Chemical Kinetics

It is branch of physical chem. which deals with rate of chem. rx^n and factors affecting it.

Rate – It is defined as change in conc. of reactant / product per unit time.

In $molL^{-1}$

$$\boxed{Rate = \left(\frac{\Delta\ Conc.\ of\ Reactant|Product}{Time\ taken}\right)}$$

OR

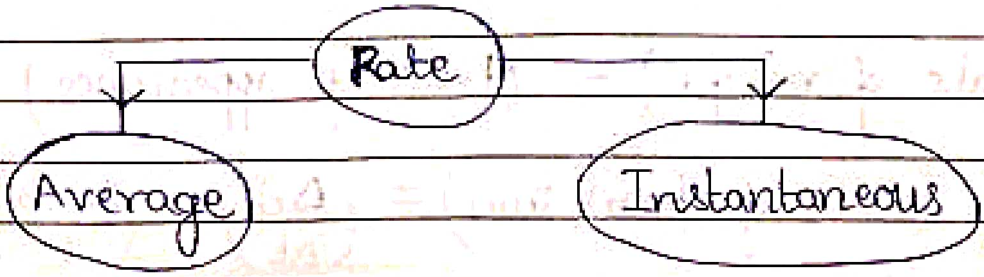
In Prsre

$$\boxed{Rate = \left(\frac{\Delta\ Prsre}{Time\ taken}\right)}$$

Units : $mol L^{-1} s^{-1}$ OR $atm\ s^{-1}$

Now, $PV = nRT \Rightarrow$ ~~$\Delta P = RT(\Delta\ Conc.)$~~

$$\boxed{\Delta P = RT(\Delta\ Conc.)}$$



Average Rate – for macroscopic time interval.

$$aA \longrightarrow bB$$

$$\left(\begin{matrix}\text{Average Rate}\\ \text{of A}\end{matrix}\right) = \left(\frac{-\Delta[A]}{\Delta t}\right) ; \left(\begin{matrix}\text{Average Rate}\\ \text{of B}\end{matrix}\right) = \left(\frac{\Delta[B]}{\Delta t}\right)$$

Instantaneous Rate – for microscopic time interval

$$aA \rightarrow bB.$$

$$(\text{Rate of A}) = \left(\frac{-d[A]}{dt}\right) ; (\text{Rate of B}) = \left(\frac{d[B]}{dt}\right).$$

Consider rx^n, $aA \longrightarrow bB$

$$(\text{Rate of } rx^n \text{ of A}) = (\text{Rate of disappearance})$$

$$= (\text{Rate of Consumption}) = \left(\frac{-\Delta A}{\Delta t}\right) = -\left(\frac{a_t - a}{t}\right.$$

$$(\text{Rate of } rx^n \text{ of B}) = (\text{Rate of appearance})$$

$$= (\text{Rate of formation}) = \left(\frac{\Delta B}{\Delta t}\right) = \left(\frac{b_t - b_0}{t}\right)$$

☆ Rate can NOT be (-ve).

Rate of individual species is INDEPENDENT of stoich. coeff.

Rate of rx^n depends on stoich coeff.

Rel^n b/w Rate of Diff. Species

Consider homo. irreversible rx^n.

$$aA \longrightarrow bB$$

At $t=0$ $\qquad a_0 \qquad 0$

At $t=t$ $\qquad (a_0 - ax) \qquad bx$

$$\left(\text{Rate of } A\right) = \frac{-d[A]}{dt} = a\left(\frac{dx}{dt}\right)$$

$$\left(\text{Rate of } B\right) = \frac{d[B]}{dt} = b\left(\frac{dx}{dt}\right)$$

Now, $\underbrace{\left(\frac{dx}{dt}\right)}_{\text{Rate of } rx^n} = \left(\frac{1}{a}\right)\left(\frac{-d[A]}{dt}\right) = \left(\frac{1}{b}\right)\left(\frac{d[B]}{dt}\right)$

In general,

$$\boxed{\left(\text{Rate of } Rx^n\right) = \left(\frac{1}{a}\right)\left(\frac{-dA}{dt}\right) = \left(\frac{1}{b}\right)\left(\frac{-dB}{dt}\right) = \left(\frac{1}{c}\right)\left(\frac{dC}{dt}\right)}$$

^{n}: $aA + bB \rightarrow cC$

Q) Consider $2A(g) \longrightarrow 3B(g)$ at 25°C
Prsre of A changes from 2 atm to 1 atm in 10s. Calc. —

1) Rate of rxn in $atm s^{-1}$ & $mol L^{-1} s^{-1}$
2) Prsre of B in same time.

A) 1) $(R.o.R) = \left(\frac{1}{2}\right)\left(\frac{-dA}{dt}\right) = \left(\frac{1}{2}\right)\left(\frac{2-1}{10}\right) atm s^{-1}$

$$\Rightarrow \boxed{RoR = \left(\frac{dP}{dt}\right) = \frac{1}{20} atm s^{-1}}$$

Now, $P = CRT \Rightarrow \left(\frac{dC}{dt}\right) = \left(\frac{1}{RT}\right)\left(\frac{dP}{dt}\right)$

$$\Rightarrow \left(\frac{dC}{dt}\right) = \frac{1}{\left(\frac{25}{300}\right)(298)}\left(\frac{1}{20}\right)\frac{mol}{Ls} \Rightarrow \boxed{\left(\frac{dC}{dt}\right) \sim \frac{1}{500} Ms^{-1}}$$

2) $\left(\frac{d[B]}{dt}\right) = 3(RoR) \Rightarrow \left(\frac{d[B]}{dt}\right) = \left(\frac{3}{20}\right) atm s^{-1}$

$$\Rightarrow P_B = (t)\left(\frac{d[B]}{dt}\right) \Rightarrow P_B = \left(\frac{3}{2}\right) atm$$

Q) For forming NH_3 from N_2 & H_2, rate of consumption of N_2 is 1.5×10^{-3} Ms^{-1}.
Calc. rate of rxn, & rate of NH_3 for rxn's

$N_2 + 3H_2 \rightarrow 2NH_3$ & $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$

A) RoR $= 1.5 \times 10^{-3}\ Ms^{-1}$ RoR $= 3 \times 10^{-3}\ Ms^{-1}$

$\left(\text{Rate of } NH_3\right) = 3 \times 10^{-3}\ Ms^{-1}$ $\left(\text{Rate of } NH_3\right) = 3 \times 10^{-3}\ Ms^{-1}$

Q) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$.

If rate of NH_3 is 1.7 kg/h for this rx^n, then calc. rate of H_2 in g/min.

A) $\left(\frac{dNH_3}{dt}\right) = 1.7\ \frac{kg}{h} =$ [redacted] [redacted] $\left(\frac{100}{60}\right)\frac{mol}{min}$

Now, $\left(\frac{1}{3}\right)\left(\frac{-dH_2}{dt}\right) = \left(\frac{1}{2}\right)\left(\frac{dNH_3}{dt}\right)$

$\Rightarrow \left(\frac{-dH_2}{dt}\right) = \left(\frac{3}{2}\right)\left(\frac{100}{60}\ \frac{mol}{min}\right) \Rightarrow \boxed{\left(\frac{-dH_2}{dt}\right) = 5\ \frac{\overset{(g)}{\text{[redacted]}}}{min}}$

Factors affecting RoR

1) Nature of reactants –

Bonds present b/w atoms of reactant & product are diff.

∴ RoR depends upon nature of bond breaking & bond formation.

2) Conc of Reactant – $\boxed{\text{RoR} \propto \text{Conc of Reactant}}$

3) Temperature – $\boxed{\text{RoR} \propto \text{Temp.}}$

4) Catalyst –

Catalyst inc. RoR w/o itself being consumed in rx^n.

5) Surface Area – $\boxed{\text{RoR} \propto \text{Surface Area}}$

6) Presence of Light – $\boxed{\text{RoR} \propto (\text{Intensity of Light})}$

Eg: $H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl$

$CH_4(g) + Cl_2(g) \xrightarrow{h\nu} CH_3Cl$

Rate Law Expression & Rate Const.

Consider the rx^n,

$$aA(g) + bB(g) + cC(g) \longrightarrow \text{Product}$$

$$\boxed{\text{Rate} \propto [A]^p [B]^q [C]^r}$$

Rate is proportional to product of active masses of reactants, each raised to some power. Powers may or may not represent stoich. coef.

$$\boxed{\text{Rate} = \underbrace{K}_{\text{rate const. of } rx^n} [A]^p [B]^q [C]^r}$$

Units of 'K' : $(\text{mol L}^{-1})^{1-(p+q+r)} s^{-1}$

* 'p', 'q', 'r' are practically determined.

- Elementary Rx^n: Any rx^n that takes place in only 1 step and reactant directly converts into product, no intermediate product formed.

★ Law of Mass action applicable only to elementary rx^{n}s.

⇒ $\boxed{p=a}$, $\boxed{q=b}$, $\boxed{r=c}$

- Complex Rx^n : Any rx^n that takes place in multiple elementary rx^n. In this, intermediate products are formed.

★ Rate Law Expression is applicable to complex rx^{n}s.

