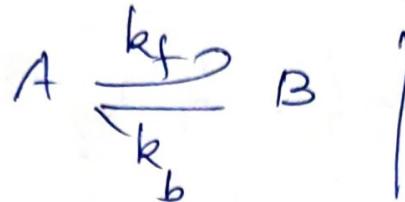


Rate expression of some Complex reactions:

1) Opposed OR Reversible Elementary Reacs:

Case I First order rearⁿ opposed by first order.



e.g.



where, k_f and k_b are the

reaction rate-constants of forward and backward reactions, respectively.

Now,

$$\text{Overall rate of the rear}^n = \left(\frac{\text{Rate of forward rear}^n}{\text{Rate of backward rear}^n} - 1 \right)$$

$$\text{i.e., } -\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_f [A] - k_b [B]$$

Now, let at $t=0$, $[A]_0$ i.e. initial concn of A.
 $[B]_0 = 0$: No B at initial time.

x be the extent of rearⁿ at time t .

$$\therefore \text{At time } t, [A] = [A]_0 - x$$

$$[B] = x.$$

$$\therefore \text{Overall rate of rear}^n, \frac{dx}{dt} = k_f \{ [A]_0 - x \} - k_b x \rightarrow ①$$

Now, when the rate of forward rearⁿ > rate of backward rearⁿ.
 With time, rate of backward rearⁿ gradually increases.

When eq^m. is established,

rate of forward rxn = Rate of backward rxn
Under this cond; Overall rate of rxn = 0.

$$\therefore \text{At eq}^m, \frac{dx}{dt} = 0,$$

$$\therefore k_f \left\{ [A]_0 - x_{eq} \right\} = k_b x_{eq} \quad (2) \quad x_{eq} = \text{eq}^m \text{ concn of B.}$$

$$\therefore \frac{[B]}{[A]} = \frac{x_{eq}}{[A]_0 - x_{eq}} = \frac{k_f}{k_b} = K_{eq} \quad (\text{eq}^m \text{ concn of A.})$$

$$\therefore K_{eq} = \frac{k_f}{k_b} \quad \text{e.g. Ratio of forward & backward rate constants.}$$

Now, from eqⁿ-②, $k_b = k_f \left\{ \frac{[A]_0 - x_{eq}}{x_{eq}} \right\}$

Putting this value of k_b in eqⁿ-①,

$$\begin{aligned} \frac{dx}{dt} &= k_f \left\{ [A]_0 - x \right\} - k_f \left(\frac{[A]_0 - x_{eq}}{x_{eq}} \right) \cdot x \\ &= k_f [A]_0 - k_f x - k_f \frac{[A]_0 x}{x_{eq}} + k_f x \end{aligned}$$

$$\frac{dx}{dt} = k_f \frac{[A]_0}{x_{eq}} (x_{eq} - x)$$

$$\therefore \frac{dx}{(x_{eq} - x)} = k_f \frac{[A]_0}{x_{eq}} \cdot dt$$

Integrating:

$$\int_0^x \frac{dx}{(x_{eq} - x)} = k_f \frac{[A]_0}{x_{eq}} \int_0^t dt$$

$$\text{or, } -\ln(x_{eq} - x) + \ln x_{eq} = k_f \frac{[A]_0}{x_{eq}} \cdot t$$

$$\text{or, } \boxed{\ln\left(\frac{x_{eq}}{x_{eq} - x}\right) = k_f \frac{[A]_0}{x_{eq}} \cdot t}.$$

From eqⁿ-②, $k_f([A]_0 - x_{eq}) = k_b \cdot x_{eq}$

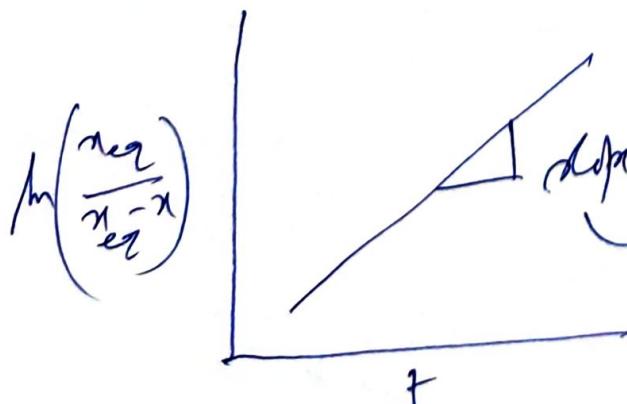
$$\text{or, } k_f [A]_0 = (k_f + k_b) x_{eq}$$

$$\text{or, } \frac{[A]_0}{x_{eq}} = \left(\frac{k_f + k_b}{k_f} \right)$$

$$\therefore \boxed{\ln\left(\frac{x_{eq}}{x_{eq} - x}\right) = (k_f + k_b) t}$$

This eqⁿ has a form of simple 1st order
redⁿ $\left[\ln \frac{[A]_0}{[A]} = k \cdot t \right]$; where,

