

enzyme-catalyse is more effective than any other cat by many powers of 10.
Due to low E_a , becomes bifunctional.
Cat i.e. The rate ~~ext~~ by large extent.

one accept proton
other waves.

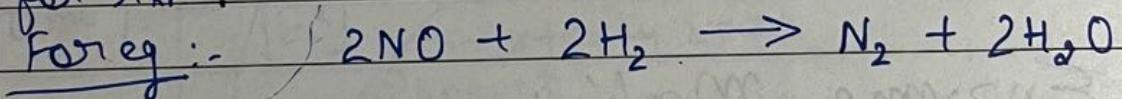
Sec-B

Composite Rxn's :-

Laidler
278 O/WN
Read from book

thermal, photochem or radiation chemically
 ↓ ↓
 low energy high energy

Most obv indications that a mech is composite is when kinetic eq is inconsistent w/ stochio eq for rxn.

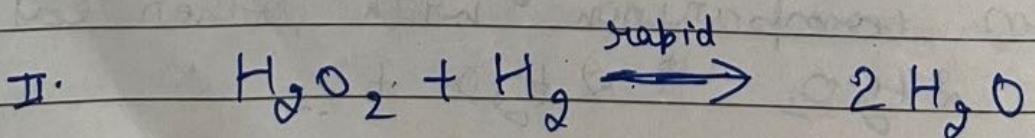
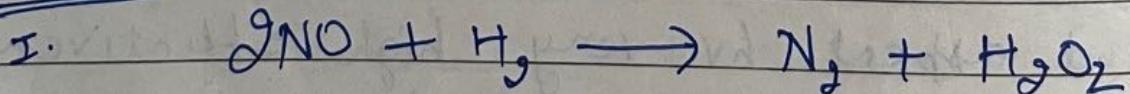


Al/c stochio \rightarrow 4th order
actually \rightarrow 3rd ,,

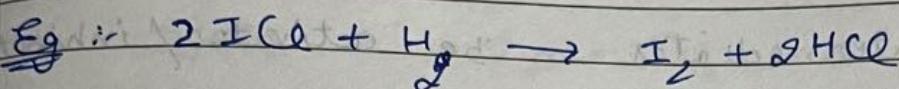
Under usual conditions rate is proportional to $[\text{NO}]^2$ but only to $[\text{H}_2]^2$

$$\therefore v = k [\text{NO}]^2 [\text{H}_2] \quad \text{i.e., 3rd order.}$$

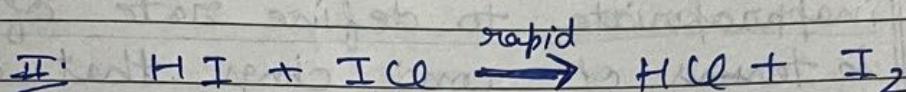
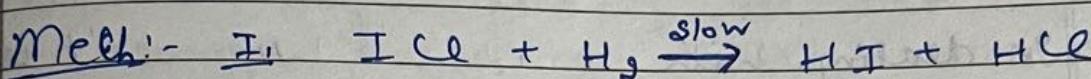
Mech :-



∴ rate of (I) rxn controls rate of (II).



Ac Stochio \rightarrow 3rd order
in actual \rightarrow 2nd ,

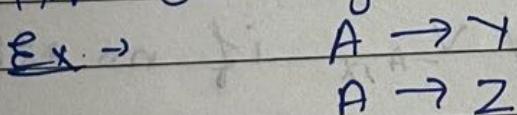


~~∴~~ rxn can occur in steps, it is found very frequently that order of rxn is less than corresponds directly to stochio eq.

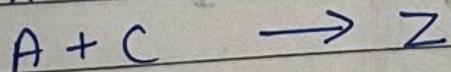
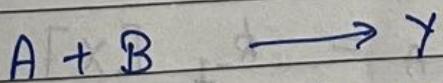
Types Of Composite Mech :-

Composite rxn mech has no of features.

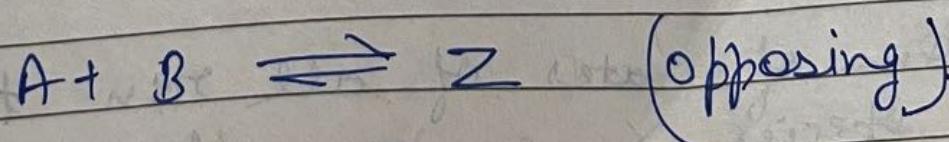
Rxn occurring in parallel.

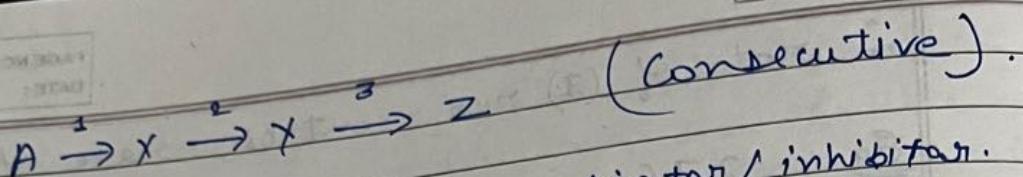


are also called simultaneous rxn.



B and C are competing with one another for A.

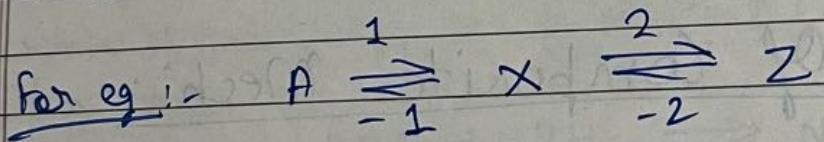




intermediates can be activator/inhibitor.

Rate Eq. for Composite Mech :-

In dealing with " ", it is generally inappropriate to define rate of individual step in terms of conc. chgs. that actually occur in rxn. sys. since these chgs may be brought about by more than one rxn. Instead it is necessary to consider, rate of individual elementary rxn., so that no other rxn. were occurring.



There are 4 elementary rxn.

rate of rxn. 1 is $v_1 / v_{-A,X}$ if no other rxn. is occurring.

$$v_1 = v_{-A,X} = k_1 [A]$$

$$v_{-1} = v_{-X,A} = k_{-1} [X]$$

$$v_2 = v_{-X,Z} = k_2 [X]$$

$$v_{-2} = v_{-Z,X} = k_{-2} [Z]$$

Sum of rates of all rxn. that produce a species X, can be called rate into 'X'. and

given symbol $\sum v_x$

$$\sum v_x = v_1 + v_2$$

$$= k_1[A] + k_2[Z]$$

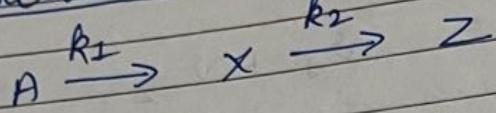
lly, sum of rates of all rxn's that remove X can be called rate out of X
 $\sum v_{-x}$.

$$\sum v_{-x} = v_{-1} + v_2 = (k_{-1} + k_2)[X]$$

For a sys. at equilibrium, the rate into each species = rate out of it.