Order of Rx^n

Consider, $aA + bB + cC \longrightarrow$ Product

$$\text{Rate} = k[A]^p[B]^q[C]^r$$

$$\left.\begin{aligned} &\text{Order } \cancel{\text{Rate}} \text{ wrt } A = p \\ &\text{Order } \cancel{\text{Rate}} \text{ wrt } B = q \\ &\text{Order } \cancel{\text{Rate}} \text{ wrt } C = r \end{aligned}\right\} \quad \cancel{\text{Rate}}\ \boxed{\begin{pmatrix}\text{Order}\\ \text{of Rx}^n\end{pmatrix} = (p+q+r)}$$

- **Order of Rx^n** : Sum of exponent of molar conc. of reactants in experimentally determined rate law expression

Order can be 0, integer or fraction.

Order of Rx^n	Units of K
Zero	$(mol L^{-1}) s^{-1}$
first	s^{-1}
Second	$(mol^{-1} L) s^{-1}$

- Molecularity : It is no. of molecular species taking part in an elementary rx^n which are colliding simultaneously, to bring a chemical rx^n. It is NOT defined for complex rx^ns.

Unimolecular rx^ns (Molecularity = 1)

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

Bimolecular rx^n (Molecularity = 2)

$$2HI \longrightarrow H_2 + I_2$$

Trimolecular rx^n (Molecularity = 3)

$$2NO + O_2 \longrightarrow 2NO_2$$

1) Molecularity is a theoretical concept.

2) It has no significance for complex rx^n's. But we can calc. molecularity for individual steps

3) Order of complex rx^n is calced using slowest step, also called rate determining step.

4) For elementary rx^n's, Order = Molecularity

5) Probability of collision of >3 molecules is extremely low.
⇒ Molecularity is <u>not</u> observed >3.

6) Molecularity of rx^n can <u>NOT</u> be fractional. It is either 1, 2 or 3.

☆ (1)

$$NO + O_2 \rightleftharpoons NO_3 \text{ ---- fast}$$

$$NO_3 + NO \longrightarrow 2NO_2 \text{ ---- slow}$$

Rate Const. for 2nd rx^n is 'k'.

Find rate law exp^n for rx^n

A) From slowest step, (Law of Mass Action) Rate $= k[NO_3][NO]$

☆ Apply Law of Mass Action to slowest step, i.e. rate determining step.

But rate law NEVER contains intermediate.

Now, $K_c = \dfrac{[NO_3]}{[NO][O_2]} \Rightarrow [NO_3] = K_c[NO][O_2]$

$\Rightarrow \text{Rate} = k K_c [NO]^2[O_2]$

☆ ~~In rate determining step, we need~~

☆ If rx^n given in multiple steps, reduce every rx^n to SIMPLEST WHOLE NO. ratio, only then use to calc. rate. !

Pseudo Molecule or Pseudo Molecular Rx^n

Eg: $CH_3COOC_2H_5(aq.) + H_2O(l) \rightarrow CH_3COOH(aq.) + C_2H_5OH(aq.)$

In above rx^n, conc. of H_2O ~ const.

$\Rightarrow$ (Rate of rx^n) independent of $[H_2O]$

$\Rightarrow$ (Order of rx^n) wrt. H_2O is Zero

$\Rightarrow$ H_2O is Pseudo Molecule !

Pseudo Molecule : Molecules wrt whom order of rx^n is zero, but are necessary for rx^n. They don't affect rate of rx^n.

Methods to find Rate law Exp^n -

1) Initial Rate Method
2) Integrated Rate law Method.

1) Initial Rate Method —

Data is given to find rate law.

Q) $A + B \rightarrow \text{Product}$

$[A] (Ms^{-1})$	$[B] (Ms^{-1})$	Rate (Ms^{-1})
3	4	1.2×10^{-6}
3	8	2.4×10^{-6}
9	4	3.6×10^{-6}

A) ① ↔ ② ; $[B]$ doubles & (Rate) doubles & $[A]$ const. $\Rightarrow \boxed{r \propto [B]}$

① ↔ ③ ; $[A]$ triples & (Rate) triples & $[B]$ const. $\Rightarrow \boxed{r \propto [A]}$

So, $r = k[A][B]$

Now, $(1.2 \times 10^{-6}) = k(3)(4) \Rightarrow k = 10^{-7}$

Hence, $\boxed{r = (10^{-7})[A][B]}$

2) Integrated Rate law Method —

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

$$\text{Rate} = k[A]^{p} \Longrightarrow \boxed{\left(\frac{-dA}{dt}\right) = k[A]^{p}}$$

★ (Since stoich coeff. = 1)

$\Rightarrow$ (RoR = Rate of A)

Differental Rate Eq^{n}

Zero Order Kinetics

for zero order rxn, $A \longrightarrow$ Product

RoR ↳ $\left(\frac{-dA}{dt}\right) = k_A[A]^{0} = K_A \Rightarrow \int dA = \int -K_A\, dt$

$\Rightarrow A = C - K_A t$ at $\boxed{\begin{matrix} t = 0 \\ A = A_0 \end{matrix}}$

$\Downarrow$

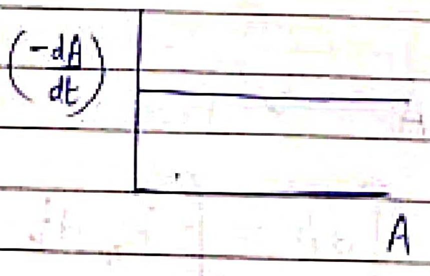
$\boxed{A = A_0 - k_A t}$ — Integrated Rate Law Eq^{n}

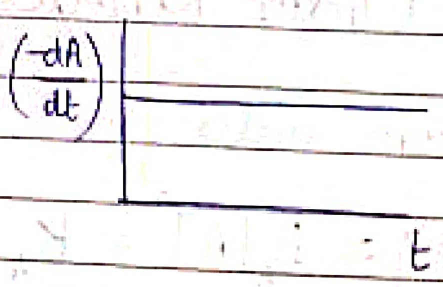
Lifetime (t_∞) : Time when reactant completely consumed.

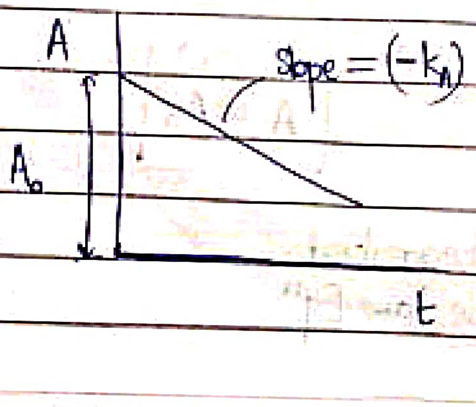
Half life $(t_{1/2})$: Time when (1/2 of the) reactant is consumed.

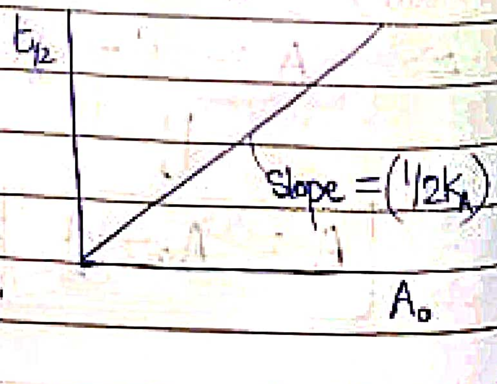
- For 0th order rxn, $\boxed{t_\infty = \left(\frac{A_0}{K_A}\right)}$ $\boxed{t_{1/2} = \left(\frac{A_0}{2K_A}\right)}$
- Unit of Rate Const : $mol L^{-1} s^{-1}$
- $A_0 \xrightarrow[t_{1/2}]{} \left(\frac{A_0}{2}\right) \xrightarrow[\frac{1}{2} t_{1/2}]{} \left(\frac{A_0}{4}\right) \xrightarrow[\frac{1}{4} t_{1/2}]{} \left(\frac{A_0}{8}\right)$
- $\boxed{t_{75\%} = t_{3/4} = (1.5)\, t_{1/2}}$

Graphs —









First Order Kinetics

For 1st order rx^n, $A \longrightarrow$ Product

RoR $\hookrightarrow$ $$\left(\frac{-dA}{dt}\right) = K_A [A]^1 \Rightarrow \int \left(\frac{1}{A}\right) dA = \int (K_A) dt$$

$$\Rightarrow \boxed{\ln(A) = C - k_A t} \quad \text{at } t=0,\ A = A_0$$

$$\Downarrow$$

$$\boxed{A = A_0 e^{-k_A t}} \leftarrow \text{Integrated Rate Law Eq}^n$$

Imp. formula : $\boxed{t = \left(\frac{2.303}{K_A}\right) \log\left(\frac{A_0}{A}\right)}$

- $\boxed{t_{1/2} = \left(\frac{\ln(2)}{K_A}\right) = \left(\frac{0.693}{K_A}\right)}$; $\boxed{t_\infty = \infty}$
- Unit of Rate Const : s^{-1}
- $A_0 \xrightarrow[t_{1/2}]{} \left(\frac{A_0}{2}\right) \xrightarrow[t_{1/2}]{} \left(\frac{A_0}{4}\right) \xrightarrow[t_{1/2}]{} \left(\frac{A_0}{8}\right)$
- $\boxed{t_{75\%} = t_{3/4} = (2) t_{1/2}}$
- $\boxed{t_{90\%} = t_{1/2}\left(\frac{10}{3}\right)}$
- $\boxed{t_{99\%} = t_{1/2}\left(\frac{10}{3}\right)(2)}$; $\boxed{t_{99.9\%} = t_{1/2}\left(\frac{10}{3}\right)(3)}$; $\boxed{t_{99.99\%} = t_{1/2}\left(\frac{10}{3}\right)(4)}$

- <u>Degree of Diss</u> : $\boxed{D.D = \left(\frac{A_0 - A}{A_0}\right) = \left(1 - e^{-k_A t}\right)}$

<u>Mean Life</u>: Avg. time for a molecule
(Avg. Life) to dissociate.