$[A]_0$ is replaced by x_{eq} and k by $(k_f + k_b)$



$$d\ln = (k_f + k_b)$$

$$\text{And } K_{eq} = \frac{k_f}{k_b}$$

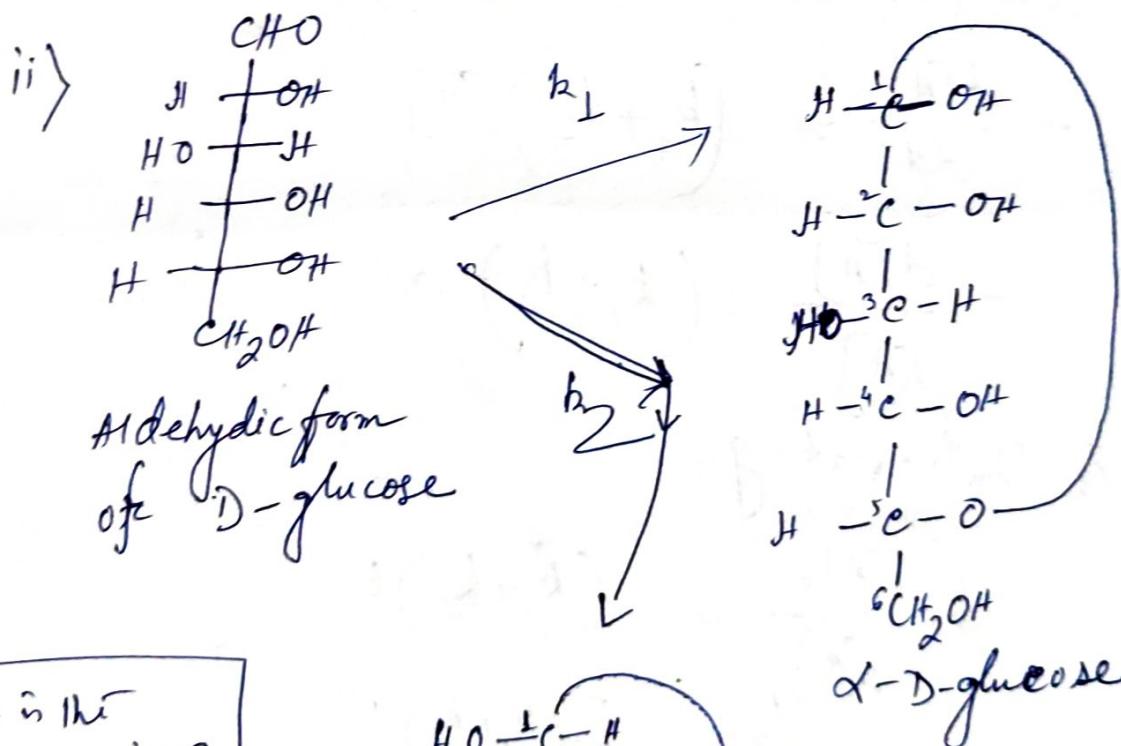
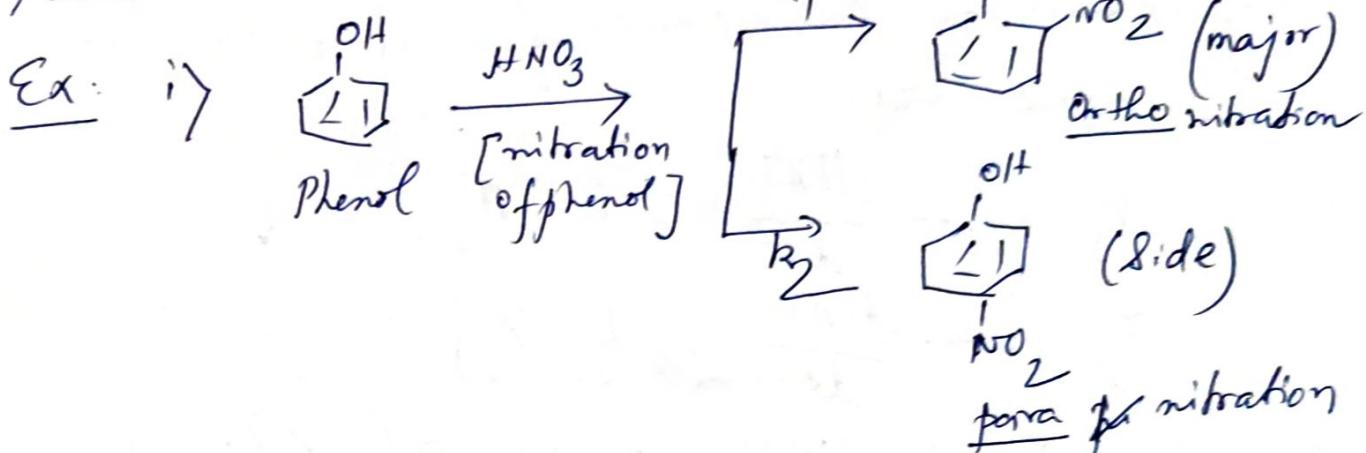
From these two,
we can evaluate both
 k_f and k_b .

(1)

Chemical Kinetics 3

Rate expression of some Complex reactions:

2) Parallel or Concurrent Elementary Reactions.



C-1 is the
anomeric C

Position of -OH
gr. at C1
guides whether
it will be
 α or β form.

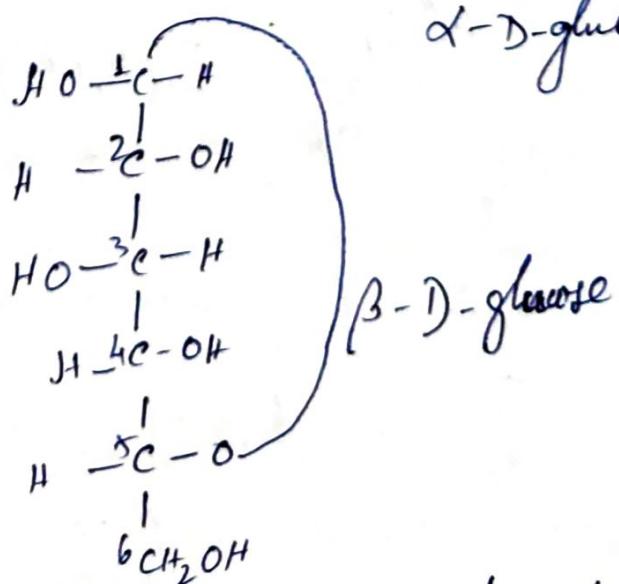
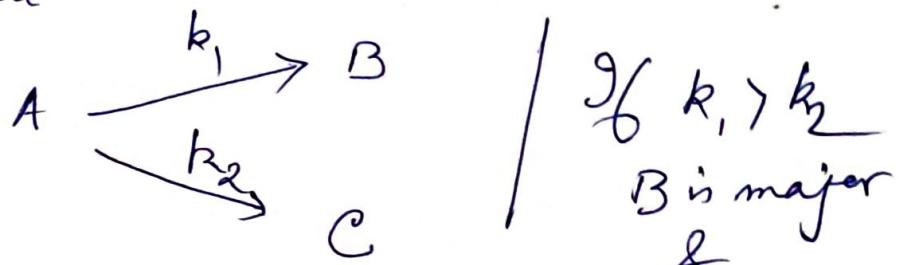


Exhibit different optical rotation property.

