The last important category of complex reaction in which study of chemical kinetics becomes highly complicated due to occurrence of complex reactions is Chain Reactions.

Chain Reactions: There are certain reactions whose rate is much greater than predicted from collision theory. In ~~the~~ chain reactions the group of reactions proceed by a long series of self-repeating and as a result millions of molecules react together.

Def^n: Chain reaction is defined as series of successive elementary processes in which active intermediate species are consumed and ~~generated~~ regenerated before the products are obtained.

Chain reactions ~~are~~ can be considered as a special case of Consecutive reactions.

The chain reactions proceeds through the following steps.

1. Chain Initiation: It consists of slow generation of active intermediate species called (Chain carriers) which may be atoms, free radicals or energised molecules of one of the products formed during the course of reaction. The chain initiation step may takes place thermally or photochemically.

2. Chain propagation: The active intermediate species formed during the chain initiation step reacts with the molecules of other reactant or reactants resulting in the formation of the products and regeneration of active intermediate species; thus, restarting the reaction leading to the formation of final products. Chain propagation is much faster and most of the products are formed in these steps.

3. Chain transfer: In some of the chain propagation steps, new chain carriers are generated. In this step ~~new~~ initial chain carriers generates new chain carrier by reaction with some existing molecular species.

(④ Chain Inhibition: This step involves removal of the products with simultaneous regeneration of more active species with a net decreasing effect on the rate of overall reactions. The Chain Inhibition may complete when the concentration of product becomes significant.

⑤ Chain Termination or Breaking: In this step the active intermediate species are removed or destroyed & no longer available for chain initiation or propagation. The chain termination stage occurs when there are not enough reactant molecules to be converted into products, and active intermediate species are converted into non active molecular species.

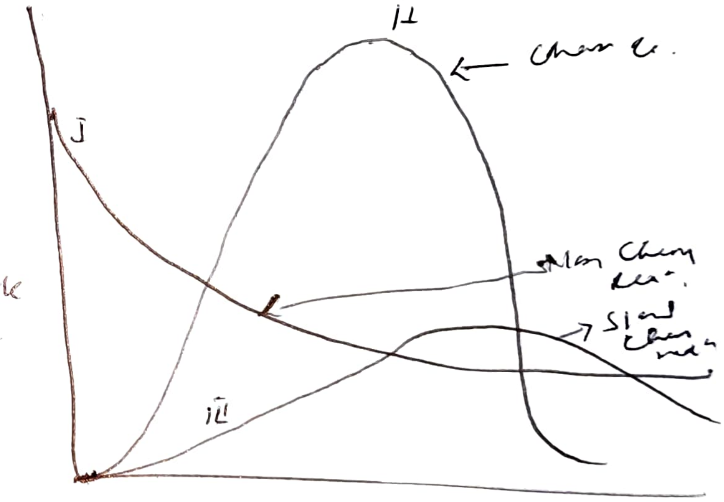
Characteristic features of chain Reactions:

The following are the distinguishing features of chain Reaⁿs:

1. Every chain reaction involves initial slow step generating active intermediate species, which are helpful in starting fast propagating steps.

2. Rate is much higher than expected from Collision theory

3. Mechanism is complex ...



Comparison of slow & fast Chain reactions with non Chain Reactions

4. The remarkable feature is is in all Non-chain reaction, the rate is highest in the begining and falls of with time, WHERE AS IN CHAIN reactions, the rate is zero in the begining rises to maximum & finally decreases with time.

Ex. Curve i, & ii & iii.

⑤ They are highly influenced by pressure or concentration of reactants.

⑥ Sensitive to foreign substance (speed may be accelerated or retarded)

⑦ Chain rexn are generally of fractional order may also be of simple order. Order depends on shape of vessel & other conditions.

⑧ Chain reactions have induction period. Since chain reactions has zero rate in the beginning, it requires enough time so that the rate could be experimentally detected. This time lag is called INDUCTION - PERIOD.