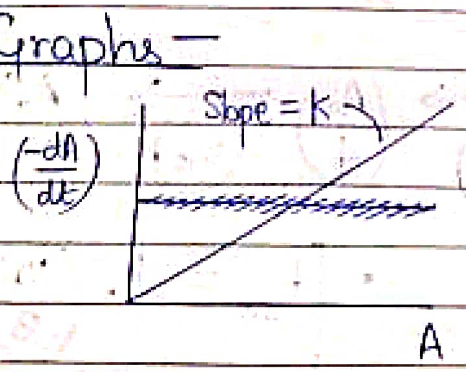
$$t_{avg} = \left(\frac{n_1 t_1 + n_2 t_2 + \ldots\ldots}{n_1 + n_2 + \ldots\ldots}\right) = \left(\frac{C_1 t_1 + C_2 t_2 + \ldots}{C_1 + C_2 + \ldots}\right)$$

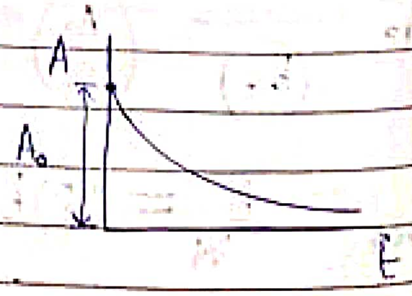
if n_1 molecules take t_1 time, n_2 molecules take t_2 time and so on.

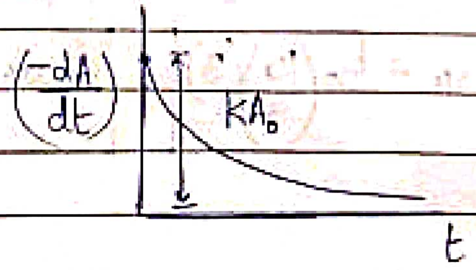
In general, $\boxed{t_{avg} = \frac{\int t \, dA}{A_0}}$

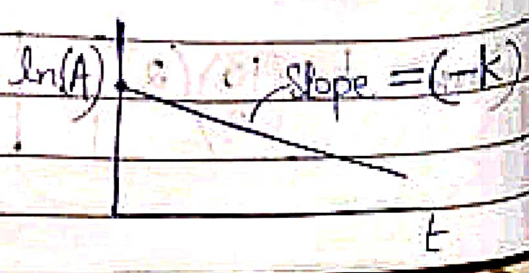
for 1st order rxn, $\boxed{t_{avg} = \frac{1}{k_A} = (1.44) t_{1/2}}$

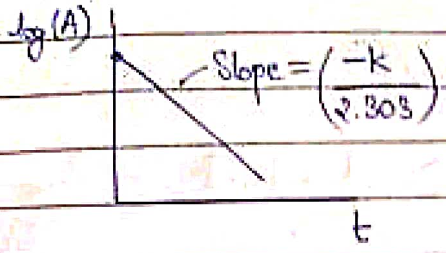
<u>Graphs</u>—

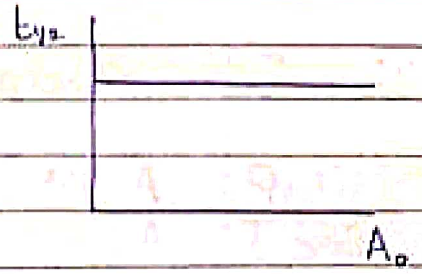












Second Order Kinetics

C1: Both reactant, same conc init.

R: A + B ⟶ Product

Conc. I: A_0 A_0

Conc. E: $(A_0 - x)$ $(A_0 - x)$

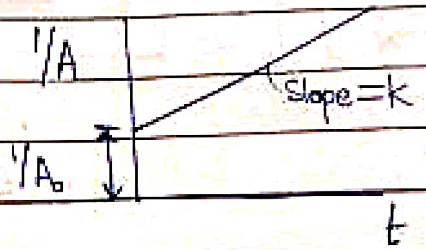
$$\left(\frac{-dA}{dt}\right) = \left(\frac{dx}{dt}\right) = k_A (A_0 - x)(A_0 - x)$$ (as 2nd order rxn given)

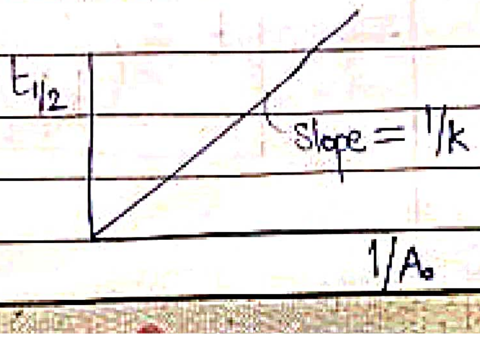
$$\Rightarrow \int \frac{1}{A^2}\, dA = \int -k_A\, dt \Rightarrow \boxed{\frac{1}{A} = C + k_A t}$$

At $t = 0$, $A = A_0$, $$\boxed{\frac{1}{A} = \frac{1}{A_0} + k_A t}$$

- $\boxed{t_{1/2} = \left(\frac{1}{A_0 k_A}\right)}$
- Units of Rate Const. : $mol^{-1} L\, s^{-1}$

Graphs –





C2: Both reactant, diff conc init.

$$R: \quad A + B \longrightarrow \text{Product}$$

Conc I: A_0 $\quad B_0$

Conc E: $(A_0 - x)$ $\quad (B_0 - x)$

$$\left(\frac{dx}{dt}\right) = k_A (A_0 - x)(B_0 - x) \qquad \left(\text{as 2nd order rx}^n \text{ given}\right)$$

$$\Rightarrow \int \frac{(B_0 - A_0)}{(A_0 - x)(B_0 - x)} \, dx = \int (B_0 - A_0) k_A \, dt$$

$$\Rightarrow \ln\left(\frac{B_0 - x}{A_0 - x}\right) = C + k_A (B_0 - A_0) t$$

At $t = 0$, $x = 0$ $\Rightarrow$ $C = \ln(B_0 / A_0)$

$$\Rightarrow \boxed{kt = \left(\frac{1}{B_0 - A_0}\right) \ln\left(\left(\frac{B_0 - x}{A_0 - x}\right)\left(\frac{A_0}{B_0}\right)\right)}$$

☆ If $B_0 >> A_0$, this becomes a <u>Pseudo First Order Rx^n</u>

Hence, $$t = \left(\frac{1}{k_A B_0}\right) \ln\left(\frac{A_0}{A_0 - x}\right)$$

$$\Rightarrow \boxed{t = \left(\frac{1}{k'}\right) \ln\left(\frac{A_0}{A_0 - x}\right)} \; ; \quad \boxed{k' = k_A B_0}$$

overall rate const. of new rx^n

General Order Kinetics

For 'n' th order rx^n, $A \longrightarrow$ Product

RoR

$$\hookrightarrow \left(\frac{-dA}{dt}\right) = k A^n \Rightarrow \int A^{-n}\, dA = \int -k\, dt$$

$$\Rightarrow \frac{A^{(1-n)}}{(1-n)} = C - kt$$

At $t=0$, $A=A_0$ $\Rightarrow$ $\boxed{kt = \left(\frac{1}{n-1}\right)\left[\frac{1}{A^{(n-1)}} - \frac{1}{A_0^{(n-1)}}\right]}$

- $\boxed{t_{1/2} = \left(\frac{2^{(n-1)}-1}{n-1}\right)\left(\frac{A_0^{(1-n)}}{k}\right) \propto A_0^{(1-n)}}$

Rate Const.

Rate Const. can be defined in 2 ways —

1) Rate Const. Of Rx^n

2) Rate Const. Of INDIVIDUAL SPECIES

Consider 1 st order rx^n,

$A \longrightarrow$ Product.

We have, $\left(\frac{-dA}{dt}\right) = k_A [A]$

Also, RoR $= \left(\frac{1}{1}\right)\left(\frac{-dA}{dt}\right) = k_R [A]$

$\boxed{k_A = k_r}$ in this case.