(2).

In general:



Differential rate expressions for the above two reactions are:

$$r_1 = -\frac{d[A]}{dt} = k_1 [A]$$

$$r_2 = -\frac{d[A]}{dt} = k_2 [A]$$

Overall rate of disappearance of A ($= r_1 + r_2$)

$$-\frac{d[A]}{dt} = (k_1 + k_2) [A]$$

$$\text{or, } -\frac{d[A]}{[A]} = (k_1 + k_2) dt$$

Now Integrating:

$$\ln \frac{[A]_0}{[A]_t} = (k_1 + k_2) t .$$

$$\text{or, } \boxed{[A]_t = [A]_0 \cdot e^{-(k_1 + k_2) t}}$$

$$[A]_t = [A]_0 e^{-(k_1+k_2)t}$$

Rate of formation of B:

$$\frac{d[B]}{dt} = k_1 [A] = k_1 e^{-(k_1+k_2)t} \cdot [A]_0 \quad \text{--- (A)}$$

Similarly: $\frac{d[C]}{dt} = k_2 [A] = k_2 [A]_0 e^{-(k_1+k_2)t} \quad \text{--- (B)}$

From eqn (A)

$$d[B] = k_1 [A]_0 e^{-(k_1+k_2)t} \cdot dt$$

Integrating: $[B] = -\left(\frac{k_1}{k_1+k_2}\right) [A]_0 e^{-(k_1+k_2)t} + IC$

when $t=0$, $[B] = 0$.

$$\therefore IC = \left(\frac{k_1}{k_1+k_2}\right) [A]_0$$

$$\therefore [B]_t = \left(\frac{k_1}{k_1+k_2}\right) [A]_0 \left\{ 1 - \left(\frac{k_1}{k_1+k_2}\right) e^{-(k_1+k_2)t} \right\}$$

$$1 - e^{-x} \approx 1 - (1-x) \approx x \quad (\text{if } x \text{ is small})$$

$$\therefore [B]_t = \left(\frac{k_1}{k_1+k_2}\right) [A]_0 \cdot (k_1+k_2) t = k_1 [A]_0 t.$$

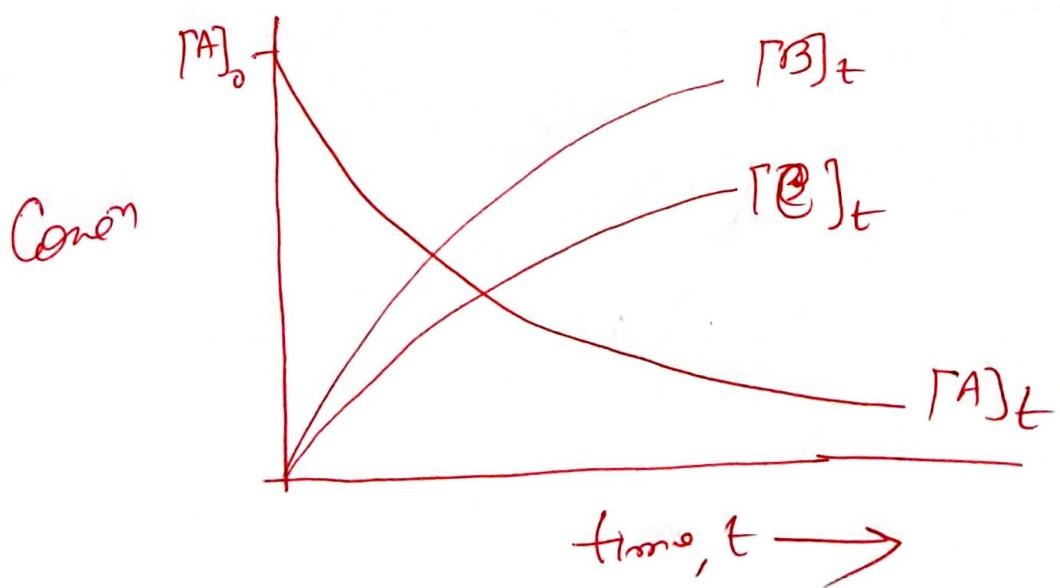
Similarly, $[C]_t = k_2 [A]_0 t$.

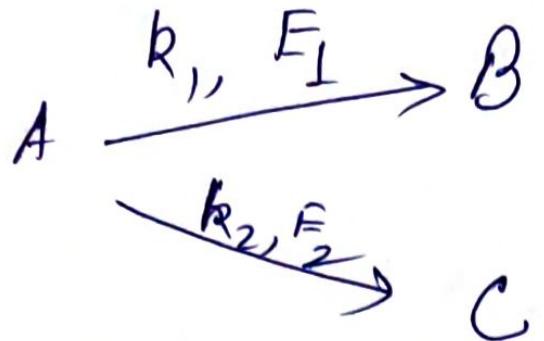
Here, Ratio of the conc' of products at any time:

$$\frac{[B]_t}{[C]_t} = \frac{k_1}{k_2} = \frac{\frac{k_1 [A]}{k_2 [A]}}{\frac{d[A]}{dt}} = \frac{\frac{d[B]}{dt}}{\frac{d[C]}{dt}}$$

$\therefore \frac{[B]_t}{[C]_t} = \frac{\text{Rate of formation of } B}{\text{Rate of formation of } C}$

$\Rightarrow \boxed{\frac{[B]_t}{[C]_t} = \frac{k_1}{k_2}}$ constant value
at all the time
during the course of the
red².