Kinetics of Chain Reactions:

A Chain reaction may be classified into two types.
- STATIONARY (NON - BRANCHED)
- NON-STATIONERY (BRANCHED)

Chain reactions depending one one or more than one radical (transient intermediate) produced in each chain propagation step, respectively.

A Chain Rexn can be represented as

Initiation $A \xrightarrow{k_1} R^*$

Propagation $R^* + A \xrightarrow{k_2} P + \alpha R^*$

Termination $R^* \xrightarrow{k_3}$ DESTRUCTION. (Termination,

A, R & P represents Reactant, Radical & Product respectively.

If $\alpha = 1$ (Stationary Chain Rexn)

$\alpha > 1$ (Non Stationary) or Branched chain Rexn

The destruction or termination occurs with the collision of intermediate (Radicals) with the wall of the vessel or direct collision of all other radicals within the gaseous phase.

Applying ~~Stea~~ S.S.A. to the Radical.

$$\frac{d[R^*]}{dt} = 0 = k_1[A] + k_2(\alpha-1)[R^*][A] - k_3[R^*]$$

$$\text{or } [R^*] = \frac{k_1[A]}{k_2(1-\alpha)[A] + k_3}$$

Since the destruction of radical can occur in either of the way (wall / gaseous phase) k_3 can be replaced by $\underline{k_w + k_g}$ (w = wall) (g = gas phase)

$$[R^*] = \frac{k_1[A]}{k_2[1-\alpha][A] + k_w + k_g} \quad — ⊛$$

<u>Imp</u> Examples of Stationary Chain Reactions.

Here ~~wke~~ $\alpha = 1$. [since $(k_2[0][A] = 0$]

$$\boxed{\text{Hence } [R^*] = \frac{k_1[A]}{k_w + k_g}}$$

⇒ Concn of radical is simply ratio of rate of formation of radical in chain initiation step & rate of destruction of radical in chain termination step.

(I) Formation of ~~HBR~~HBr.

Rexn between H_2 & Br_2.

$$H_2 + Br_2 \longrightarrow 2HBr.$$

The elementary step proposed for the rexn are

Initiation $\quad Br_2 \xrightarrow{k_1} 2Br.$

Propagation $\quad Br + H_2 \xrightarrow{k_2} HBr + H$

$\quad H + Br_2 \xrightarrow{k_3} HBr + Br.$

Inhibition $\quad H + HBr \xrightarrow{k_4} H_2 + Br.$

Termination $\quad Br + Br \xrightarrow{k_5} Br_2.$

⑤

The rate law can be derived using steady state Approximation (S.S.A.)

Rate of formation of HBr is given by

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

Apply S.S.A to intermediate H & Br

$$\frac{d(H)}{dt} = 0 \quad \& \quad \frac{d[Br]}{dt} = 0$$

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

$$\frac{d[Br]}{dt} = 0 = 2k_1[Br_2] - k_2[Br][H_2] + k_3[H][Br_2] + k_4[H][HBr] - 2k_5[Br]^2 \quad III$$

using (II) & (III) cancelling and terms left

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

or

$$[Br] = \left[\frac{k_1}{k_5}[Br_2]\right]^{1/2} \quad \text{— (IV)}$$

putting [Br] & in (II) simply rearranging (II).

$$[H] = \frac{k_2[Br][H_2]}{k_3[Br_2] + k_4[HBr]} \quad (I$$

$$[H] = \frac{k_2\left(\frac{k_1}{k_5}[Br_2]\right)^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]} \quad \text{— V}$$

or

$$[H] = \frac{k_2\left(\frac{k_1}{k_5}\right)^{1/2}[Br_2]^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]} \quad \text{— (V)}$$