But if we had, $2A \rightarrow$ Product

We have, $\left(\frac{-dA}{dt}\right) = k_A[A]$ $\rightarrow$ $\boxed{k_A = 2k_R}$

Also, $RoR = \left(\frac{1}{2}\right)\left(\frac{-dA}{dt}\right) = k_R[A]$ $\rightarrow$

it changes from earlier

Q) $2A \rightarrow B + 3C$ find $k_A : k_B : k_C$

A) We know, $\left(\frac{-dA}{dt}\right) = k_A[A]$

$\left(\frac{-dB}{dt}\right) = k_B[A]$

$\left(\frac{-dC}{dt}\right) = k_C[A]$

$$RoR = \left(\frac{1}{2}\right)\left(\frac{-dA}{dt}\right) = \left(\frac{1}{1}\right)\left(\frac{dB}{dt}\right) = \left(\frac{1}{3}\right)\left(\frac{dC}{dt}\right) = k_R[A]$$

$\Rightarrow \boxed{k_A = 2k_R}, \boxed{k_B = k_R}, \boxed{k_C = 3k_B} \Rightarrow \boxed{Req = 2:1:3}$

Q) The following data was obtained from 1st order thermal decomposition of $N_2O_4(g)$ at const. vol. Find rate const. of rx

$$2N_2O_4 \rightarrow 2NO_2 + O_2$$

S.No.	Time	Total Prsre
1.	0	P_0
2.	t	P_1

A)

	R: $2A$	$\longrightarrow 2B$	$+ C$	Total
Prsre I:	P_0	0	0	P_0
Prsre E:	(P_0-2x)	$2x$	x	$\boxed{(P_0+x)=P_1}$

Now, $\left(-\frac{dA}{dt}\right) = k_A[A] \Rightarrow A_1 = A_0 e^{-k_A t}$

$$\Rightarrow (P_0 - 2x) = P_0 e^{-k_A t} \Rightarrow P_0 - 2(P_1 - P_0) = P_0 e^{-k_A t}$$

$$\Rightarrow (3P_0 - 2P_1) = P_0 e^{-k_A t} \Rightarrow \boxed{k_A = \left(\frac{1}{t}\right)\ln\left(\frac{P_0}{3P_0-2P_1}\right)}$$

Now, $k_R[A] = \left(\frac{-dA}{dt}\right)\left(\frac{1}{2}\right) = \left(\frac{k_A}{2}\right)[A] \Rightarrow \boxed{k_R = \left(\frac{k_A}{2}\right)}$

$$\Rightarrow \boxed{k_R = \left(\frac{1}{2t}\right)\ln\left(\frac{P_0}{3P_0-2P_1}\right)}$$

☆ If nothing specified, we are given or we have to find k_A, NOT k_R

Q) for rx^n (1st order), $A \longrightarrow B + C$

Find rate const.

Time	t	∞
Total Prsre	P_2	P_3

A)

R :	A	$\longrightarrow$ B +	C	Total
Prsre I :	P_0	0	0	P_0
Prsre E_1 :	$(P_0 - x)$	x	x	$(P_0 + x)$
Prsre E_2 :	0	P_0	P_0	$2P_0$

$(P_0 + x) = P_2$ & $P_3 = 2P_0$

Now, $(P_0 - x) = P_0 e^{-kt} \Rightarrow P_0 - (P_2 - P_0) = P_0 e^{-kt}$

$\Rightarrow (2P_0 - P_2) = P_0 e^{-kt}$

$\Rightarrow (P_3 - P_2) = \left(\frac{P_3}{2}\right) e^{-kt} \Rightarrow \boxed{k = \left(\frac{1}{t}\right) \ln\left(\frac{P_3}{2(P_3 - P_2)}\right)}$

Calc. of 1st Order Rx^n using diff. parameters

1) Decomposition of H_2O_2 —

(In terms of $KMnO_4$ used.)

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2} O_2$$

We conduct 2 rx^n, one in which H_2O_2 has NOT decomposed and other in which H_2O_2 has decomposed for a time 't'. We use 'V' vol. in each case.

$R_1 : H_2O_2 \longrightarrow H_2O + 1/2\, O_2$

Conc.I : $a \quad 0 \quad 0$

Since immediately reacted, $eq(H_2O_2) = 2aV$

Let 'M_1' M, 'V_0' vol. of $KMnO_4$ be used to neutralise it. $\Rightarrow$ $eq(KMnO_4) = 5M_1V_0$

$eq(H_2O_2) = eq(KMnO_4) \Rightarrow \boxed{a \propto V_0}$

$R_2 : H_2O_2 \longrightarrow H_2O + 1/2\, O_2$

Conc. I : $(a-x) \quad x \quad (x/2)$

Now, $eq(H_2O_2) = 2(a-x)V$

Let 'M_1' M, 'V_t' vol of $KMnO_4$ be used to neutralise it. $\Rightarrow$ $eq(KMnO_4) = 5M_1V_t$

$eq(H_2O_2) = eq(KMnO_4) \Rightarrow \boxed{(a-x) \propto V_t}$

Now, $kt = \ln\left(\frac{a}{a-x}\right) \Rightarrow \boxed{kt = \ln\left(\frac{V_0}{V_t}\right)}$

2) Decomposition of H_2O_2 —

(In terms of O_2 produced)

R :	H_2O_2	$\longrightarrow$ H_2O	+ $\frac{1}{2}O_2$
Conc I :	a	0	0
Conc E_1 :	$(a-x)$	x	$x/2$
Conc E_2 :	0	a	$a/2$

If prsre const., $\begin{pmatrix}\text{vol. of } O_2 \\ \text{produced}\end{pmatrix} \propto \begin{pmatrix}\text{mol. of} \\ O_2\end{pmatrix}$

$$\Rightarrow \quad \boxed{V_t \propto x/2} \quad \& \quad \boxed{V_\infty = a/2}$$

Now, $kt = \ln\left(\frac{a}{a-x}\right)$

$$\Rightarrow \quad \boxed{kt = \ln\left(\frac{V_\infty}{V_\infty - V_t}\right)}$$

3) Hydrolysis of Ethyl Acetate —

(In terms of NaOH used)

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+ \leftarrow \text{Catalyst.}} CH_3COOH + C_2H_5OH$$

We conduct 3 rx^ns, in 3 samples with vol. V.

1. NaOH added immediately
2. NaOH added after time 't'.
3. NaOH added after very long time.

To complete rx^n we add V_0, V_t & V_∞ vol. of NaOH (with same molarity) in resp. samples. As in 1), we have;

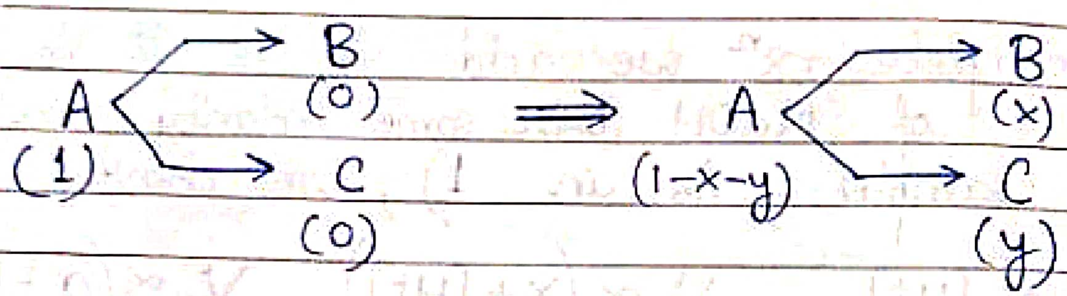
$$V_0 \propto [H^+] \quad , \quad V_t \propto (x + [H^+]) \quad , \quad V_\infty \propto (a + [H^+])$$

Now, $$kt = \ln\left(\frac{a}{a-x}\right) \Rightarrow \boxed{kt = \ln\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)}$$

4) Hydrolysis of Sucrose (Inversion of Cane Sugar) —

Parallel & Series Rx^ns (1st Order Kinetics)

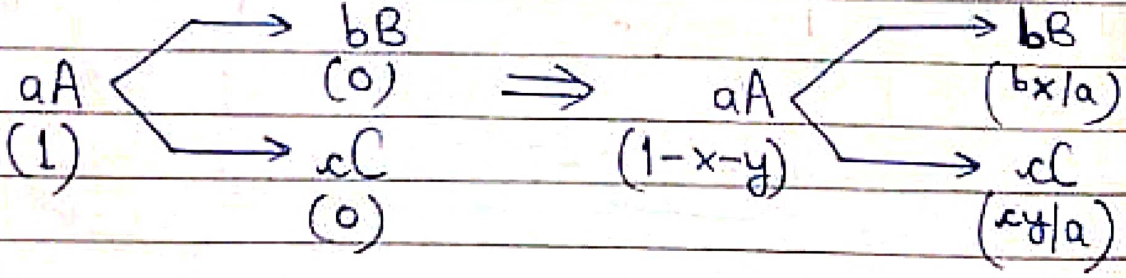
1) Parallel Rx^n —



Init. mol. $= \boxed{1}$

Final mol. $= (x+y) = \boxed{1}$ (as at final $(1-x-y) \sim 0$)