E_1 & E_2 are the activation energies for formation of B & C , respectively.

Show that, Overall activation energy for overall disappearance of A

$$E = \left(\frac{k_1 E_1 + k_2 E_2}{k_1 + k_2} \right)$$

Soln

(7)

Consecutive or Sequential Reactions:

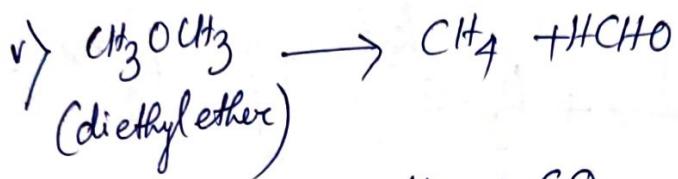
Example: i) Polymerization process

ii) Thermal cracking

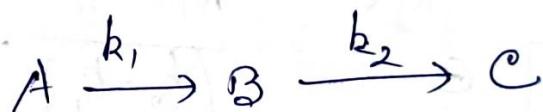
iii) Chlorination of hydrocarbon:



iv) Radioactive decay



In general:



Let, when $t=0$, $[\text{A}]_0$ $[\text{B}]_0 = 0$ $[\text{C}]_0 = 0$ (i.e. no product at initial time)

At any time t , $[\text{A}]_t$ $[\text{B}]_t$ $[\text{C}]_t$

$$\text{It is obvious, } [\text{A}]_0 = [\text{A}] + [\text{B}] + [\text{C}]$$

$$\text{Now, } -\frac{d[\text{A}]}{dt} = k_1[\text{A}] \quad \text{--- (1)}$$

$$\frac{d[\text{B}]}{dt} = k_1[\text{A}] - k_2[\text{B}] \quad \text{--- (2)} \quad \begin{array}{l} \text{[As B is formed} \\ \text{from A, and} \\ \text{is decomposed to C]} \end{array}$$

$$\frac{d[\text{C}]}{dt} = k_2[\text{B}] \quad \text{--- (3)} \quad \begin{array}{l} \text{[C is formed from} \\ \text{decomposition of B]} \end{array}$$

$$\text{Integrating (1), } [\text{A}]_t = [\text{A}]_0 e^{-k_1 t} \quad \text{--- (4)}$$

Putting this value of $[A]$ in eqⁿ (2) :

$$\frac{d[B]}{dt} = k_1 [A]_0 e^{-k_1 t} - k_2 [B]$$

$$\text{or, } \frac{d[B]}{dt} + k_2 [B] = k_1 [A]_0 e^{-k_1 t}$$

Multiplying both sides with $e^{k_2 t}$:

$$e^{k_2 t} \cdot \frac{d[B]}{dt} + k_2 \cdot e^{k_2 t} [B] = k_1 [A]_0 \cdot e^{(k_2 - k_1)t}$$

Integrating:

$$[B] \cdot e^{k_2 t} = \frac{k_1 [A]_0}{(k_2 - k_1)} \cdot e^{(k_2 - k_1)t} + \text{I.C.}$$

when, $t = 0$, $[B] = 0$.

$$\therefore \text{I.C.} = -\frac{k_1 [A]_0}{(k_2 - k_1)}$$

$$\therefore [B] e^{k_2 t} = \frac{k_1 [A]_0}{(k_2 - k_1)} \left\{ e^{(k_2 - k_1)t} - 1 \right\}$$

$$\therefore [B] = \frac{k_1 [A]_0}{(k_2 - k_1)} \left\{ \frac{e^{(k_2 - k_1)t} - 1}{e^{k_2 t}} \right\}$$

$$\therefore [B]_t = \frac{k_1 [A]_0}{(k_2 - k_1)} \left(e^{-k_1 t} - e^{-k_2 t} \right)$$

↑ indicates formation of B from A ; ↓ indicates disappearance of B to C

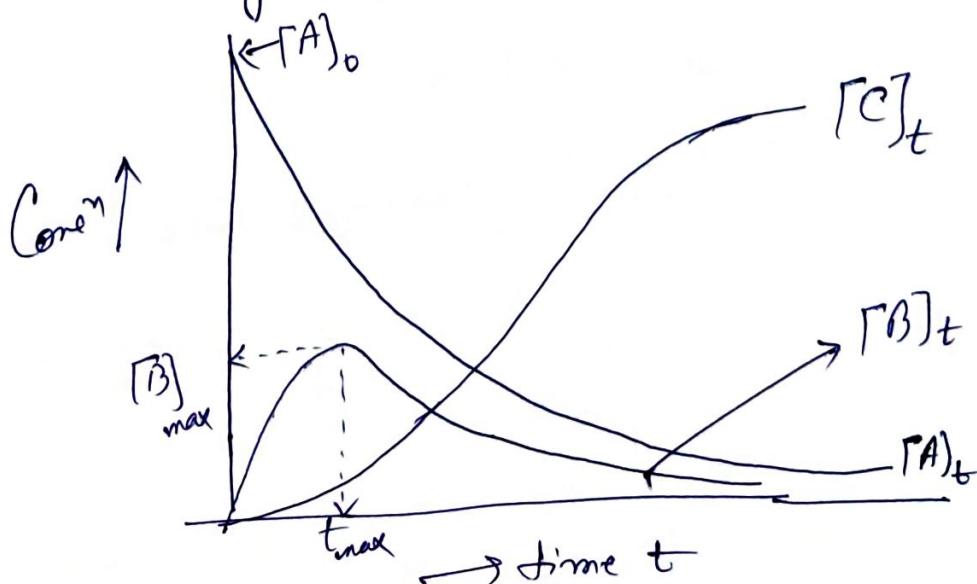
(9)

