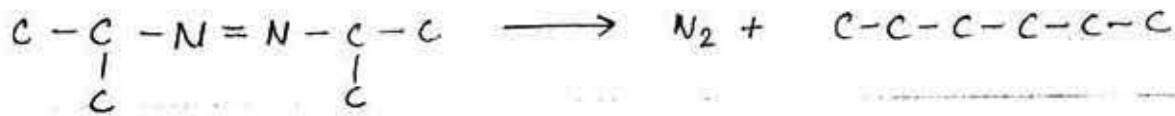


$$\begin{aligned} \therefore P_t &= P_i - 2x + 2x + x \\ &= P_i + x \\ \therefore x &= P_t - P_i \end{aligned}$$

$$\begin{aligned} K &= \frac{2.303}{t} \log \frac{P_i}{P_i - 2x} \\ &= \frac{2.303}{t} \log \frac{P_i}{P_i - 2(P_t - P_i)} \\ &= \frac{2.303}{t} \log \frac{P_i}{3P_i - 2P_t} \end{aligned}$$

Pg 119

4.20



$$i) k = \frac{2.303}{t} \log \frac{P_i}{2P_i - P_t}$$

$$ii) = \frac{2.303}{360} \log \frac{35}{70 - 54}$$

$$iii) = \frac{2.303}{720} \log \frac{35}{70 - 63}$$



$$t=0 \quad P_i \quad 0 \quad 0$$

$$t \quad P_i - 2x \quad 3x \quad x$$

$$\therefore P_t = P_i - 2x + 3x + x$$

$$\therefore P_t = P_i + 2x$$

$$\therefore 2x = P_t - P_i$$

$$\therefore x = \frac{P_t - P_i}{2} \quad \therefore x = \frac{P_t - P_i}{2}$$

$$\therefore K = \frac{2.303}{t} \log \frac{P_i}{P_i - x}$$

$$= \frac{2.303}{t} \log \frac{P_i}{P_i - (P_f - P_t)(P_t - P_i)}$$

$$= \frac{2.303}{t} \log \frac{P_i}{P_f - P_i}$$

[Pg 117] [4.2]

20 15 —
0.01 - 0.2

$$R = K[A]^x[B]^y$$

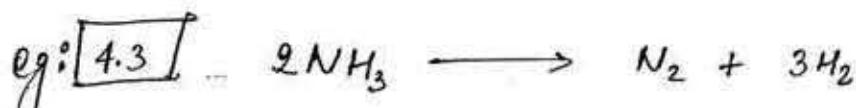
$$I.R = 2 \times 10^{-6} [0.1]^x [0.2]^y$$

$$= 2 \times 10^{-6} [0.06]^x [0.18]^y$$

$$\therefore 2A + B \rightarrow P$$

$$\therefore [A] = 0.1 - \frac{0.04}{\text{consumed}} = 0.06 \quad (\because 1 - 0.4 = 0.6)$$

$$[B] = 0.20 - \frac{0.02}{0.06} = 0.18$$



$$-\frac{d[NH_3]}{dt} = K[NH_3]^0$$

$$-\frac{d[NH_3]}{2 dt} = \frac{d[N_2]}{dt} - \frac{1}{3} \frac{d[H_2]}{dt}$$

$$\frac{d[N_2]}{dt} = \frac{K}{2}$$

$$\frac{d[H_2]}{dt} = \frac{3}{2} K$$

Pg 119 | 4.17

$$\frac{2.303}{28.1} \log 2 = \frac{2.303}{10} \log \frac{1}{A}$$

Pg 120 | 4.24

$$2 \times 10^{-2} = \frac{2.303}{100} \log \frac{1}{A}$$

Pg 120 | 4.25

$$\frac{2.303}{3} \log 2 = \frac{2.303}{8} \log \frac{A_0}{A}$$

$$\frac{0.3}{3} = \frac{1}{8} \log \frac{A_0}{A}$$

$$\therefore \log \frac{A_0}{A} = 0.1 \times 8 = 0.8$$

$$\therefore \frac{A_0}{A} = \text{Antilog}(0.8)$$

$$\frac{A_0}{A} = \text{Antilog}(0.8)$$

$$\frac{A_0}{A} = 6.310 \times 10$$

* Amount consumed = $\frac{A}{A_0} = \frac{1}{6.310}$

Antilog:

(+ve)

<u>14.340</u>	\rightarrow	<u>2.188</u>	$\times 10^{14}$
1.56	\rightarrow	3.631	$\times 10^1$
2.72	\rightarrow	5.248	$\times 10^2$
<u>30.843</u>	\rightarrow	6.966	$\times 10^{30}$
0.84 ka 3			

[0.34 diff 0]

(-ve)