2/11/22

Simultaneous and Consecutive Rxn' :-



Eg. for rate of chng of conc. of A, X and Z were first given by Heincourt and Eison.
If initial conc. of A = A_0
conc. at any time, t = A

$$-\frac{d[A]}{dt} = k_1 [A]$$

$$\checkmark [A] = [A_0] e^{-k_1 t} \quad (\text{from first order derivation})$$

Net rate of formation of X

$$\frac{d[X]}{dt} = k_1 [A] - k_2 [X]$$

$$= k_1 [A_0] e^{-k_1 t} - k_2 [X]$$

Integrating

$$\cancel{[X]} = [A_0] \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

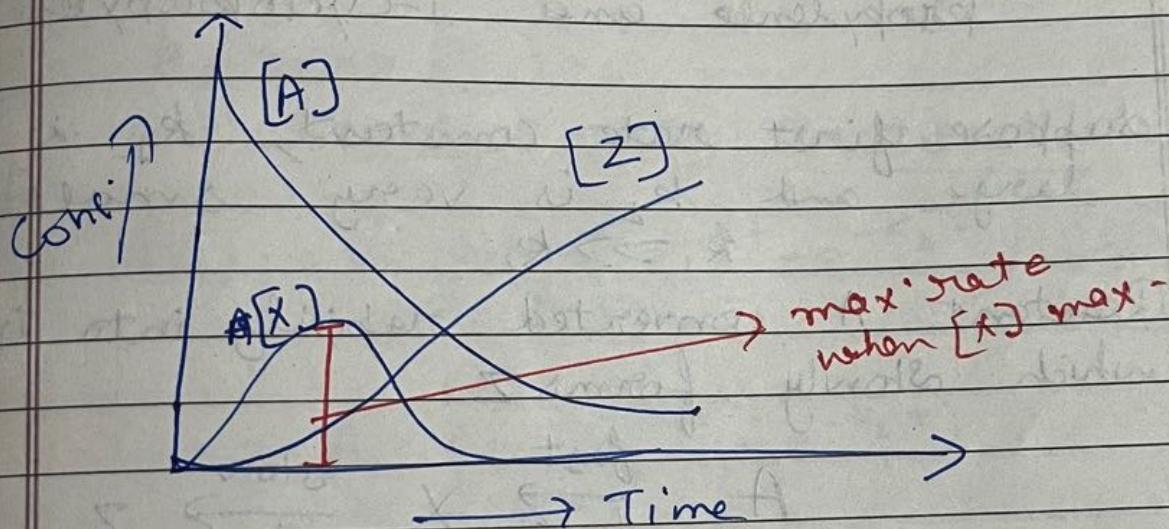
$$[A] = [A_0] + [X] + [Z]$$

$$[Z] = [A_0] - [A] - [X]$$

$$= [A_0] - [A_0] e^{-k_1 t} - [A_0] \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

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

$$\begin{aligned}
 &= [A_0] \left[\frac{(k_2 - k_1) - k_2 e^{-k_1 t} + k_1 e^{k_1 t} - k_1 e^{-k_1 t} + k_2 e^{k_2 t}}{k_2 - k_1} \right] \\
 &= \frac{[A_0]}{k_2 - k_1} (k_2 - k_1 - k_2 e^{-k_1 t} + k_1 e^{-k_2 t}) \\
 &= \frac{[A_0]}{k_2 - k_1} \left[k_2 (1 - e^{-k_1 t}) - k_1 (1 - e^{-k_2 t}) \right]
 \end{aligned}$$



- conc. of A falls exponentially,
- conc. of X goes to max.,
- since rate of formation $Z \propto$ conc. of X, this \therefore is initially zero and is max. when X conc. reaches its max. value.

For initial period of t_{ym} it may be impossible to detect any of prod Z and t_{ym} is said to b h^r induction period. Such \therefore s are commonly obs for rxns occurring by composite mech.

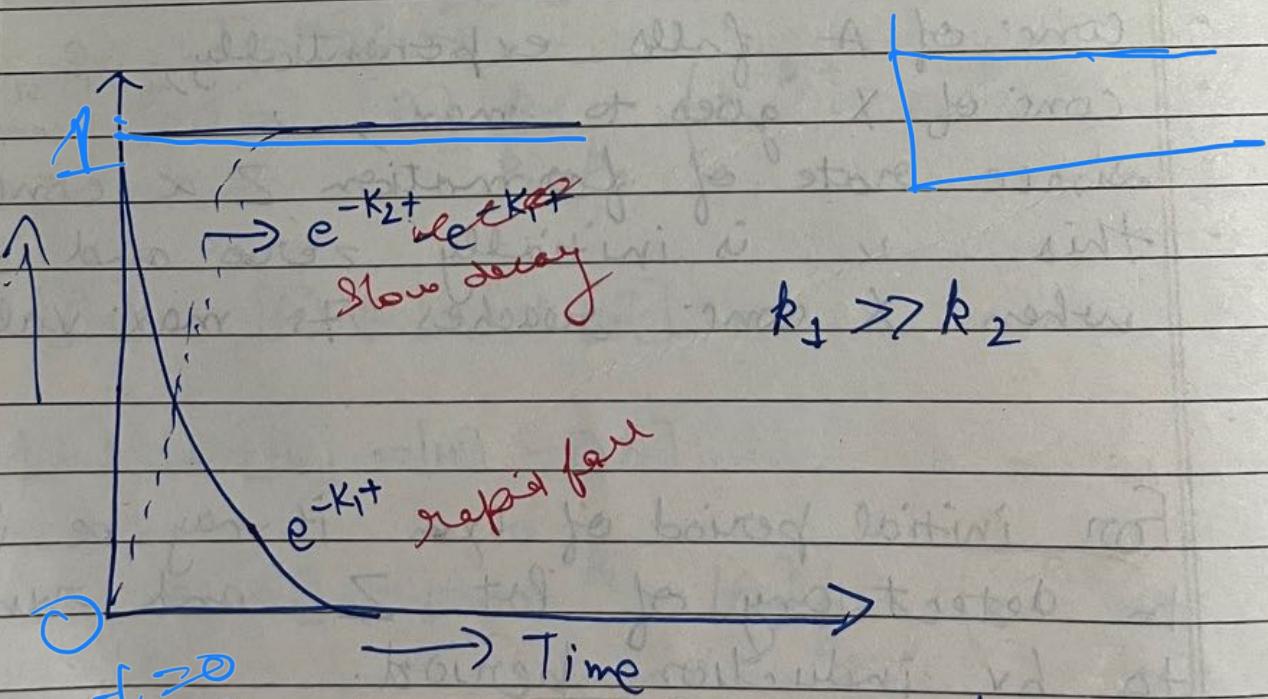
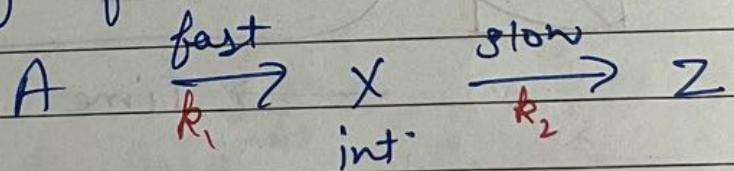
Eg. for conc. of X and Z are observed frequently by nuclides undergoing radioactive decay.

There are not many such reactions, that show consecutive first order behaviour.