Here, $A_0 = A_t + B_t + C_t$



Init. mol $= 1$

Final mol $= \left(\frac{bx}{a} + \frac{cy}{a}\right)$ (as at final $(1-x-y) \sim 0$)

Here, $A_0 = A_t + \left(\frac{a}{b}\right)B_t + \left(\frac{a}{c}\right)C_t$

for rxn,
$$A \begin{cases} \xrightarrow{k_1} B \\ \xrightarrow[k_2]{} C \end{cases}$$

$$\begin{pmatrix}\text{Net dissappearance} \\ \text{rate of A}\end{pmatrix} = \left(\frac{-dA}{dt}\right) = k_1[A] + k_2[A]$$

$$\Rightarrow \left(\frac{-dA}{dt}\right) = \left(k_1 + k_2\right)[A]$$

$$\Rightarrow \boxed{A_t = A_0\, e^{-(k_1+k_2)t}}$$

Now, $k_{net} = k_1 + k_2 \Rightarrow \dfrac{0.693}{(t_{1/2})_{net}} = \dfrac{0.693}{(t_{1/2})_1} + \dfrac{0.693}{(t_{1/2})_2}$

$$\Rightarrow \boxed{\frac{1}{(t_{1/2})_{net}} = \frac{1}{(t_{1/2})_1} + \frac{1}{(t_{1/2})_2}}$$

Now, $\left(\dfrac{dB}{dt}\right) = k_1[A] = \left(k_1 A_0\right) e^{-(k_1+k_2)t}$

$$\Rightarrow \boxed{B_t = \left(\frac{k_1}{k_1+k_2}\right) A_0 \left[1 - e^{-(k_1+k_2)t}\right]}$$

Similarly, $\boxed{C_t = \left(\dfrac{k_2}{k_1+k_2}\right) A_0 \left[1 - e^{-(k_1+k_2)t}\right]}$

Hence, $\boxed{B_t / C_t = k_1 / k_2}$

% Product formation –

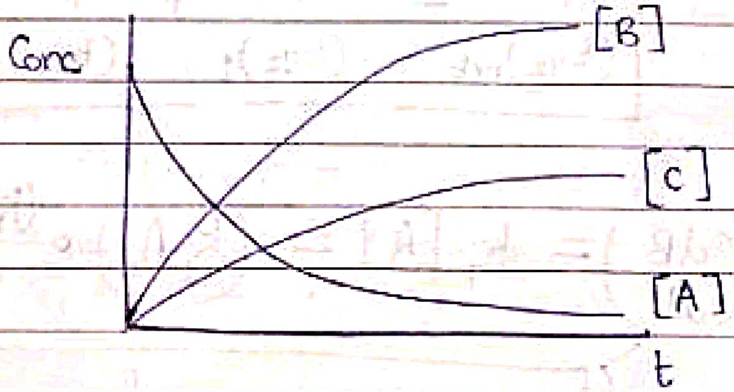
$$\boxed{\%B = \left(\frac{k_1}{k_1+k_2}\right)\times 100\%} \qquad \boxed{\%C = \left(\frac{k_2}{k_1+k_2}\right)\times 100\%}$$

If $A \begin{cases} \xrightarrow{k_1} bB \\ \xrightarrow[k_2]{} cC \end{cases}$, $\%B = \left(\frac{bk_1}{bk_1+ck_2}\right)\times 100\%$

$$\%C = \left(\frac{ck_2}{bk_1+ck_2}\right)\times 100\%$$

Q) $A \begin{cases} \xrightarrow{k_1} B \\ \xrightarrow[k_2]{} C \end{cases}$ $k_1 = 2k_2$. Find graph of conc.

A)



2) Series Rx^n —

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$\left(\frac{-dA}{dt}\right) = k_1[A] \Rightarrow \boxed{A_t = A_0 e^{k_1 t}}$$

$$\left(\frac{dB}{dt}\right) = k_1[A] - k_2[B]$$

(kitna bana) (kitna toota)

$$\Rightarrow \left(\frac{dB}{dt}\right) + k_2[B] = k_1[A]$$

$$\Rightarrow \left(\frac{dB}{dt}\right) e^{k_2 t} + [B] \frac{d}{dt}\left(e^{k_2 t}\right) = k_1[A] e^{k_2 t}$$

$$\Rightarrow \frac{d}{dt}\left(B_t e^{k_2 t}\right) = k_1 A_0 e^{(k_2 - k_1)t}$$

$$\Rightarrow B_t e^{k_2 t} = C + \left(\frac{k_1}{k_2 - k_1}\right) A_0 \left[e^{(k_2 - k_1)t} - 1\right]$$

At $t = 0$, $B_t = 0 \Rightarrow \boxed{C = 0}$

$$\Rightarrow \boxed{B_t = \left(\frac{k_1}{k_2 - k_1}\right) A_0 \left[e^{-k_1 t} - e^{-k_2 t}\right]}$$

For $[B]_{max}$, $\left(\frac{dB_t}{dt}\right) = 0$

$$\Rightarrow \boxed{t_{max} = \left(\frac{1}{k_1-k_2}\right)\ln\left(\frac{k_1}{k_2}\right)}$$

$$\Rightarrow \boxed{B_{max} = A_0\left(\frac{k_1}{k_2}\right)^{\left(\frac{k_2}{k_2-k_1}\right)}}$$

Observe,

t	A_t	B_t	C_t
0	1	0	0
t_1	$1-x$	$x-y$	y

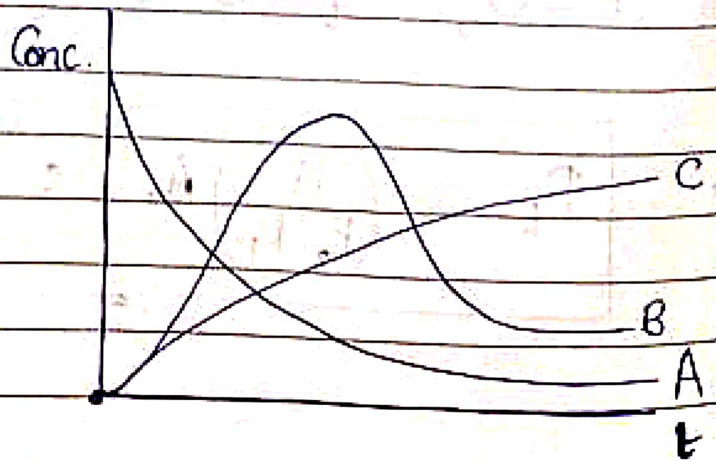
Conc. final $= (1-x)+(x-y)+y = 1$

Conc. init. $= 1$.

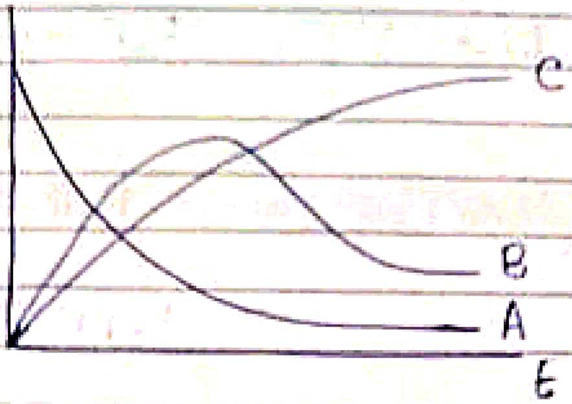
$\Rightarrow$ At every inst. total conc. = init. conc.

$$\Rightarrow \boxed{C_t = A_0 - A_t - B_t}$$

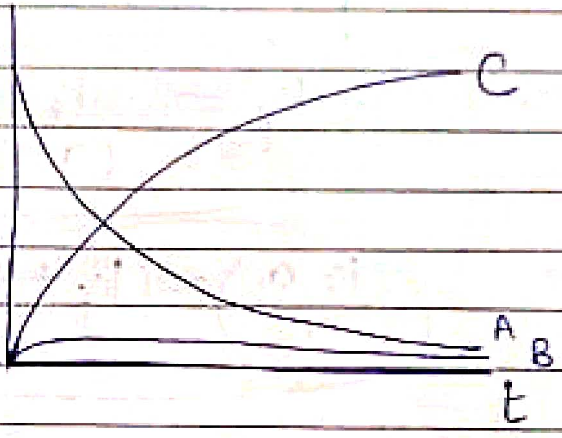
If $k_1 > k_2$,



If $k_1 < k_2$, Conc.



If $k_1 << k_2$, Conc.