$$\text{Now, } [A]_0 = [A]_t + [B]_t + [C]_t$$

$$\begin{aligned} \therefore [C]_t &= [A]_0 - [A]_t - [B]_t \\ &= [A]_0 - [A]_0 e^{-k_1 t} - \frac{k_1 [A]_0}{(k_2 - k_1)} (e^{-k_1 t} - e^{-k_2 t}) \\ &= [A]_0 \left[1 - e^{-k_1 t} - \frac{k_1}{(k_2 - k_1)} (e^{-k_1 t} - e^{-k_2 t}) \right] \\ &= [A]_0 \left[1 - \frac{1}{(k_2 - k_1)} \left\{ (k_2 - k_1) e^{-k_1 t} + k_1 (e^{-k_1 t} - e^{-k_2 t}) \right\} \right] \\ &= [A]_0 \left[1 - \left(\frac{1}{k_2 - k_1} \right) \left\{ k_2 e^{-k_1 t} - k_1 e^{-k_1 t} + k_1 e^{-k_1 t} - k_2 e^{-k_2 t} \right\} \right] \end{aligned}$$

$$[C]_t = [A]_0 \left[1 - \frac{1}{(k_2 - k_1)} \left\{ k_2 e^{-k_1 t} - k_1 e^{-k_2 t} \right\} \right]$$

Plotting $[A]_t$, $[B]_t$ & $[C]_t$ with time t :



At any time:

$$[A]_0 = [A]_t + [B]_t + [C]_t$$

When $t = t_{\max}$, $[TB]_t = [TB]_{\max}$.

i.e. At $t = t_{\max}$, $\frac{d[TB]}{dt} = 0$

From this, we can show: $t_{\max} = \left(\frac{1}{k_2 - k_1} \right) \ln \left(\frac{k_2}{k_1} \right)$

& $[TB]_{\max} = [TA]_0 \left(\frac{k_2}{k_1} \right)^{\frac{k_2}{k_2 - k_1}}$

Home Work

(11)

From the previous discussion, we can derive two important conclusions :

i) For a multi-step reaction, the slowest step is the rate determining step.

Variation of concn. of the final product C, with time t:

$$[C] = [A]_0 \left[1 - \frac{1}{(k_2 - k_1)} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right].$$

This is the general expression.

Now consider a situation when $k_2 \gg k_1$

i.e. if A \rightarrow B is slow, as k_1 is lower

& that B \rightarrow C is high, as k_2 is higher.

Under this situation,

$$[C] = [A]_0 \left[1 - \frac{1}{k_2} \cdot k_2 e^{-k_1 t} \right]$$

$$[C] = [A]_0 \left[1 - e^{-k_1 t} \right]$$

Thus, $[C]$ will depend on the

rate constant of the slowest step (i.e. k_1)

Again, if $k_1 \gg k_2$, it can be shown:

$$[C] = [A]_0 (1 - e^{-k_2 t})$$

This proved: Overall rate depends on the rate of the slowest step.

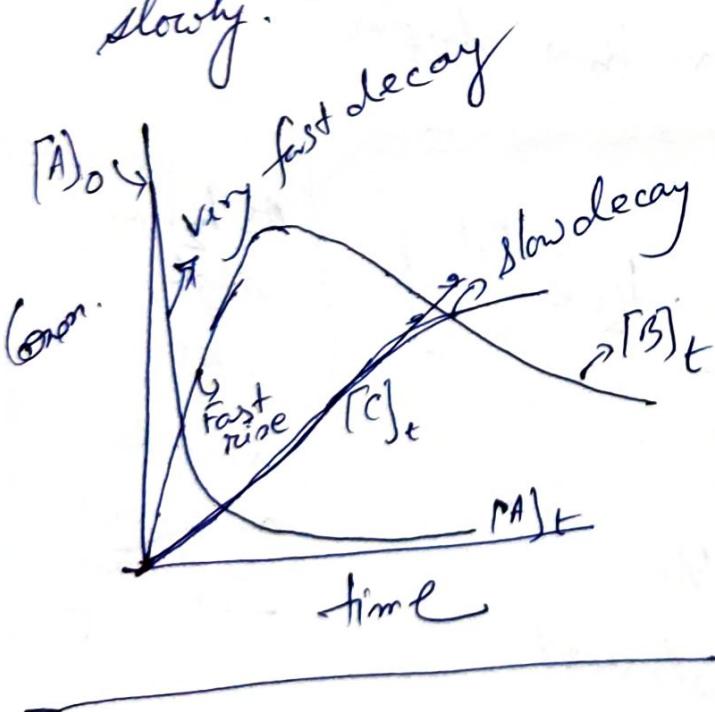
{ As k_2 is very high,
 $e^{-k_2 t}$ is very low
 and can be neglected }

iii) Concept of Steady State Approximation towards a reactive intermediate:

Previous diagram for variation of conc' of different species with time is a general one, where k_1 & k_2 are comparable. Now, let us examine the nature of conc' variation under two extreme conditions:

Case I $k_1 \gg k_2$

i.e. A will decay very rapidly, but the intermediate B will degrade to C very slowly.