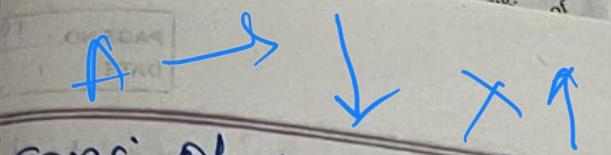
Eg.: Thermal isomerisation of 1,1-dicyclopropane and 1-cyclopropane pentene

Case 1 suppose first rate constant, k_1 is very large and k_2 is very small.
 $k_1 \gg k_2$

Reactant A is converted rapidly into int. X which slowly forms Z



Since k_2 is small, exp $e^{-k_2 t}$ shows a very slow decay, while $e^{-k_1 t}$ shows a rapid fall.



$$\text{conc. of } X = (e^{-k_2 t} - e^{-k_1 t}) \times A_0$$

since $k_1 \ggg k_2$

and $X \therefore$ rises rapidly to value A_0 and then slowly declines, the rise in [Z] follows approx simple 1st order law

Case II
#

$$k_2 \ggg k_1$$

i.e., steady state treatment.



$$[X] = A_0 \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) [A]_0$$

$$= A_0 \frac{k_1}{k_2} (e^{-k_1 t} - e^{-k_2 t}) [A]_0$$

A_0 at, $t = 0$ $[X] = 0$

after a very short tym relative to duration of rxn;

$$e^{-k_1 t} - e^{-k_2 t} = 1$$

$$\therefore [X] = A_0 \frac{k_1}{k_2} \Rightarrow [X] \ll [A]_0$$

which is much less than $[A_0]$

after this short induction period,

$[X]$ remains practically constant,

so that to a good approximation;

$$\frac{d[X]}{dt} = 0$$

This is basis of steady state treatment.

use of which was first suggested by Chapman and Underhill.

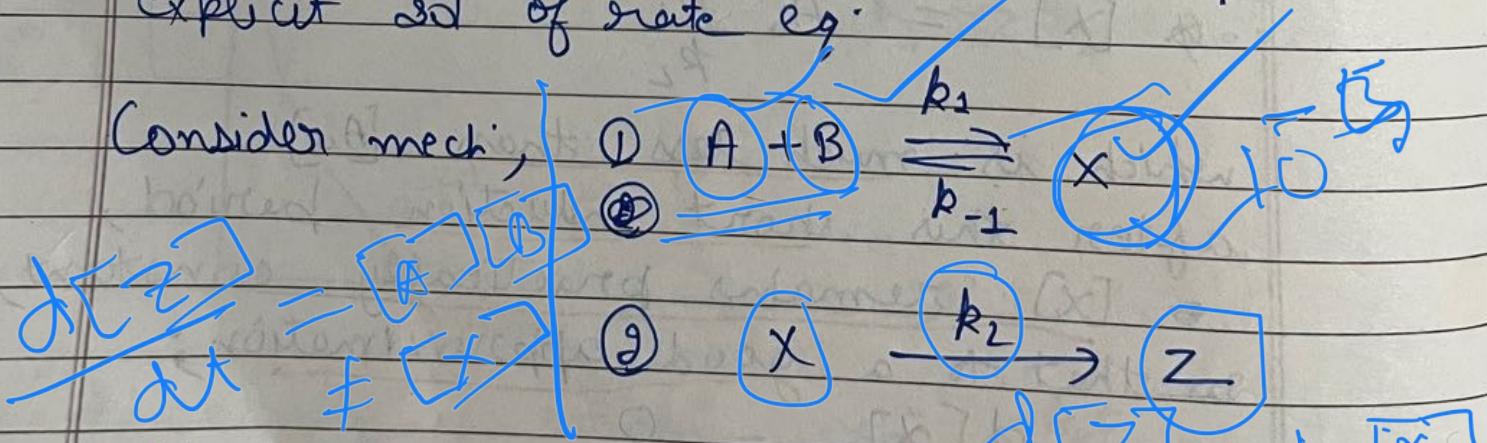
→ Rate of chng of conc of intermediate to a good approximation can be set = 0.
Whenever int. is formed slowly and disappears rapidly.

In other words, whenever intermediate X is such that it is ~~also~~ always present in amounts much smaller than those of reactants, sum of rates of all rxns that form X i.e., $\sum v_x$ is approx = sum of rates of all rxns that removes X. $\sum v_x = \sum v_{-x}$

$$\therefore \frac{d[x]}{dt} = \sum v_x - \sum v_{-x} = 0$$

Steady state treatment is of ~~great imp~~ great imp in analysis of composite mech. Since there is mathematical difficulties that make it impossible to explain it explicit sd of rate eq.

Consider mech.



Differential rate eq. that applied to these set of eq's are:

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_1[A][B] - k_2[X] \quad (1)$$

$$\frac{d[X]}{dt} = k_1[A][B] - k_{-1}[X] - k_2[X] \quad (2)$$

$$\frac{d[Z]}{dt} = k_2[X] \quad (3)$$

~~in terms of A & B~~

To treat this problem exactly, it would be necessary to eliminate X and to solve resulting differential eq's and to find $[Z]$ as a function of t .

∴ It is not possible to obt explicit sol. steady state treatment which is valid, provided that conc of X is always small so then,

$$\frac{d[X]}{dt} = 0 \quad (\text{from eq } (2))$$

$$\therefore k_1[A][B] - k_{-1}[X] - k_2[X] = 0$$

$$\therefore [X] = \frac{k_1[A][B]}{k_{-1} + k_2}$$

$$v = v_2 = \frac{d[Z]}{dt} = \frac{k_2 k_1 [A][B]}{k_{-1} + k_2}$$

$$= k_2[X] = k_2$$

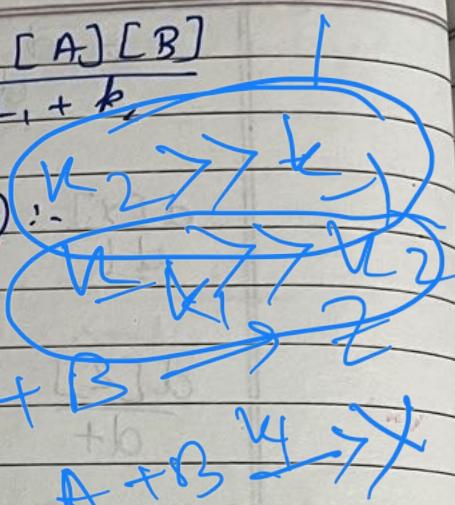
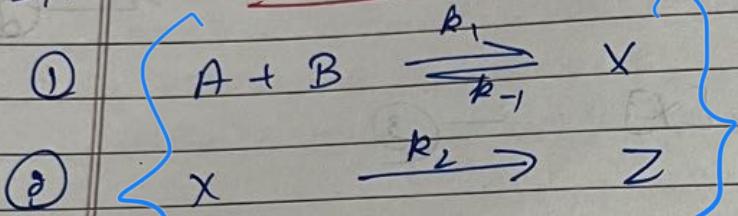
7/11/22

PAGE NO.: 194
DATE: / /

$$v = v_z = \frac{d[z]}{dt} = \frac{k_1 k_2 [A][B]}{k_{-1} + k_1}$$

#

R.d.s (rate controlling)



where intermediate X converted very rapidly into Z , much more rapidly than it can go back into $A + B$.