Equilibrium (1st Order Kinetics)

$$R: A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

$t=0$: a 0

$t=t$: $(a-x)$ x

$t=t_{eq}$: $(a-x_e)$ x_e

Now, $\boxed{RoR = Ro(\text{frwd}) rx^n - Ro(\text{Bkwrd}) rx^n}$

At time 't', $RoR = \left(\frac{-dA}{dt}\right) = \left(\frac{dx}{dt}\right)$

At time 't_{eq}', $RoR = 0$

$$\Rightarrow RoFR = RoBR$$

$$\Rightarrow k_f(a - x_e) = k_b x_e$$

$$\Rightarrow \boxed{k_f = \frac{k_b x_e}{(a - x_e)}} \quad — ①$$

$$\Rightarrow \boxed{\left(\frac{k_f a}{x_e}\right) = (k_f + k_b)} \quad — ②$$

At time 't', $\left(\frac{dx}{dt}\right) = RoR = RoFR - RoBr$

$$\Rightarrow \left(\frac{dx}{dt}\right) = k_f(a - x) - k_b x$$

Using ①

$$\Rightarrow \left(\frac{dx}{dt}\right) = \left(\frac{k_b x_e}{a - x_e}\right)(a - x) - k_b x$$

$$\Rightarrow \left(\frac{dx}{dt}\right) = \left(\frac{k_b x_e a - \cancel{k_b x_e x} - k_b x a + \cancel{k_b x_e x}}{a - x_e}\right)$$

$$\Rightarrow \left(\frac{dx}{dt}\right) = \left(\frac{k_b a}{a - x_e}\right)(x_e - x)$$

$$= \boxed{\frac{k_b x_e}{a - x_e}}\left(\frac{a}{x_e}\right)(x_e - x)$$

$$\Rightarrow \left(\frac{dx}{dt}\right) = \boxed{\frac{k_f\, a}{x_e}}\left(x_e - x\right) \quad \left(\text{Using } ①\right)$$

$$\Rightarrow \left(\frac{dx}{dt}\right) = \left(k_f + k_b\right)\left(x_e - x\right) \quad \left(\text{Using } ②\right)$$

$$\Rightarrow \int_0^x \frac{dx}{x_e - x} = \int_0^t \left(k_f + k_b\right) dt$$

$$\Rightarrow \boxed{\left(k_f + k_b\right) t = \ln\left(\frac{x_e}{x_e - x}\right)}$$

Effect of Temp. on RoR

Temp. Coeff. – The factor with which ror is multiplied for every 10°C rise in temp.

It is const for a given rxn.

$$R(0^\circ) = R_0 \Rightarrow R(0 + 10^\circ) = \alpha^1 R_0 \Rightarrow R(0 + 20^\circ) = \alpha^2 R_0$$

$$\Rightarrow \boxed{R(t + \Delta t) = R(t)\,\alpha^{\Delta t/10}}$$

In general, $\boxed{2 \leq \alpha \leq 3}$

Effective Collision Theory

At $T = 10^\circ C$, Total Collisions $= 100$, Rate $= R_0$

$$\left(\underset{\text{ineffective}}{95} + \underset{\text{effective}}{5}\right).$$

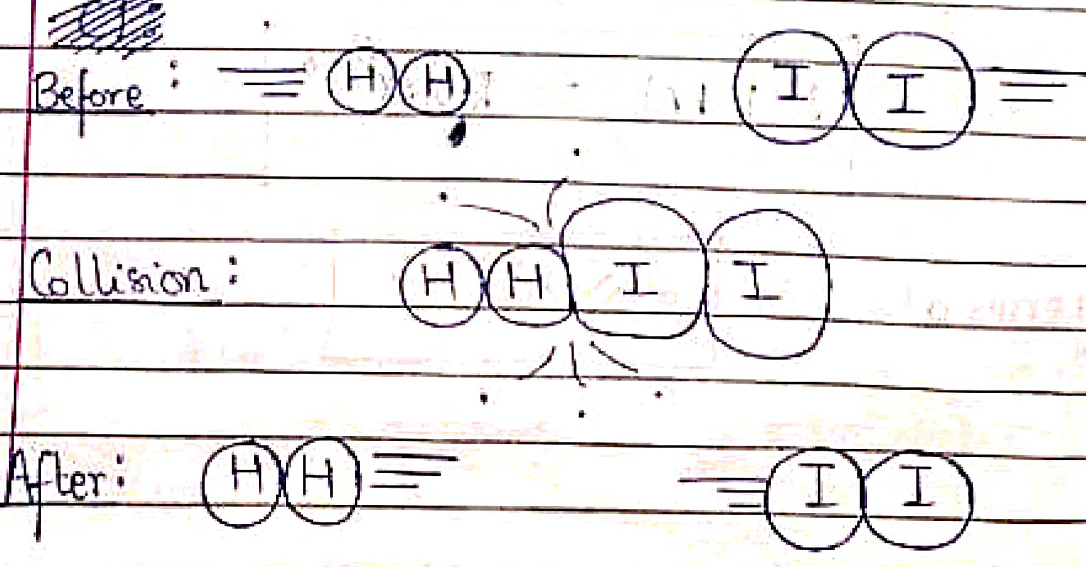
At $T = 20^\circ C$, Total collisions $= 150$, Rate $= 2R_0$

$$\left(\underset{\text{ineffective}}{140} + \underset{\text{effective}}{10}\right)$$

The fraction of total collisions that bring about the rxn are known as effective collisions.

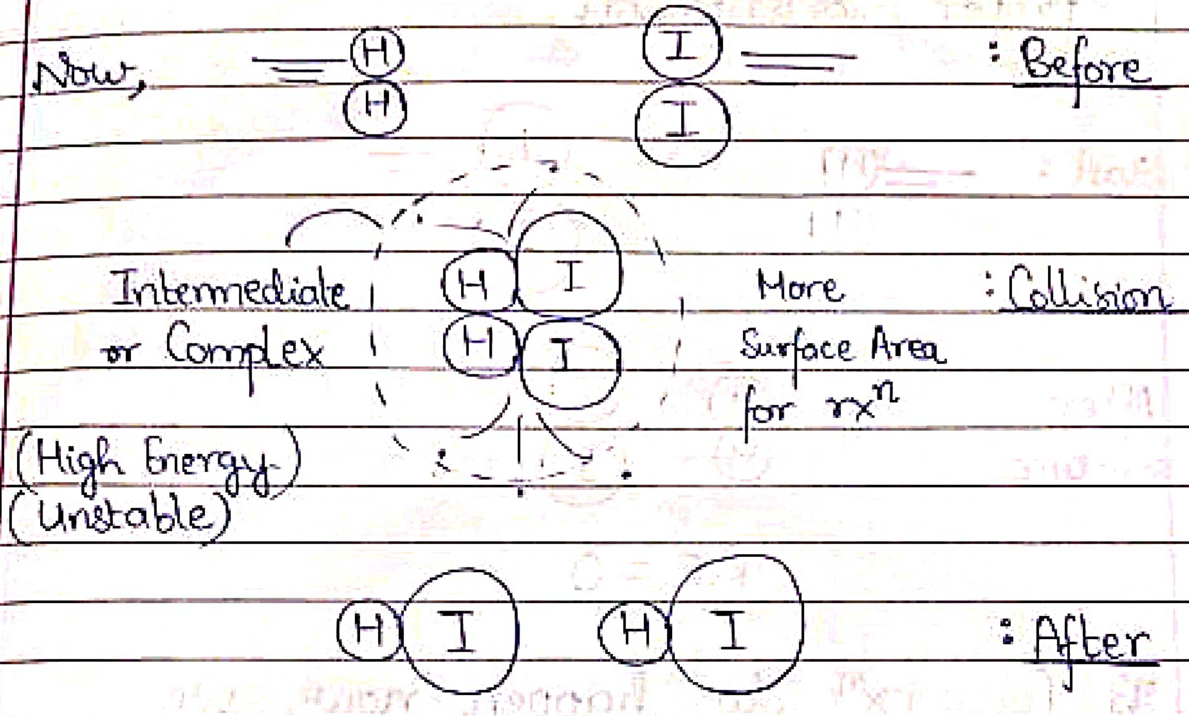
Effective collisions occur if 2 barriers are overcome —

1) Orientation Barrier :—



This is ineffective collision as WRONG orientation. Less surface area for rx^n.

Now,



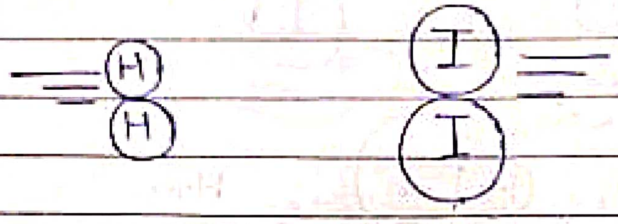
Threshold Energy (E_T) : Min. energy which colliding molecules must have so they have effective collision.

It is equal to energy of Intermediate.

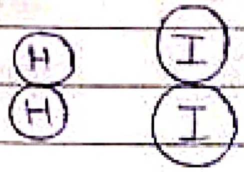
2) Energy Barrier —

If molecules are colliding in proper orientation.