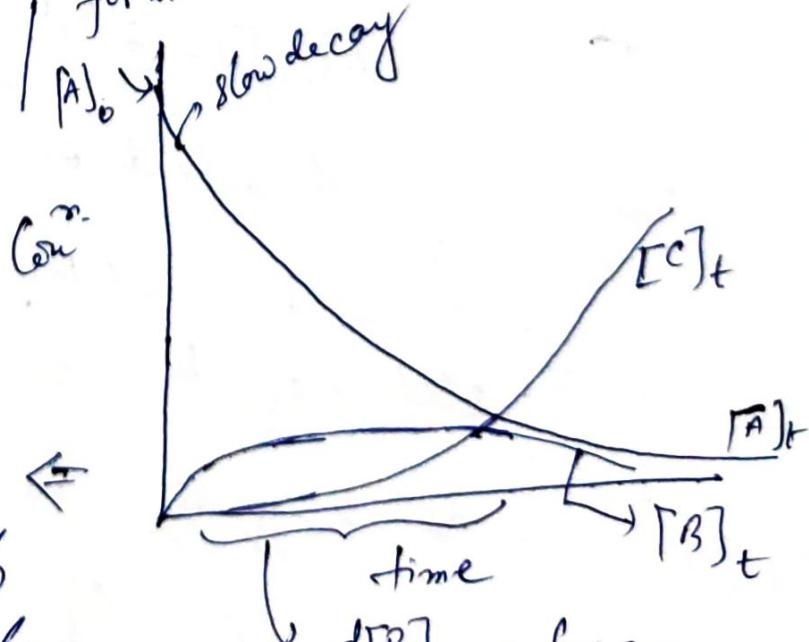
Thus, conc' of the reactive intermediate is low and remains almost constant for a considerable range of time.

$\therefore \frac{d[B]}{dt} = 0$ applicable for a reactive intermediate.

(Steady-State Approximation) (considerable range of time.)

Case II $k_1 \ll k_2$

i.e. Decay of A is slow. But degradation of the intermediate is very fast. This is now a reactive intermediate i.e.; just when it will be formed from A, it will instantaneously produce C. Thus, B can't be accumulated in the system, i.e. its overall rate of formation will be equal to zero.



$$\frac{d[B]}{dt} = 0 \text{ for a}$$

Rate expression of chain Reactions:

Many gas phase reactions and liquid-phase polymerisation reactions are chain reactions. Chain reaction proceeds through the formation of reactive intermediates, called chain carriers. Atoms / radicals (species with unpaired electrons) or ions can act as chain carrier. In nuclear fission the chain carriers are neutrons.

Four intermediate steps in a chain reaction:

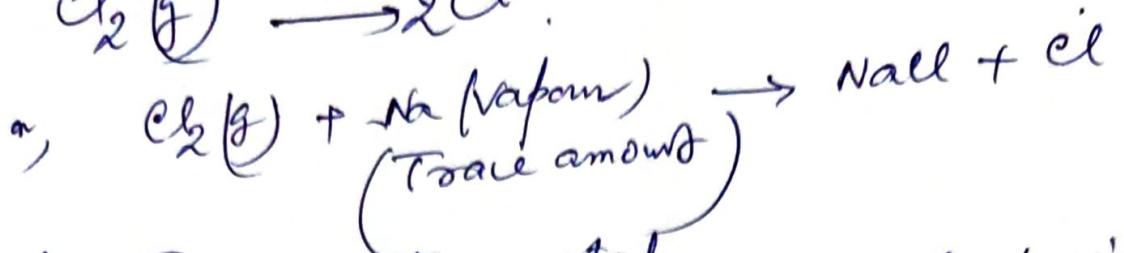
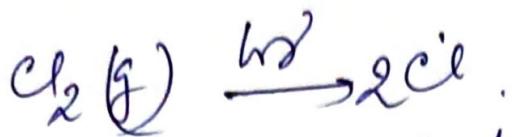
i) Chain Initiation Step:

Here, the reactive intermediates are formed by the action of heat or by vigorous intermolecular collisions, or by the action of radiation of suitable frequency.

For example: Br_2 radical is formed from the Br_2 molecule by heat or intermolecular collision like:



where M is either $\text{Br}_2(\text{g})$ or $\text{H}_2(\text{g})$
 \Rightarrow Termination.



ii) Chain Propagation Step: formed in previous step, highly reactive intermediate reacts with one of the reactant molecule to produce a product molecule and another reactive intermediate. This produced reactive intermediate, in-turn, reacts with another reactant producing again a product molecule and another reactive intermediate. Thus one reactive intermediate produced in the initiation step may result in thousands of product molecules via the propagation step.

iii) Chain Inhibition Step:

Here, the reactive intermediate combines with a product molecule producing a reactant molecule and another reactive intermediate. Though a reactive intermediate is generally, the net effect of this step is to decrease the rate of overall reaction.

(3)

iv) Chain Termination Step:

Here, the reactive intermediates are destroyed by combining with another reactive intermediate. This combination may occur at the wall of the reaction vessel or by direct collision between the two reactive intermediates within the vessel. Certain substances when added also help in terminating the reactive intermediates. e.g. nitric oxide (NO_2) molecules can react very rapidly with free radicals.

Chain length

The number of chain propagation steps in between the chain initiation step and termination step is usually expressed by as the chain length.