In that case, rate of gxn is rate of formation of X from $A + B$. i.e.,

$$v_x = \frac{k_1 [A][B]}{k_{-1}} = v_z$$

Since, as soon as X is formed, it is transformed into Z . Initial step o° is R.d.s,

$$k_2 \gg k_{-1}$$

This condition is applicable and this is steady-state,,

Alternatively, suppose rate constant for 2nd gxn i.e., $X \rightarrow Z$ is very small & compared to the reverse of 1st gxn .

$$\therefore k_2 \ll k_1$$

$$\text{so, } v = k_2 [X]$$

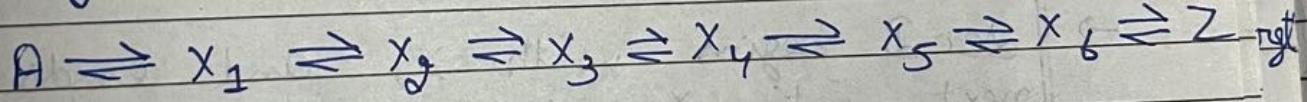
$\therefore \text{rxn } ②$ is too slow to disturb the eq. in ①

$$[X] = \frac{k_1 [A][B]}{k_{-1} + k_1}$$

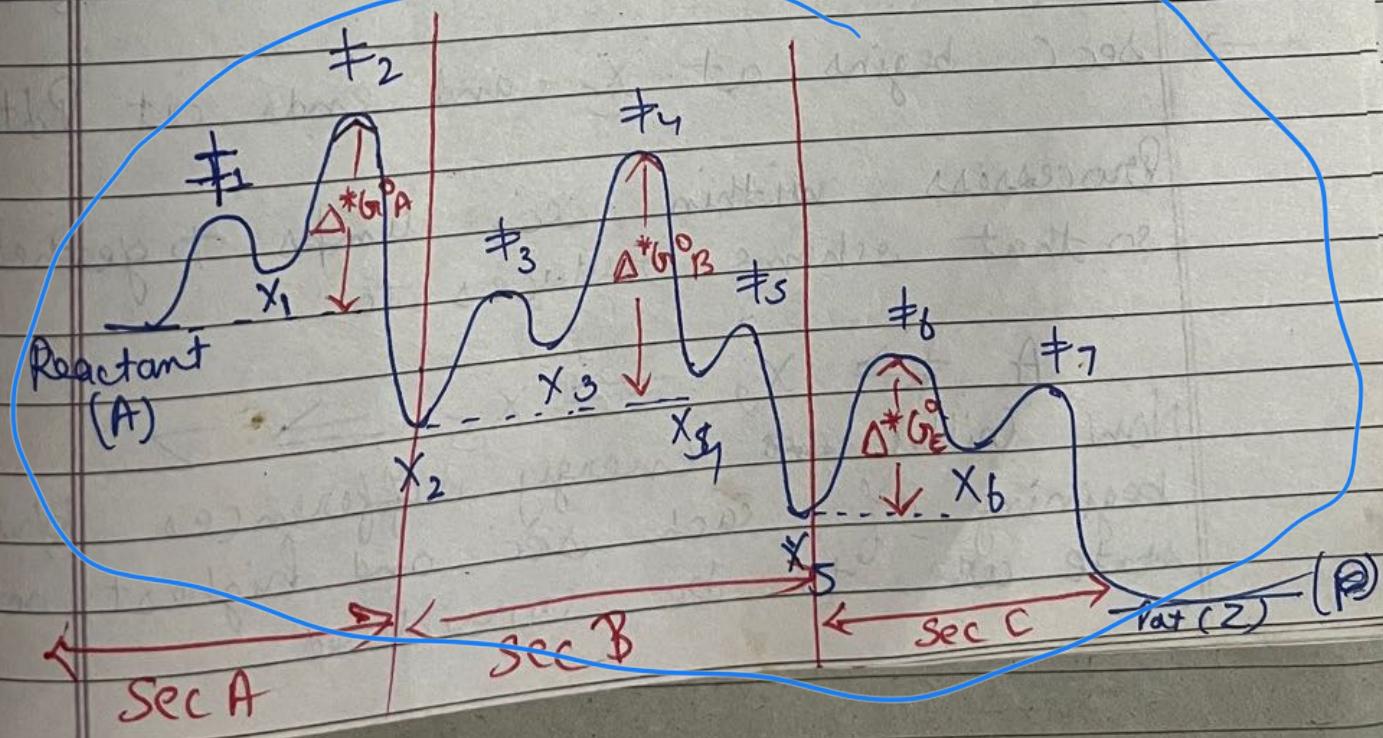
$$= \frac{k_1}{k_{-1}} [A][B]$$

$$\therefore v = \frac{k_2 k_1}{k_{-1}} [A][B]$$

It is impt to work out each kinetic scheme separately. \therefore there are some pit fall. When there is chain rxn there is usually no r.d.s. Rate \neq or controlled by any particular step.



6 int are there.



Reaction would be controlled by ΔG° leading to highest act. comb.

For eg, for a sys shows in fig.

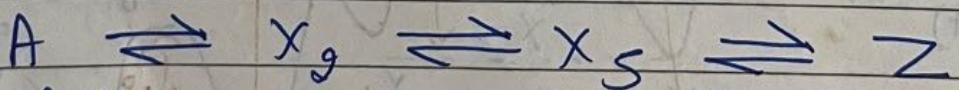
\rightarrow x_2 is highest act. comb.
so that r.d.s will be
 $x_1 \rightarrow x_2$

~~This is not correct.~~

since, argument leading to conclusion ignored possibility of build up of conc. of int. s, correct sol was given by Murdoch. by dividing dia into 3 sections:

- \rightarrow Sec A begins with reactants, A and ends with first int i.e., more stable than reactant i.e., x_2 .
- \rightarrow Sec B begins with x_2 and ends with next int, x_5 i.e., more stable than x_2 .
~~There is no int more stable than x_5~~
- \rightarrow Sec C begins at x_5 and ends at Ppts.

Processes within sec's lumps together, so that scheme reduces to

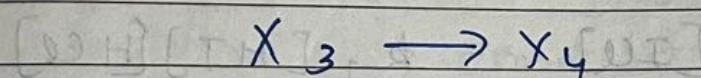


Now Gibbs energy differences b/w beginning of each sec and highest act. state are to be considered.

Largest value is $\Delta^* G_{1B}^\circ$
 So, there will be accumulation of int X_2
 Since X_2 is converted into X_5 more slowly than it is formed from reactants.

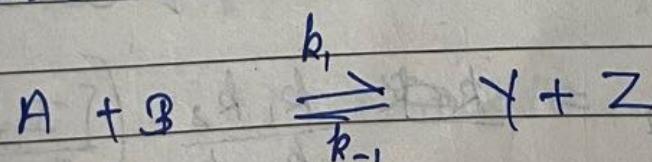
Int X_5 will give Pds rapidly and X_2 will be present in small amounts.
 It follows from this analysis that bottleneck in rxn scheme - lies in sec B.

More specifically, it is highest act complex that controls overall rate so r.d.s for entire process \therefore is rxn.



Microscopic Reversibility and Detailed Balance:-

For elementary rxn, eq constant must be ratio of rate constants in forward and reverse direction



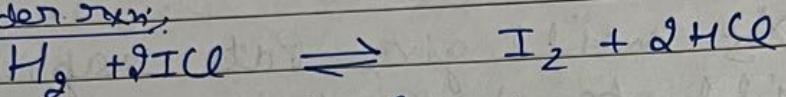
$$\therefore v_1 = k_1 [A][B]$$

$$v_{-1} = k_{-1}[Y][Z]$$

$$\frac{k_1}{k_{-1}} = \left(\frac{[Y][Z]}{[A][B]} \right)_{eq}$$

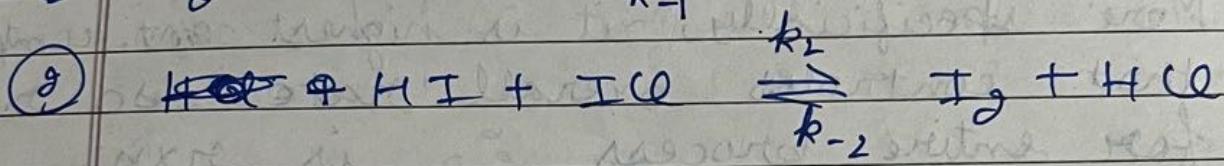
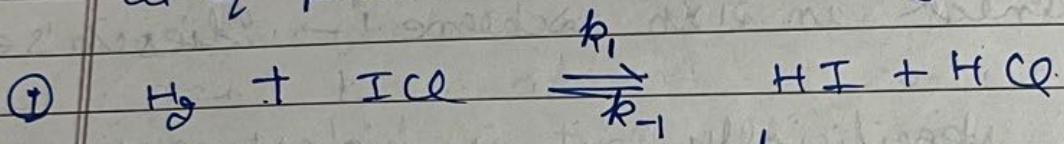
$$= K_c$$

consider now,



occurs in 2 steps

at eq. processes are occurring at equal rates.