Start:



After some time :

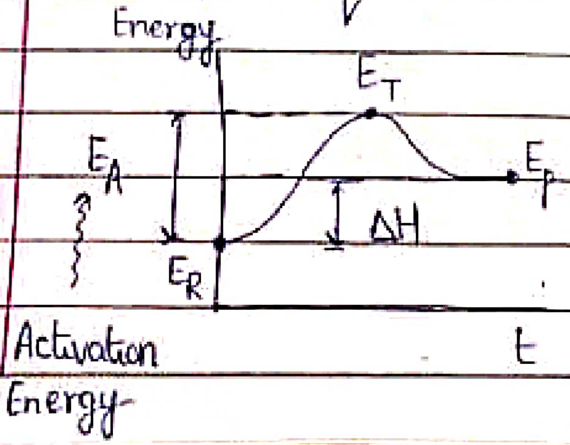


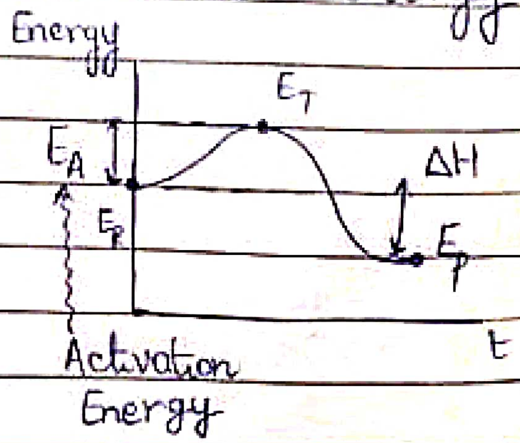
K.E = 0

For rx^n to happen now, we need to add extra energy.

Activation Energy —

Min. extra amt of energy absorbed by reactants s.t their energy becomes equal to threshold energy.

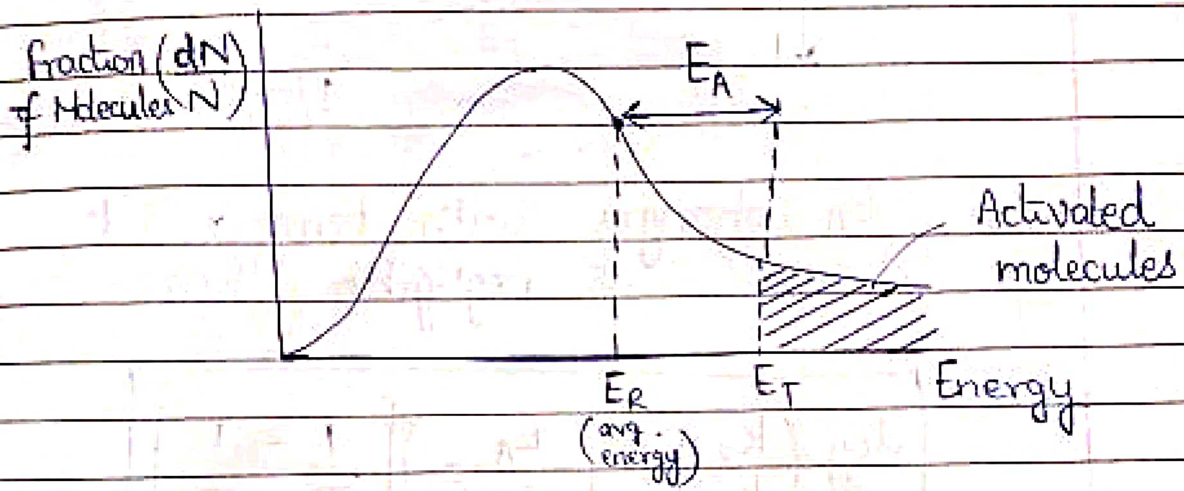




Enthalpy

where $\Delta H = (E_P - E_R)$.

$$\boxed{\begin{pmatrix}\text{Activation}\\ \text{Energy of}\\ \text{Fwd Rx}^n\end{pmatrix} = E_A \Rightarrow \begin{pmatrix}\text{Activation}\\ \text{Energy of}\\ \text{Bwrd Rx}^n\end{pmatrix} = E_A - \Delta H}$$



Activated Molecules : Molecules whose energy $\geq E_T$
(Effective)

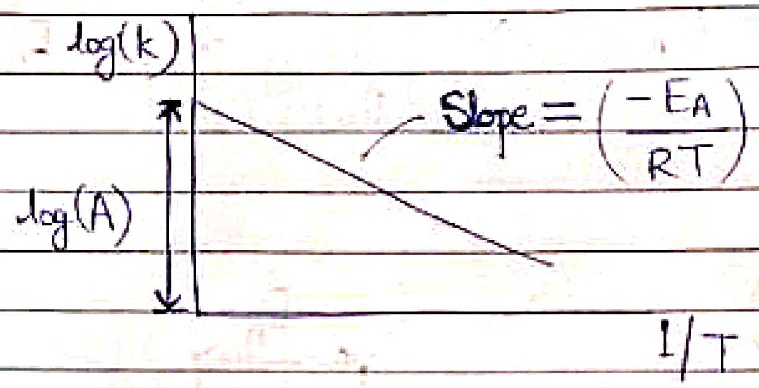
$$\boxed{\begin{pmatrix}\text{Fraction of}\\ \text{effective molecules}\end{pmatrix} = e^{-E_A/RT}}$$

We have, Rate Const $(K) \propto \begin{pmatrix}\text{Fraction of}\\ \text{effective molecules}\end{pmatrix}$

$$\Rightarrow \boxed{k = Ae^{-E_A/RT}}$$

Arrhenius Eq^n

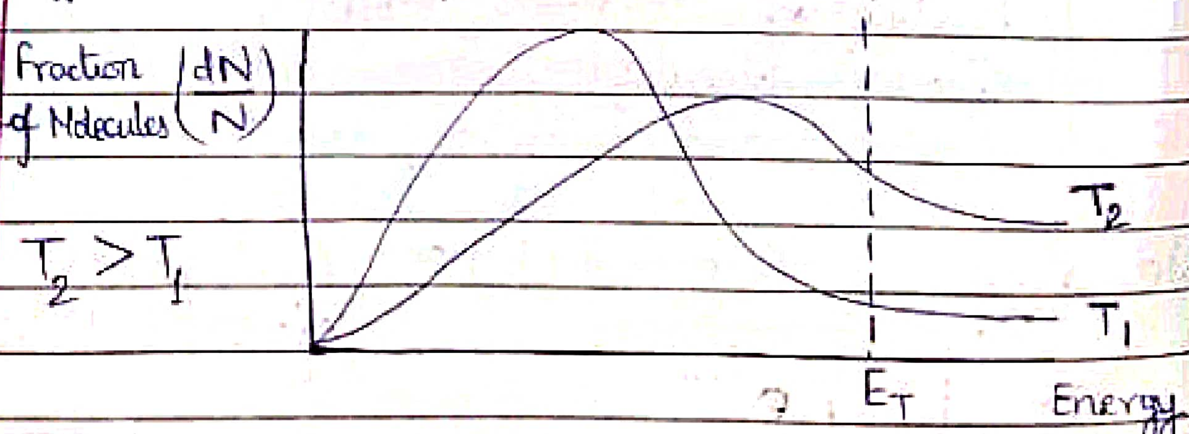
A - Arrhenius Const., Collision factor, Pre-exponential factor, Taking log on both sides, $\boxed{\log(k) = \log(A) - \frac{E_A}{(2.303)RT}}$



Now, E_A changes with temp. But if change is negligible then,

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

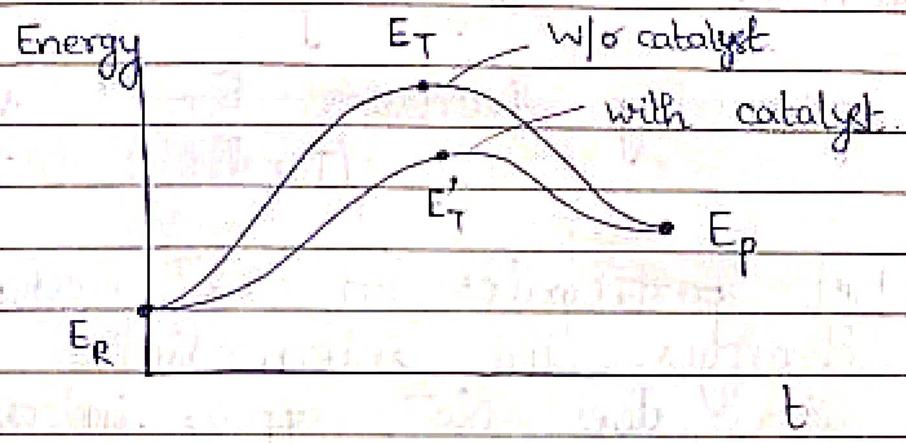
Effect on Temp.



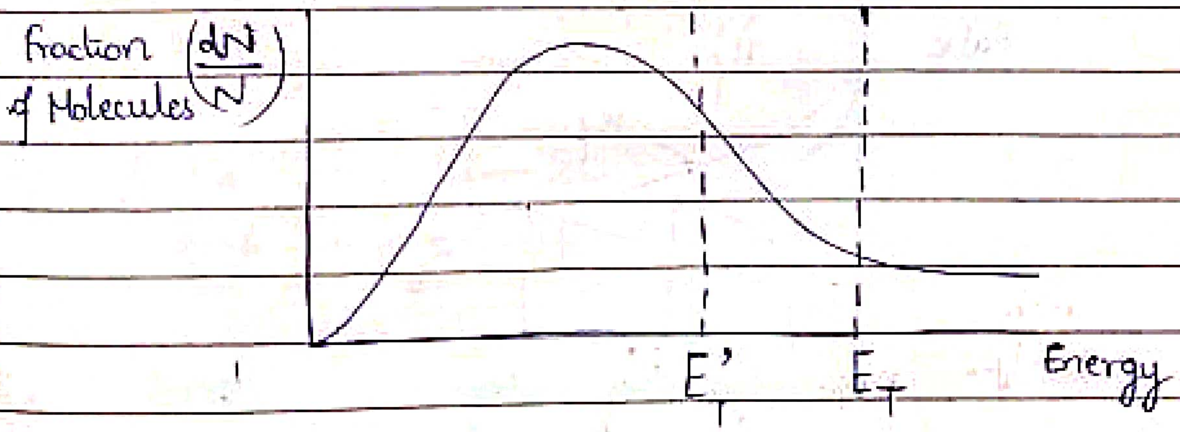
Area of Curve remains same as it represents ①.