-2.34	\rightarrow	3.66	\rightarrow	$\times 10^{-3}$
-8.76	\rightarrow	9.24	\rightarrow	$\times 10^{-9}$
-10.23	\rightarrow	11.77	\rightarrow	$\times 10^{-11}$
-50.26	\rightarrow	51.74	\rightarrow	$\times 10^{-51}$

* $\frac{1}{2.303} = 0.45$

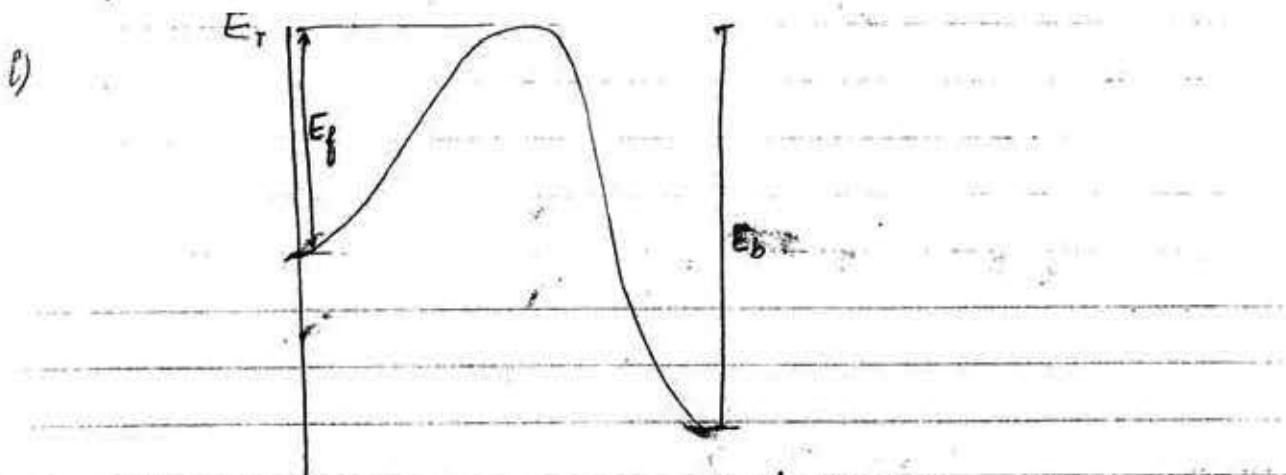
* $2.303 \times R \approx 20 \approx 0.1915$

* $2.303 R T_{298} \approx 5700$

Transition state theory:

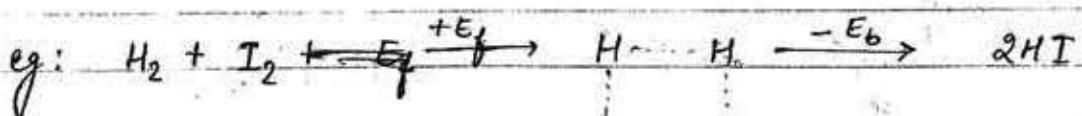
According to this theory, the reaction molecules absorbs activating energy and forms unstable intermediate known as activating complex and threshold energy barrier, then it converts into stable product by releasing the activating energy

To convert the reactant into product, the energy of forward is less than that of backward for a kinetically favourable reaction.



$$\therefore \Delta E = E_f - E_b = -ve$$

$$\therefore E_f < E_b$$



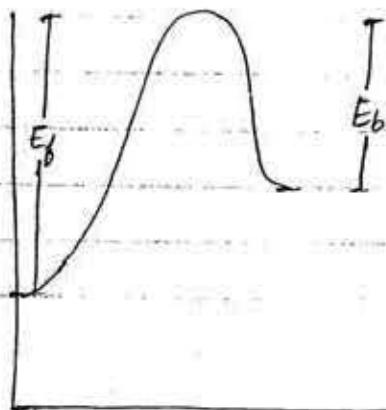
I. . . . I

activating complex

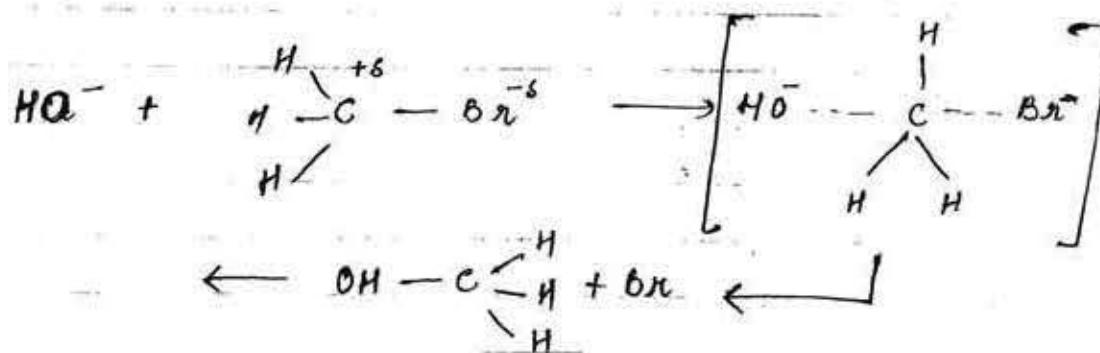
The reactions which are thermodynamically feasible but kinetically unfavourable have high forward activation energy