$$k_1 [H_2] [ICl] = k_{-1} [HI] [HCl]$$

$$k_2 [HI] [ICl] = k_{-2} [I_2] [HCl]$$

$$K_1 = \frac{k_1}{k_{-1}} = \left(\frac{[HI][HCl]}{[H_2][ICl]} \right)_{eq}$$

$$K_2 = \frac{k_2}{k_{-2}} = \left(\frac{[I_2][HCl]}{[HI][ICl]} \right)_{eq}$$

Prod of each these two eq. constant;

$$K_1 \times K_2 = \frac{k_1 k_2}{k_{-1} k_{-2}} \left(\frac{[I_2][HCl]^2}{[H_2][ICl]^2} \right)_{eq}$$

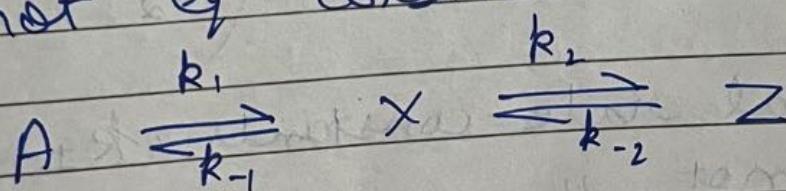
$$= K_c$$

for any mech., involving any no. of elementary and consecutive step, the overall eq. constant is pdt of eq. constants for individual steps and is pdt. of rate constants for rxn in forward direction divided by pdt. of those for reverse rxn.

If rxn occurs by composite mech and we measure rate coeff. k , for overall rxn from left to rgt and also measure rate coeff k_{-1} for overall rxn from rgt to left at same T, ~~the~~ the ratio, $\frac{k_1}{k_{-1}}$ is not necessarily the eq. constant for overall rxn,

So, reason is that, rate laws for composite rxn's chng with experimental conditions such as rxn condition and rate coeff. also chng.

Eg:- where ratio of rate constants is not eq. constant.



if sys is at complete eq.

$$\left(\frac{[X]}{[A]} \right)_{eq} = \frac{k_2}{k_{-1}}$$

$$\left(\frac{[Z]}{[X]} \right)_{eq} = \frac{k_1}{k_{-2}}$$

$$\left(\frac{[Z]}{[A]} \right)_{eq} = \frac{k_1 k_2}{k_{-1} k_{-2}} \\ = K_c$$

If we make measurements of rate of consumption of A at beginning of run before any X and Z have accumulated.

$$-\frac{d[A]}{dt} = k_1 [A]$$

Similarly if we starts with pure Z and measures initial rates of consumption of Z, rate constant obt. is: $k_{-1} [Z]$

In general, ratio $\frac{k_1}{k_{-2}} \neq K_c$

Initial rate constants k_1 and k_{-2} are not " " that apply when sys is at eq.

Now, when " " " " .

$$k_1[A] - k_{-1}[I] - k_2[X] + k_{-2}[Z]$$

PAGE NO.: 201
DATE: / /

$$\therefore \frac{d[X]}{dt} = k_1[A] - (k_1 + k_2)[X] + k_{-2}[Z]$$

$$[X] = \frac{k_1 A + k_2 [Z]}{k_1 + k_2}$$

So, net rate of consumption of A;

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[X]$$

Put value of [X]

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1} \left(\frac{k_1 A + k_2 [Z]}{k_1 + k_2} \right)$$

$$-\frac{d[A]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} [A] - \frac{k_{-1} k_2}{k_{-1} + k_2} [Z]$$

first term is rate of rxn from left to right
and rate constant = $\frac{k_1 k_2}{k_{-1} + k_2}$

likewise, " from rgt to left,
 $= \frac{k_{-1} k_2}{k_{-1} + k_2} \times -$

and ratio of these 2 constants = $\frac{k_1 k_2}{k_{-1} k_2}$

$$= K_e$$

[eq. constant]

Laddar Ch-8.

- Dec-N
- chain rxn.
 - HBr HCl
 - (Both thermal and photochem.)
 - decomposition of ethane and acetalddehyde

Dec-C

9/11/99.

Fast Reactions:-

Exp techniques considered so far are directly applicable to rxns that are not too rapid and that have halflives of at least several min.

Some rxns occur very fast with $t_{1/2}$ less than a sec. Thus, these techniques cannot be applied so special techniques are req'd.

Imp. Two main reasons why conventional techniques are not directly applicable to very rapid rxns.

- ① Rxn cannot be initiated, within a period of time i.e., negligible compared with $t_{1/2}$.
" taken for measurement during kinetic investigation may not be negligible in comparison with duration of exp.

Flow Method :-

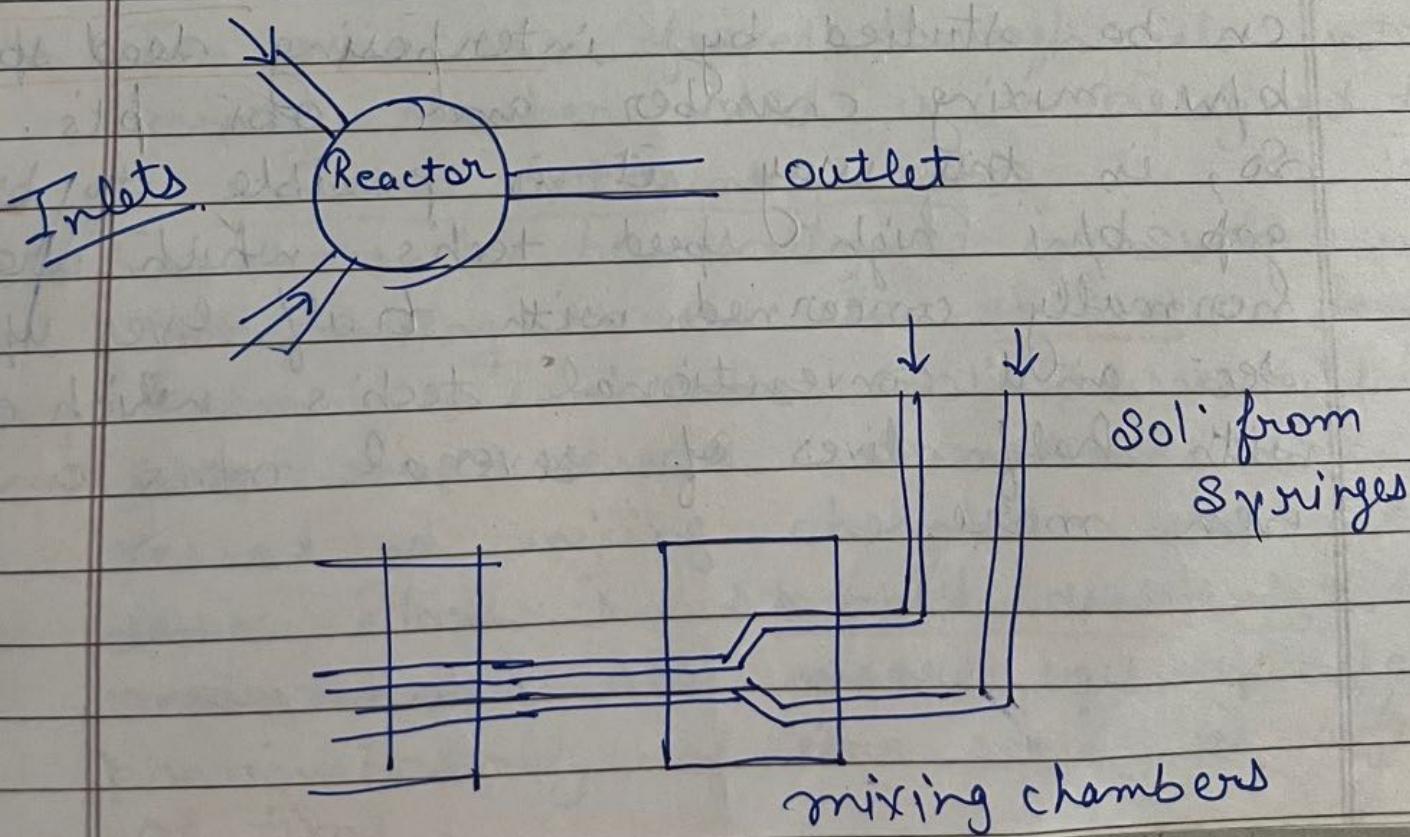
In " " first difficulty for fast rxn is often overcome by studying rxn in flow sys. rather than in a static sys.