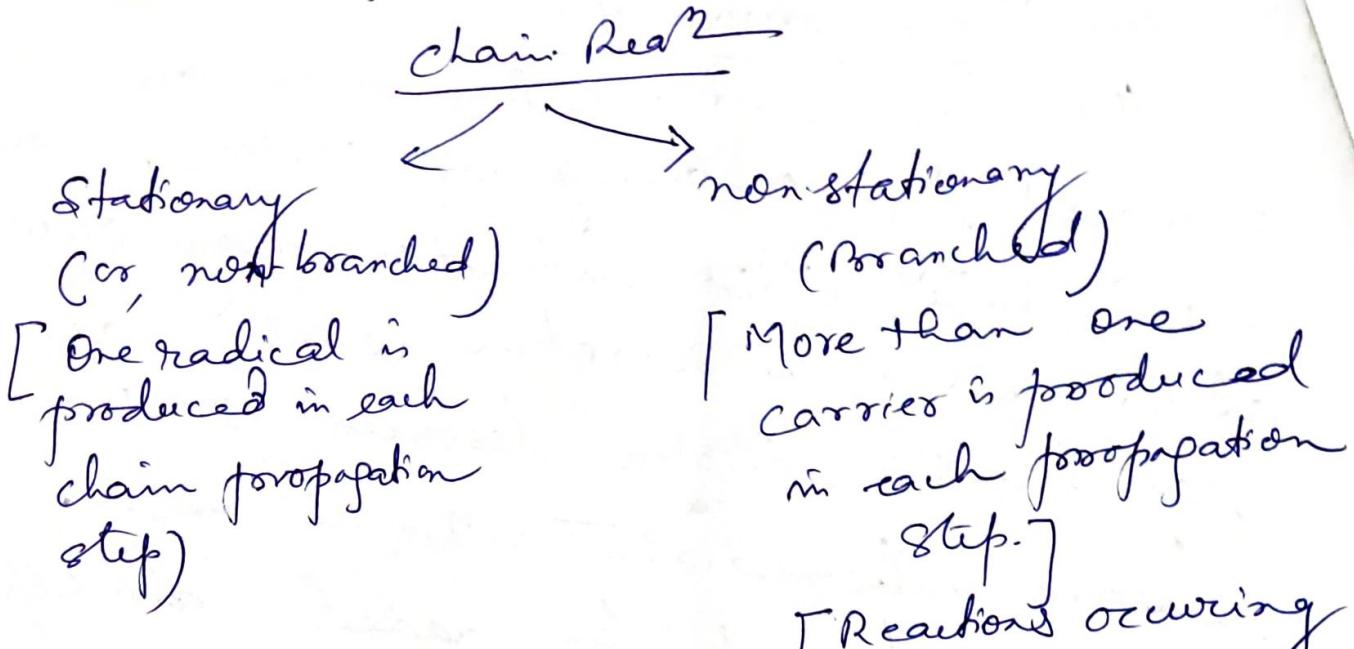
Mathematically:

chain length \Rightarrow Number of product molecules formed per chain carrier produced in the chain initiation step: etc.

$$\text{chain length} = \frac{d[\text{product}]/dt}{d(\text{initiation step})/dt}$$

$$= \frac{\text{Overall rate of formation of product}}{\text{rate of chain initiation step}}$$

Kinetics of chain Reactions:



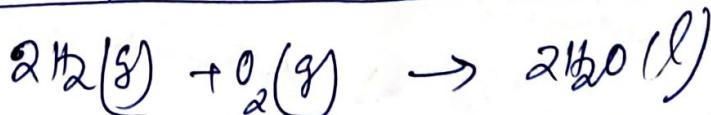
[Reactions occurring in explosives;
Nuclear fission].

Here, rate of rad^n increases in an uncontrolled manner - leading to explosion.

Home work

What is the role of control rods in nuclear power plants?
What should be the criteria for material selection for these control rods?

Another example of branched chain radⁿ



Reacⁿ proceeds via some complex intermediate steps. In some propagation steps, more than one free radicals are produced.

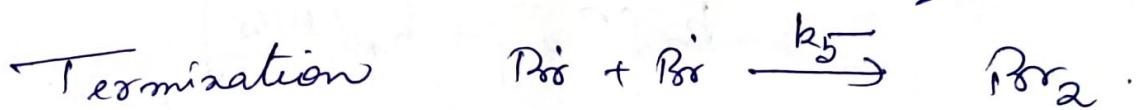
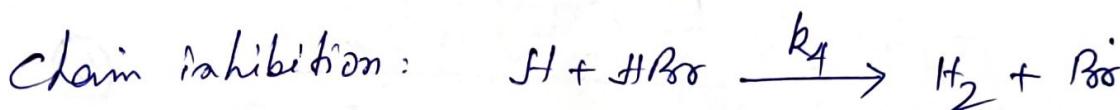
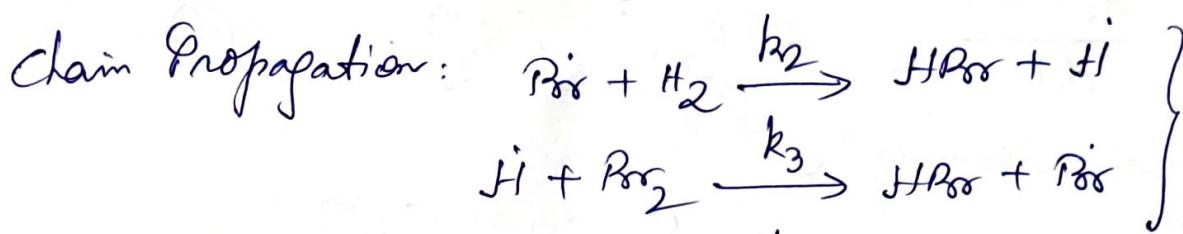
(7)

Example of Non-stationary chain redⁿ:

i) Redⁿ betw. H₂(g) and Br₂(g) :



Proposed elementary steps:



In 2nd & 3rd step, product HBr is produced, while in 4th step, it is consumed.

Hence, Overall rate of formation of product -
i.e.: HBr is given as:

$$\frac{d[HBr]}{dt} = k_2 [Br] [H_2] + k_3 [H][Br_2] - k_4 [H][HBr] \quad \dots \quad (1)$$

Here, [H] & [Br] are the concn. terms of reactive intermediates. These are to be replaced by the concn. terms of reactants & products.

Previously, we have shown that one can apply steady state approximation towards a reactive intermediate. It tells that overall rate of formation of any reactive intermediate is zero. i.e.