e.g: In case of substitution reactions in haloalkanes. The reaction is kinetically favourable only when nucleophile attack from rear side and hydrocarbons should have less steric hindrance

ii)



$$\Delta E = E_f - E_b \\ \because E_f > E_b = +ve$$



Relation b/w Rate constant and activation energy :

$$K = A e^{-\frac{E_a}{RT}} \quad [\text{Arrhenius eq}]$$

where K = rate constant $[\text{sec}^{-1} (\text{unit})]$

A = Arrhenius constant /
Pre exponential factor /
collision frequency

= it is the no. of collision per sec
per unit vol^m
unit : sec^{-1}

E_a = Activation energy
unit : joule/mole

R = gas constant
= $8.314 \text{ J K}^{-1} \text{ mole}^{-1}$

T = Absolute Temperature (in Kelvin)

$$\therefore K = A e^{-\frac{E_a}{RT}}$$

$$\log K = \text{to}$$

$$\ln K = \ln A + \ln e^{-\frac{E_a}{RT}}$$

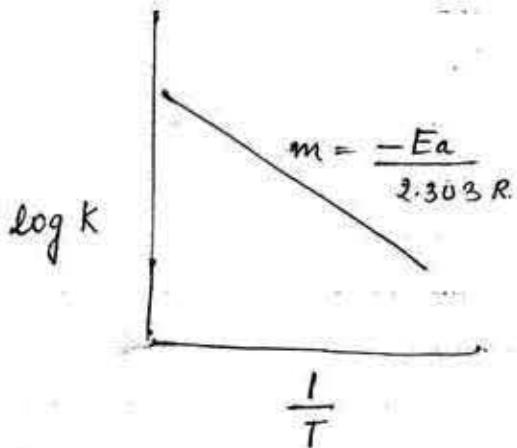
$$\ln K = \ln A - \frac{E_a \ln e}{RT}$$

$$[\because \log_e e = 1 \text{ and } \ln = 2.303 \cdot \log]$$

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

$$\therefore \log K = \log A - \frac{E_a}{2.303 R} \left(\frac{1}{T} \right)$$

$$y = c + m x$$



i) $T = \infty$ $K = ?$
 $K = A$

ii) $K = A e^{-\frac{E_a}{RT}}$ $\therefore E_a = ?$

$$\therefore \frac{E_a}{RT} = \frac{28000}{T}$$

$$\therefore E_a = 28000 \times 8.314 \text{ J/mole}$$

iii) $\log K = 14.34 - \frac{1.25 \times 10^4}{T} \quad \therefore E_a = ?$

$$\therefore \frac{E_a}{2.303 RT} = \frac{1.25 \times 10^4}{T}$$

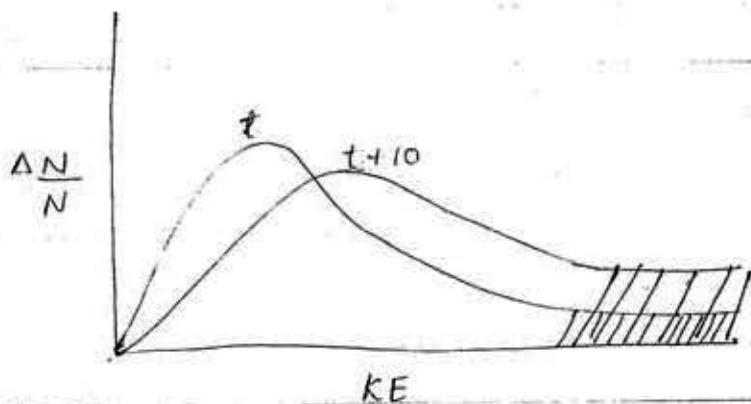
$$\therefore E_a = 2.303 R \times 1.25 \times 10^4$$

$$\Rightarrow 1.25 \times 10^4 \times 20 \text{ J/mole}$$

Relation b/w Rate constant and at two different temperature.