So, such tech. hr been employed for both gas rxns and rxns in liq. phase.

First use of flow tech in kinetic investigation hr been made by ~~Rashig~~ in 1905, who study the rapid rxn b/w HNO_3 and O_2 by forcing the two gases through a mixing chamber in a min vessel.

No of such vessels are used that is of different vol. Rxn mixt. was passed into sol which stop rxn. Extent of rxn was studied by chemical analysis of this sol.

By varying flow rates and vol of rxn vessel, regendence time could be vary from 0.025 to 25 sec.



Reactants are pumped at a rate of 10 ml/s continuously into mixing vessel. Mixing chamber is designed in such a way ~~so as~~ to complete mixing within 10^{-3} sec.

During this interval partial mixing occurs and steady state is reached then mix of reactants and pdts. flows out of mixing vessel, into obs tube. Composition of sol in "obs" is determined by optical, thermal or other methods (Spectro) at various pts.

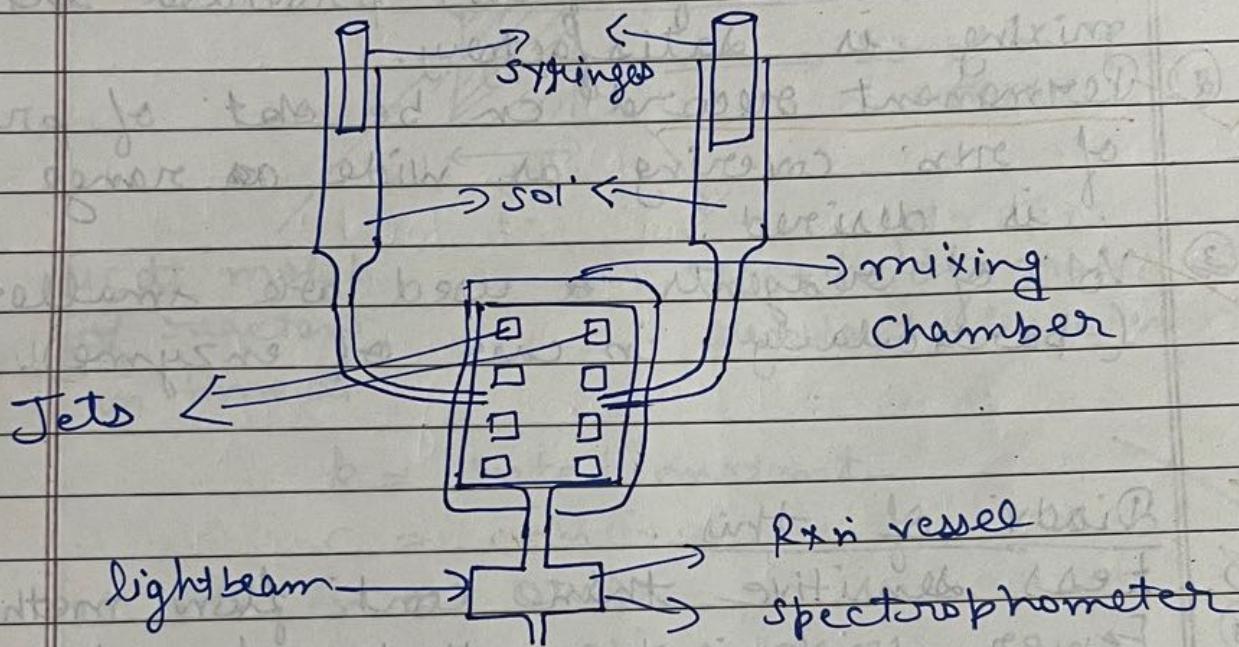
Thus, these obs corresponds to lapse of some definite time interval after mixing at constant flow rate.

Alternatively flow can be varied and obs can be made at one pt. only.

With all these tech's much slower mix's can be studied by interposing dead spaces b/w mixing chamber and obs pts. So, in this way it is possible to bridge gap b/w high speed tech's which are normally concerned with half lives upto a sec and conventional tech's which deal with half lives of several min's and even more.

Stopped Flow Tech :-

One valuable procedure that embodies some of the best features of both static and flow sys's is stopped flow tech, which was first used for rxn's in sol by Chance.



Two sol's are forced through jets into a mixing chamber which is so designed that it is extremely rapid.

Chambers hv been designed in such a way that mixing occurs in 10^{-3} sec. From 11 chamber sol passes at once into rxn vessel. Sometimes rxn vessel and mixing chamber are one and same. Flow is stopped suddenly and measurements are made usually spectrophotometrically of conc. as a function of time.

Rxn's are fast, spectrophotometer reading are recorded continuously using high speed recorder or oscilloscope.

- * Main adv of stopped flow tech over continuous flow are:
- ① Method is not affected by rate and character of flow, provided that mixing is satisfactory.
 - ② Permanent record can be obt. of progress of rxn covering as wide a range as is desired.
 - ③ Vol. of reagents used are smaller. (particularly in case of enzyme).

* Disadv of this.

- ① Less sensitive than cont flow method.
- ② Fewer convenient methods of obs.

Kinetic Eq for Flow Sys:-

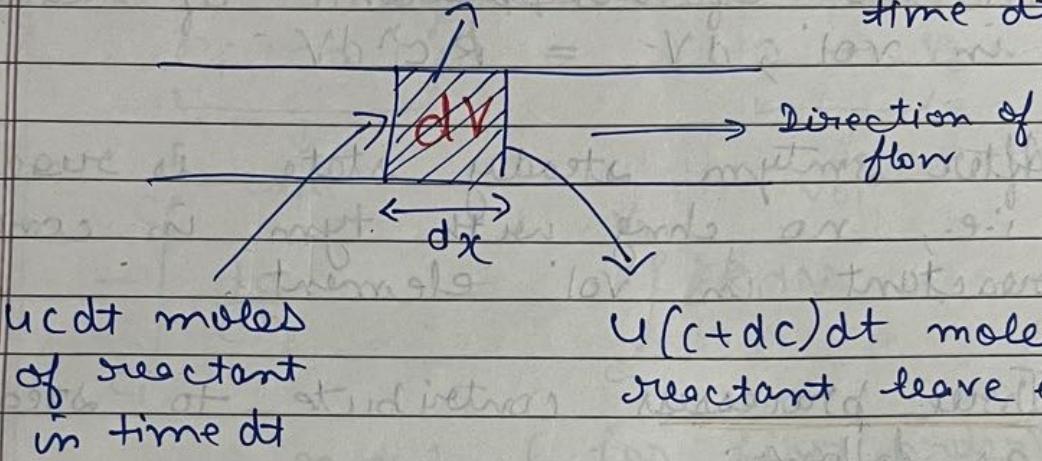
Two situation:-

- ① No stirring in reactor and flow through it is known as plug flow
- ② Stirring, which is sufficient vigorous for complete mixing within reactor.