Invoking (II) on (I), (I − II)

$$\frac{d[HBr]}{dt} = 2k_3[H][Br_2]$$

Substituting the value of [H] ~~from~~ eqn (V)

$$\frac{d(HBr)}{dt} = 2k_3\left[\frac{k_2\left(\frac{k_1}{k_5}\right)^{1/2}(Br_2)^{1/2}(H_2)}{k_3(Br_2) + k_4(HBr)}\right][Br_2]$$

$$= \frac{2k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{1 + (k_4/k_3)[HBr]/[Br_2]}$$

[Dividing by $k_3[Br_2]$
$\Rightarrow$ simplifying.

$$= \frac{k'[Br_2]^{1/2}[H_2]}{1 + k''[HBr]/[Br_2]}$$

where $k' = 2k_2(k_1/k_5)^{1/2}$ & $k'' = k_4/k_3$

Imp

At initial stage of the rxn [HBr] is negligibly small

Hence $1 + k''[HBr]/[Br_2] \approx 1$.

& initial rate.

$$\left[\frac{d(HBr)}{dt}\right]_{initially} = \left[\frac{d[HBr]}{dt}\right]_0 = k'[Br_2]_0^{1/2}[H_2]_0$$

At initial stage order of rxn = 1.5.

—o—

Thermal Decomposition of Acetaldehyde.

Rexn $CH_3CHO \longrightarrow CH_4 + CO$

Observed rate law

$$\frac{d[CH_4]}{dt} = k[CH_3CHO]^{3/2} \quad — (*)$$

&

Chain length $\frac{d[\text{product}]/dt}{d[\text{initiation step}]/dt} = [\dot{K}]^{1/2}[CH_3CHO]^{1/2}(\times\alpha)$

The proposed mechanism is

Initiation

(i) $CH_3CHO \xrightarrow{k_1} {}^{\bullet}CH_3 + {}^{\bullet}CHO$

Propagation (ii) ${}^{\bullet}CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + {}^{\bullet}CH_2CHO$

(iii) ${}^{\bullet}CH_2CHO \xrightarrow{k_3} {}^{\bullet}CH_3 + CO$

Termination ${}^{\bullet}CH_3 + {}^{\bullet}CH_3 \xrightarrow{K_4} CH_3CH_3$

Rate of formation from (ii) propagation step

$$\frac{d[CH_4]}{dt} = k_2[{}^{\bullet}CH_3][CH_3CHO] \quad — ①$$

Applying S.S.A. to ${}^{\bullet}CH_3$ & ${}^{\bullet}CH_2CHO$

$$\frac{d[{}^{\bullet}CH_3]}{dt} = 0 = k_1[CH_3CHO] - k_2[{}^{\bullet}CH_3][CH_3CHO] + k_3[{}^{\bullet}CH_2CHO] - 2K_4[{}^{\bullet}CH_3]^2 \quad ~~②~~ - ②$$

$$\frac{d[{}^{\bullet}CH_2CHO]}{dt} = 0 = k_2[{}^{\bullet}CH_3][CH_3CHO] - k_3[{}^{\bullet}CH_2CHO] \quad - ③$$

Making use of ③ in ②

$$k_1[CH_3CHO] - 2K_4[{}^{\bullet}CH_3]^2 = 0$$

$$\text{or } [{}^{\bullet}CH_3] = \left(\frac{k_1}{2K_4}[CH_3CHO]\right]^{1/2}$$

Substituting in ①

$$\frac{d[CH_4]}{dt} = k_2\left\{\left(\frac{k_1}{2k_4}\right)[CH_3CHO]\right]^{1/2}[CH_3CHO]$$

$$= k_2\left(\frac{k_1}{2k_4}\right)^{1/2}[CH_3CHO]^{3/2}$$

$$= K[CH_3CHO]^{3/2}$$ — * (Result.

The Chain length of rxn

$$\frac{d(\text{product})/dt}{d(\text{initiation step})/dt} = \frac{k_2(k_1/2k_4)^{1/2}(CH_3CHO)^{3/2}}{k_1[CH_3CHO]}$$

$$= \left[\frac{k_2}{2k_1k_4}\right)^{1/2}\{CH_3CHO]^{1/2}$$