On increasing the temperature by 10°C the rate of the reaction becomes double due to increase in effective no of collision. The fraction of molecule increases, hence the most probable velocity increases due to increase in K.E

The ratio of the temperature is known as temperature co-efficient.



$$\frac{T_{t+10}}{T_t} = 2$$

T_t

$$V \propto \sqrt{T}$$

$$300 \rightarrow 310. \text{ (temp)}$$

$$\frac{10}{300} \times 100 = 3.33\%$$

$$\therefore V \propto \sqrt{T} \quad \therefore \sqrt{3.33} = 1.8 \approx 2$$

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

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

$$T_1 - T_2$$

$$\begin{array}{c} \log k_2 = \cancel{\log A} - \frac{E_a}{2.303 RT_1} \\ \log k_1 = \cancel{\log A} - \frac{E_a}{2.303 RT_2} \\ \hline - & + \end{array}$$

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

Pg 120 4*30

$$\log \frac{4k_1}{k_1} = \frac{E_a}{20} \left[\frac{1}{293} - \frac{1}{313} \right]$$

$$\therefore E_a = 0.6 \times 293 \times 313.$$

* The value of E_a lies between 50 - 55 kg/mole

\propto $\frac{k_2}{k_1} = 2^{\Delta T/10}$

Q) calculate the activation energy if rate of the reaction becomes triple on increasing the temp. from 300 K to 315 K

$$\log \frac{3K_1}{K_1} = \frac{E_a}{2.303R} \left[\frac{1}{300} - \frac{1}{315} \right]$$

Q) calculate the temp. if rate of the reaction increases from 4.5×10^3 to 1.5×10^4 by providing an activation energy 60 kJ/mole at 300 K

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60,000}{2.303R} \left[\frac{1}{300} - \frac{1}{T_2} \right]$$

$$\log \frac{10}{3} = \frac{60 \times 10^3}{20} \left[\frac{1}{300} - \frac{1}{T_2} \right]$$

$$\frac{0.52}{3000} = \frac{1}{300} - \frac{1}{T_2}$$

$$\frac{0.052}{300} = \frac{1}{300} - \frac{1}{T_2}$$

Q) calculate the activation energy if half life of 1st order reaction at 300 K is 20 minutes and that of 5 minutes at 320 K respectively.

$$k_1^{300} = \frac{2.303 \log 2}{20}$$

$$k_2^{320} = \frac{2.303 \log 2}{5}$$

$$\therefore \frac{k_2^{320}}{k_1^{300}} = \frac{20}{5} = 4$$

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

$$\log 4 = \frac{E_a}{20} \left[\frac{1}{300} - \frac{1}{320} \right]$$

$$0.6 = \frac{E_a}{20} \frac{20}{300 \times 320}$$

$$\therefore E_a = 0.6 \times 300 \times 320 \\ = 57.6 \times 10^3$$

Pg 120

4.29

$$t_{10}^{300} = t_{25}^{320}, E_a = ?$$

$$\therefore \frac{2.303}{K_1} \log \frac{100}{90} = \frac{2.303}{K_2} \log \frac{100}{75} \frac{4}{3}$$

$$\therefore \frac{K_2}{K_1} = \frac{\log 4 - \log 3}{\log 10 - \log 9}$$

$$\frac{0.6 - 0.48}{1 - 0.96} = \frac{0.12}{0.04} = 3.$$

FORMULAS

1) $R = K[A]^n$

~~unit of rate (R) = $(\text{mole})^t \text{ sec}^{-1}$~~

~~unit of $K = (\text{mole})^{1-n} \text{ sec}^{-1}$~~
~~= (atm) $^{1-n} \text{ sec}^{-1}$~~

2) For first order kinetics

(for solution)

$$K = \frac{2.303}{t} \log \frac{A_0}{A}$$

$$\text{At } t_{50} \quad A = \frac{A_0}{2}$$

$$(for \text{ gas}) \quad K = \frac{2.303}{t} \log \frac{P_i}{2P_i - P_t}$$



3) $K = A e^{-E_a/RT}$

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

$$\log \frac{K_2}{K_1} = \frac{-E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

\therefore Fraction of molecules having $E > E_a$.

$$\log x = \frac{-E_a}{2.303 RT}$$

4) Slope :

$$m = \tan \theta = -K \quad \text{for time (t)}$$

$$= \frac{-E_a}{R} \quad \text{for Temp. (T)}$$

$$= \frac{m(\text{slope})}{2.303} \quad \text{for log}$$

Derivations :

- i) Integrated rate law for 1st order
- ii) Integrated rate law for 1st order for gaseous reactant and product.
- iii) Relation b/w activation energy, rate constant at two different temperature

Exemplar

- Q) For which type of reaction order and molecularity have same value
Elementary reaction (Slow step - RDS)
- Q) For a certain reaction, large fraction of molecule have energy more than threshold energy. Yet the rate of reaction is slow. explain why
because at threshold energy barrier the molecules are not properly oriented in space so, it do not make effective collision.
- Q) Thermodynamic feasible on its own can't decide the rate of the reaction. explain with the help of eg.
Thermodynamically, graphite is more stable form. hence, ~~graphite~~ diamond converts into graphite but ^{due to} high forward activation energy, diamond do not convert into graphite
- * for 2 marks : take the eg of substitution reaction.