~~Eqn 2~~

$$\frac{d[H]}{dt} = 0 = k_2 [Br] [H_2] - k_3 [H][Br_2] - k_4 [H][HBr] \quad \text{--- (2)}$$

$$\text{or, } k_2 [Br] [H_2] - k_4 [H][HBr] = k_3 [H][Br_2] \quad \text{--- (3)}$$

From (1) & (3), we can write:

$$\frac{d[HBr]}{dt} = 2 k_3 [H][Br_2] \quad \text{--- (4)}$$

Again from eqⁿ (2),

$$[H] = \frac{k_2 [Br] [H_2]}{k_3 [Br_2] + k_4 [HBr]} \quad \text{--- (5)}$$

Applying steady state approximation towards Br:

$$\begin{aligned} \frac{d[Br]}{dt} = 0 &= 2 k_1 [Br_2] - k_2 [Br] [H_2] + k_3 [H][Br_2] \\ &+ k_4 [H][HBr] - 2 k_5 [Br]^2 \end{aligned} \quad \text{--- (6)}$$

From eqⁿ (2) & (6)

$$2 k_1 [Br_2] - 2 k_5 [Br]^2 = 0$$

$$\text{or, } [Br_2] = \left\{ \frac{k_1}{k_5} [Br]^2 \right\}^{1/2} \quad \text{--- (7)}$$

$$\begin{cases} 2 Br \xrightarrow{k_5} Br_2 \\ -\frac{1}{2} \frac{d[Br]}{dt} = k_5 [Br]^2 \\ \therefore \frac{d[Br]}{dt} = -2 k_5 [Br]^2 \end{cases}$$

Putting this value of $[Br_2]$ in eqⁿ - (5):

$$[H] = \frac{k_2 \left\{ \frac{k_1}{k_3} [Bor_2] \right\}^{1/2} [H_2]}{k_3 [Bor_2] + k_1 [H Bor]} - \textcircled{8}$$

Putting this value of $[H]$ in eqn $\textcircled{4}$.

$$\frac{d[H Bor]}{dt} = \frac{2 k_3 k_2 \left\{ \frac{k_1}{k_3} [Bor_2] \right\}^{1/2} [H_2] \cdot [Bor_2]}{k_3 [Bor_2] + k_1 [H Bor]}$$

$$= \frac{2 k_2 \left(\frac{k_1}{k_3} \right)^{1/2} [Bor_2]^{1/2} [H_2]}{1 + \left(\frac{k_1}{k_3} \right) \frac{[H Bor]}{[Bor_2]}}$$

$$\boxed{\frac{d[H Bor]}{dt} = \frac{k' [Bor_2]^{1/2} [H_2]}{1 + k'' \frac{[H Bor]}{[Bor_2]}}}$$

Initial rate of 1st red²:

At initial time, $[H Bor]$ is very low & $[Bor_2]$ is very high.

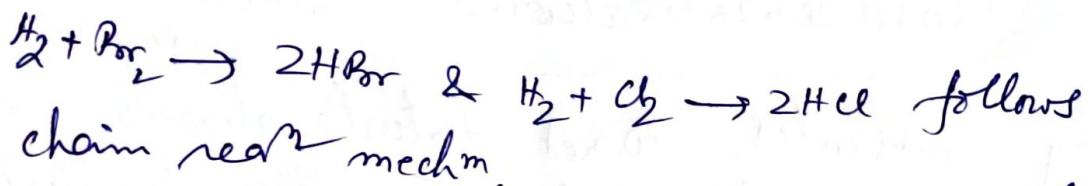
$$\therefore 1 + k'' \frac{[H Bor]}{[Bor_2]} \approx 1.$$

$$\therefore \left\{ \frac{d[H Bor]}{dt} \right\}_{\text{initial}} = k' [Bor_2]_0^{1/2} [H_2]_0$$

initial i.e., initially the order

of red² is 1.5.

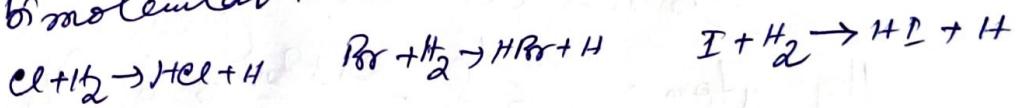
(11)



But $H_2 + I_2 \rightarrow 2HI$ follows a simple bimolecular mechm - why?

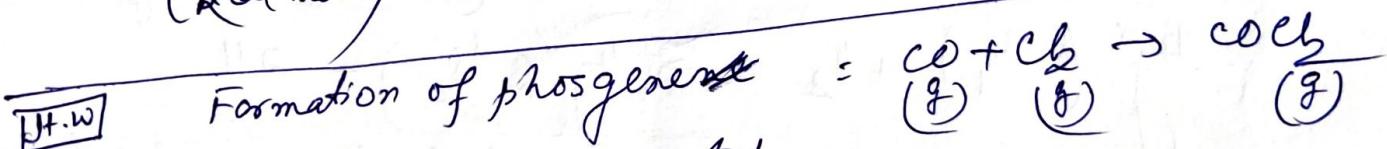
Ans: It is revealed that the energy of activation in the process

$I + H_2 \rightarrow HI + H$ is relative high and hence it follows the easier path of bimolecular rearⁿ.

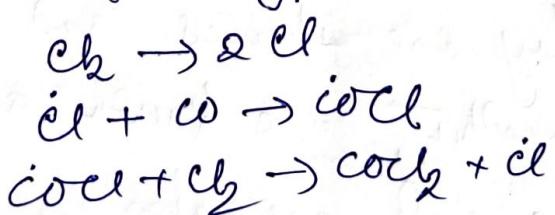


Redn:

Energy of activation (kCal/mole)	5	18	33
-------------------------------------	---	----	----



follows the following steps:



Show overall rate of formation of phosgene:

$$\frac{d[COCl_2]}{dt} = k [CO] [Cl_2]^{1/2}$$