Int situations are also possible, but it is very difficult to analyse.

→ Plug Flow :-

$k c^n dV dt$ leave by rxn in time dt .



k = rate constant

c = conc

n = order

dV = vol

dt = time

u = vel. of liq

Rxn mixt is passed through a reactor at rd rate of flow (for eg; l/s) = u .

Consider ele of vol, dV in reactor and suppose for simplicity that rxn rate depends on conc, c of single reactant.

For rxn. of nth order, rate of disappearance of reactant = $k c^n$

$$v = -\frac{dc}{dt} = k c^n$$

The Rate of disappearance of reactant in vol, $dV = k c^n dV$

After some steady state is reached, i.e., no change with time in conc. of reactant in vol element.

* Three processes contribute to steady state as follows:

- ① mol of reactant enter the slab from left face. So no of moles entering in tym, $dt = u c dt$
- ② mol of leaving by right face. So, no of moles leaving in tym, $dt = u(c + dc) dt$.
- ③ mol disappear by chem. rxn.
For rxn. of nth order, so no of moles disappearing in tym, $dt = k c^n dV dt$

From steady state,

Rate of entry of reactant

i.e., process ①

= Sum of rates of removal i.e., process ② and ③

$$\begin{aligned}uc dt &= u(c+dc)dt + kc^n dv dt \\uc dt &= uc dt + udc dt + kc^n dv dt \\-udc dt &= kc^n dv dt \\-udc &= kc^n dv \\-\frac{dc}{c^n} &= \frac{k}{u} dv\end{aligned}$$

Integrate within limits.

$$\underbrace{c_i \text{ to } c_f}_{\substack{\downarrow \\ \text{conc.}}} \quad \underbrace{0 \text{ to } v_0}_{\substack{\downarrow \\ \text{vol.}}}$$

$$-\int_{c_i}^{c_f} \frac{dc}{c^n} = \int_0^{v_0} \frac{k}{u} dv$$

$n = 1$ (for first order)

$$-\int_{c_i}^{c_f} \frac{dc}{c} = \int_0^{v_0} \frac{k}{u} dv$$

~~$$\ln \frac{c_f}{c_i} = -\frac{k}{u} v_0$$~~

$$\frac{c_f}{c_i} = e^{-\frac{k v_0}{u}}$$

$$\frac{c_f}{c_i} = c_i e^{-\frac{k v_0}{u}}$$

Comparing it with first order eq:

$$\checkmark t = \frac{v_0}{u}, \text{ Known as contact time for reactant.}$$

It is avg. time mol takes to pass through reactor.

14/11/92

PAGE NO.: 910
DATE: / /

$$C_f = C_i e^{\frac{kv_0}{u}} \quad \text{--- (1)}$$

eq. 1 can be tested by varying $\frac{v_0}{u}$ i.e., by changing vol. of reactor or flow rate.

Just as in static sys. tym is varied. Reactions that are too rapid for convenient study in static sys. may frequently be studied in flow sys.

The contact tym being reduced by using high flow rate and small vol.
For rxn of nth order;

$$\frac{C_f - C_i}{C_i} = \frac{kv_0}{u}$$

$$\frac{1}{n-1} \left[\frac{1}{C^{n-1}} \right]_{C_i}^{C_f} = \frac{1}{n-1} \left[\frac{1}{C_f^{n-1}} - \frac{1}{C_i^{n-1}} \right]$$

$$= \frac{kv_0}{u}$$

$$= kt \quad \left[t = \frac{v_0}{u} \right]$$

In this derivation the assumption has been made that there is no vol chng during the course of rxn. However, any such chng will cause vol. flow rate to vary through reactor.

→ In stirred-flow reactor in which conc. are maintained constant within reactor. It is no longer necessary to consider a thin slab but rather the reactor as a whole. Rate of flow of ~~out~~ reactants into a reactor is, UC_i ; And rate of flow out = UC_f

Difference b/w these is the rate of rxn. in reactor which is = $\frac{vV}{\text{rate vol}}$

$$UC_i - UC_f = \frac{vV}{\text{rate}} = \frac{UC_i - UC_f}{V}$$

Measurement of C_i and C_f at a given flow rate, thus allow rxn. rate to be calculated.

Order and rate constant ~~can~~ be determined by working at diff initial conc's and rates of flow.

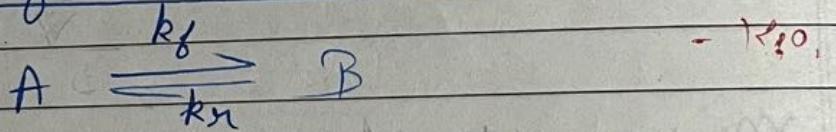
Relaxation Method :-

~~Tym~~
~~Perturbation~~ These methods involve measuring of relaxation tym of rxn; ~~#~~^{tym} that it takes for rxn. to cover certain fraction of its path towards eq. $\left[\text{rxn. having half-life less than } 10^{-3} \text{ sec can only be studied} \right]$

by method that avoids mixing.
One way to achieve it is to subject a reversible rxn at eq to a sudden chng of conditions. For eg, temp, P, electric or mag. field.

Sys then moves rapidly to new eq position. [The speed with which the sys approaches its new eq. called relaxation] is then followed by suitable fast phy methods such as spectrophotometry, conductometry etc.

Theory of This Method :-



first order in both directions.

Suppose eq suddenly displaced to rgt.

a_0 and b_0 = eq conc of A and B.

a_e and b_e = new eq " " A " B.

At any tym, let conc of ~~B~~ = a_+ and b_+ .
In initial displacement from new eq position $\phi = x_0$.

and x_+ is disp at any time 't'.

$$\therefore x_+ = a_+ - a_e \Rightarrow a_+ = x_+ + a_e$$

$$\text{likewise, } x_+ = b_+ - b_e \Rightarrow b_+ = b_e - x_+$$

Net rate of attainment of new eq position called Rate of Relaxation, can be ~~written~~ written as:

$$-\frac{dx}{dt} = k_f a_+ - k_n b_t$$

$$-\frac{dx}{dt} = k_f (x_+ + a_e) - k_n (b_e - x_+)$$

$$= k_f x_+ + k_f a_e - k_n b_e + k_n x_+$$

$$= k_f a_e - k_n b_e + x_+ (k_f + k_n)$$

At eq:- $k_f a_e = k_n b_e$

$$\therefore -\frac{dx}{dt} = x_+ (k_f + k_n)$$

Integrate within limits

$$\text{at, } t = 0, \quad x = x_0$$

$$\text{at, } t = t, \quad x = x_t$$

$$\int_{x_0}^x -\frac{dx}{dt} = \int_0^t x_+ (k_f + k_n) dt$$

$$-\left[\ln x_+ \right]_{x_0}^{x_t} = (k_f + k_n) t$$

$$-\ln \frac{x_+}{x_0} = \frac{\ln x_0}{x_+} = (k_f + k_n) t$$

Thus rate of relaxation depends upon two \leftrightarrow constants i.e., k_f and k_r .