Hence, by ↑ temp., fraction of activated molecules ↑.

Effect of Catalyst on RoR



We observe E_R & E_P remain same in both cases, but changes. E_A & E_T
catalyst



1) Catalyst does NOT change avg. energy of reactant & product.

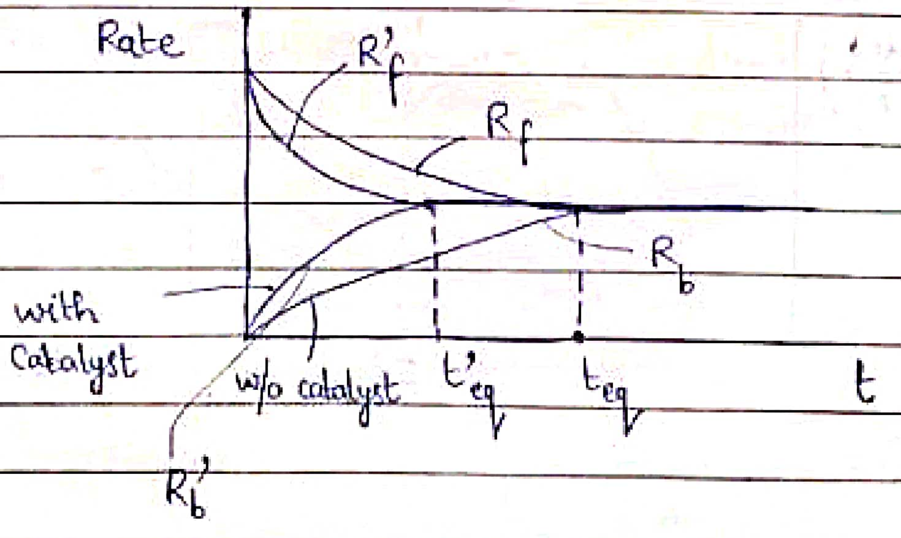
2) Catalyst does NOT change heat of rx^n i.e. ΔH remains same.

3) Catalyst does NOT affect type of spontaneity i.e. sign of ΔG!

4) It generally decreases E_T (Threshold) & E_A (Activation)

5) Catalyst participates in rx^n mechanism & changes the intermediate But it does NOT appear in overall eq^n.

6) Catalyst does NOT change K_{eq} of reversible rx^n. It brings eq. faster.



rate of change

7) Catalyst increases both RoFR & RoBR.
Hence, eq. acheived faster

fraction

8) Catalyst increases [illegible] of activated molecules.
Hence, rate const. ↑ ⇒ RoR ↑.

Q) A hydrogenation rx^n is carried out at 500 K. If same rx^n is carried out in presence of catalyst at same rate, the temp. req. is 400 K. Calc. the activation energy of rx^n if catalyst lowers the activation energy by 20 kJ/mol.

A) W/o Catalyst : $k = A e^{-E_A/R(500)}$

With catalyst : $k = A e^{-(E_A-20)/R(400)}$

$$\Rightarrow \left(\frac{E_A}{500R}\right) = \left(\frac{E_A - 20}{400R}\right) \Rightarrow \boxed{E_A = 100 \text{ kJ/mol}}$$

We know, Rate Same ⇒ Rate Const. Same

Radioactivity

Spontaneous disintegration of unstable nuclei by emission of radiations like α, β, γ, positron, ...

$$\alpha \longrightarrow {}^{4}_{2}He^{2+}$$

$$\beta \longrightarrow {}^{0}_{-1}e \text{ (fast moving)}$$

$$\gamma \longrightarrow {}^{0}_{0}\gamma \text{ (EM rays with high energy)}$$

Velocity : $\gamma > \beta > \alpha$

Penetration : $\gamma > \beta > \alpha$

☆ Radioactivity does NOT depend on ext. condition like temp. & prsre, or physical state of radioactive nuclei

X radioactive ⇒ $X(g)$, $X(l)$, $X(s)$, $X^{+}(g)$ are all radioactive.

All radioactive disintegration follow first order kinetics.

$$\underset{\text{radioactive}}{A} \longrightarrow \underset{\text{stable}}{B} + C$$

$$\boxed{-\frac{dN}{dt} = \lambda N}$$

no. of nuclei/atom at time t

rate of decay (A)

decay const. (not depend on temp.)

* Activity (A)

Rate at which disintegration of radioactive substance take place

$$A = \lambda N$$

$$N = \frac{w}{M} N_A$$

$$\boxed{A = \lambda \frac{w}{M} N_A}$$

note :→ No significance of Arrhenius eqn.

Units of activity (A)

1 Ci = 3.7×10^{10} dPs : disintegration per second

1 mCi = 3.7×10^{7} dPs

1 μCi = 3.7×10^{4} dPs

S.I unit : Becquerel

$$\boxed{1\ Bq = 1\ dPs}$$

* $\boxed{3.7 \times 10^{10}\ Bq = 1\ Ci}$

* Specific activity

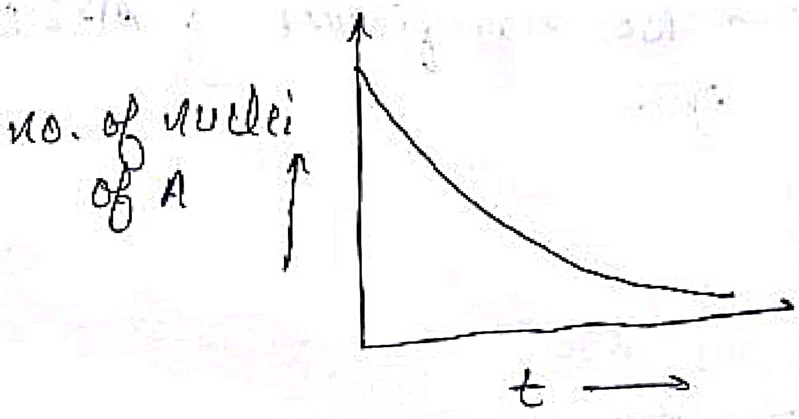
Activity of 1 gm radioactive sample is called specific activity.

$$\boxed{-\frac{dN}{dt} = \lambda N}$$

$$\boxed{N = N_0 e^{-\lambda t}}$$

No. of nuclei of A after time t.

$$\boxed{\lambda = \frac{1}{t} \ln \frac{N_0}{N_t}}$$



$$N_0 = \frac{W_0}{M} N_A = n_0 N_A$$

$$\frac{A_0}{A} = \frac{N_0}{N} = \frac{n_0}{n} = \frac{W_0}{W}$$

* $$\boxed{\lambda = \frac{1}{t} \ln \frac{W_0}{W} = \frac{1}{t} \ln \left(\frac{W_0}{W_0 - x} \right)}$$

where, W = wt. of A left after time (t)
$(W_0 - x)$

x = wt. of radioactive substance A disintegrated after time t.

* Half life

$$\boxed{t_{1/2} = \frac{0.693}{\lambda}}$$

* Average life

$$t_{av} = \frac{1}{k}$$

$$\boxed{t_{avg} = 1.44\, t_{1/2}}$$

(iv) Application of radioactivity

*→ Carbon dating : used to find ag
of wood based object

CO_2 : stable

$^{14}CO_2$: radioactive

In nature,

$$\boxed{{}^{14}_{6}C : {}^{12}_{6}C = 1 : 10^{12}}$$

ratio is maintained

Upper atmosphere,

$${}^{14}_{7}N + {}^{1}_{0}n \longrightarrow {}^{14}_{6}C + {}^{1}_{1}p$$

Age of wood based object

$$\boxed{t = \frac{1}{\lambda} \ln\left(\frac{A_0}{A}\right)}$$

A_0 = Activity of fresh wood piec

A = " " old " "

*→ Age of rocks & minerals

$${}^{A}_{Z}X \longrightarrow {}^{A-4}_{Z-2}X + {}^{4}_{2}He$$

$$^{A}_{Z}Y \longrightarrow \, ^{A}_{Z+1}Y + \, ^{0}_{-1}e$$ (emitted from nucleus)

* no. of α-particles emitted = $\dfrac{\text{diff. b/w atomic masss}}{4}$

Eg: $^{238}_{92}U \longrightarrow \, ^{206}_{82}Pb + x \, ^{4}_{2}He +$

$$\frac{238-206}{4} = x$$

& $92 = 82 + 2x - 4$