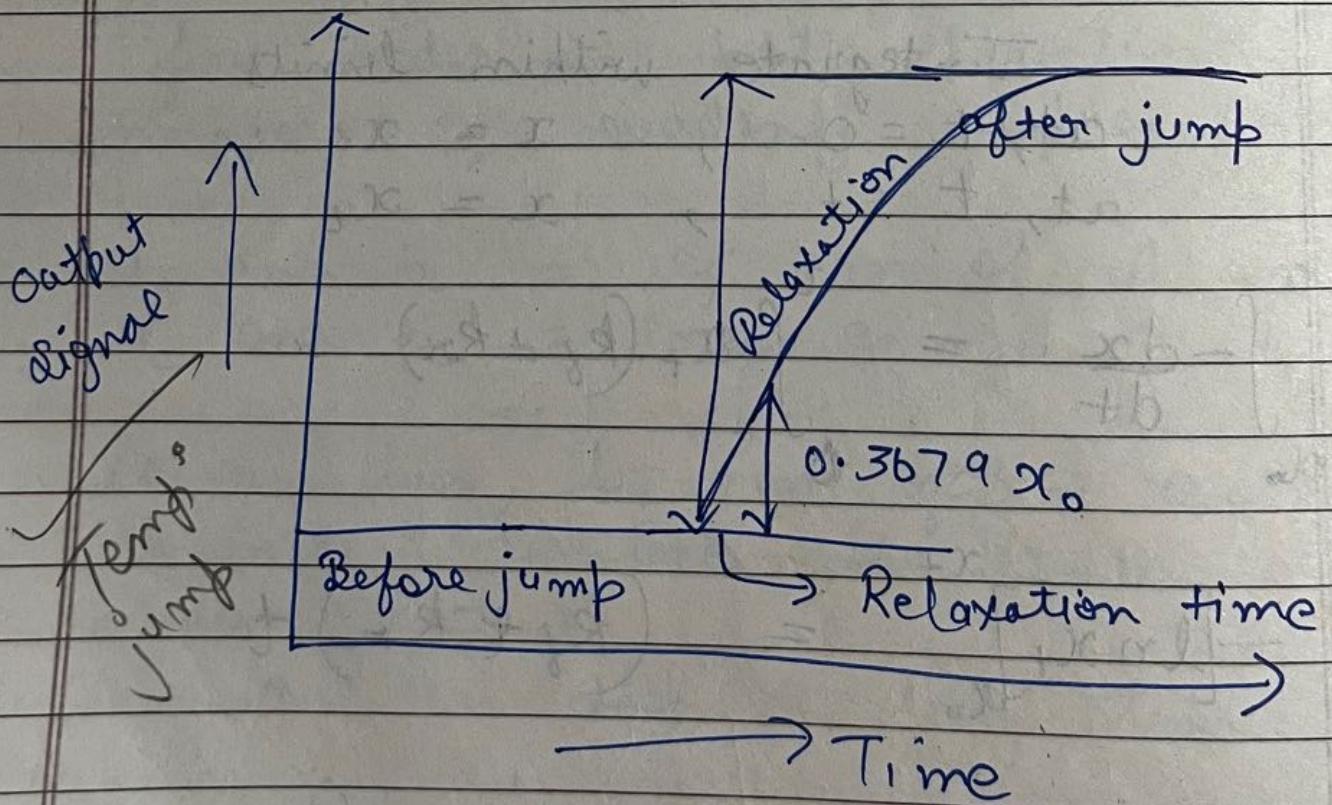
$$\text{and, } R = \frac{k_f}{k_r}$$

$$\text{Relaxation time, } T = \frac{1}{k_f + k_r}$$

$$\text{Time at which, } \ln \frac{x_0}{x_t} = 1$$

$$\frac{x_0}{x_t} = e$$

$$\frac{x_t}{x_0} = \frac{1}{e} = \frac{1}{2.718} = 0.3679$$



This means the relaxation time is the time in which sys goes 30.79 % of the way to the new eq position.

In Relaxation method, perturbation from eq must take time much smaller than relaxation time in certain fast rxns. ~~so~~ the perturbation should be caused within period of 10^{-6} to 10^{-7} sec.

No of exp' tech are applied, simplest being temp jump and Pressure jump methods used for time larger than 10^{-5} sec.

For shorter time high electric or mag fields or ultrasonic vib are employed.

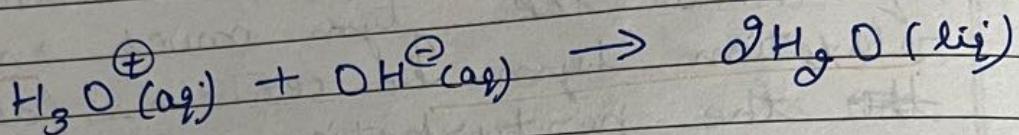
In Temp jump method, eq is changed by causing sudden chng of Temp, approx. 10°C within 10^{-6} to 10^{-7} sec.

One way of doing this is to discharge an electric current through a sample made conducting by addition of ions but laser discharge can also be used.

Time dependence of conc may then be followed by absorption spectra or by measuring electrical conductivity as a function of time.

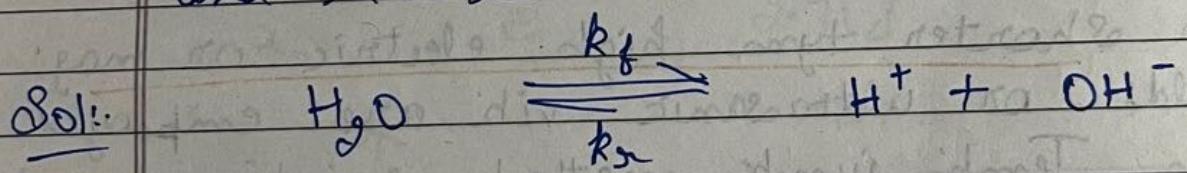
~~Temp. chng of 1°C chngs eq. (near R.T)~~
by 3%

* Imp. Appl. of temp. jump tech has been to determine rate of



by monitoring activity of sample.

Q:- When sample of pure H_2O is subjected to temp. jump exp. The relaxation time for return to eq. at 25°C is 36 ms. Calculate rate constants for forward and reverse rxn.



first order
sec⁻¹

$$\tau = \frac{1}{k_f + k_r ([\text{H}^+] + [\text{OH}^-])}$$

$$= \frac{1}{k_r \left[\frac{k_f}{k_r} + ([\text{H}^+] + [\text{OH}^-]) \right]}$$

$$K_{\text{eq}} = \frac{K_w}{55.5}$$

$$= \frac{10^{-14}}{55.5} = 1.8 \times 10^{-16}$$

$$K_{eq} = \frac{k_f}{k_r} = \frac{36 \times 10^{-6}}{1.8 \times 10^{-6}}$$

$$[H^+] = [OH^-] = 10^{-7}$$

$$\therefore 36 \times 10^{-6} = \frac{1}{k_r [1.8 \times 10^{-6} + (10^{-7} + 10^{-7})]}$$

$$k_r = 1.4 \times 10^{11} M^{-1}s^{-1}$$

$$k_f = R_g \times K_{eq}$$

=

Eq. constant of OH^- is Temp-dependent as $\Delta H \neq 0$. So, Temp-jump jump method is applicable.

Eq. composition also depend on pressure so P-jump can also be used.

