Retardation (Inhibition)

$$H^{\bullet} + HBr \longrightarrow H_2 + Br^{\bullet}$$

this step is specific and corresponds to the first propagation step in reverse

Termination

$$2\,Br^{\bullet} \longrightarrow Br_2$$

recombination of two radicals and corresponds to initiation in reverse.

- Using steady-state approximation, the thermal reaction has an initial rate of fractional-order (3/2) and a complete rate equation with a two-term denominator (Mixed order kinetics)

Example: 02

The reaction between $2H_2 + O_2 \longrightarrow 2H_2O$ which provides the example of chain-branching. The propagation is a sequence of two steps whose net effect is to replace an H-atom by other H-atoms plus two OH radicals. Under certain conditions ~~this leads to an explosion~~ of temp^{r} and pressure this leads to an explosion.

$$H^{\bullet} + O_2 \longrightarrow OH^{\bullet} + O$$

$$O^{\bullet} + H_2 \longrightarrow OH^{\bullet} + H$$

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Degree Part - III (Hons)
Paper - IVth

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Lecture - 04
Date - 02.05.2020

EFFECT OF TEMP. AND PRESSURE ON RATE CONSTANT :-

The rate of chemical reaction increases with increase of temperature. It has been observed that for a homogeneous chemical change, the rate is approximately double or treple for the 10^0 rise of temperature

The effect of temperature of on chemical reaction is expressed by temperature coefficient The temperature coefficient is the ratio of two rate constant at two temperature separated by 10^0. Thus temperature coefficient =

$$\frac{K_{t+10}}{t} \simeq 2 \text{ to } 3$$

Where, K_t is the rate constant at t^0c and K_{t+10} at 10^0c In most of homogeneous gas reaction the value of temp^r coefficient lies between 2 or 3.

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Degree Part III (HONS)

Lecture-04 Paper-V th

Date - 02.05.2020

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CHAIN-REACTION

A chain reaction is one in which the products of the reaction carry on the reaction on the part of reacting molecules and thus a long series of self repeating is started.

Or, we can say a chain reaction is a sequence of reactions where a reactive product or by-product causes additional reactions to take place.

Main types of steps in chain reaction are as follows:

(I) Initiation (Formation of active particles or chain-carriers, free radicals, thermal or photochemical step

(II) Propagation (may comprise several elementary steps in a cycle where the active particles through reaction forms another active particles which continues the reaction chain by ~~entering~~ entering the next elementry step. The active particle serves as a catalyst for the overall reaction of the propagation cycle. Particular cases are:

Chain branching, ~~chain~~

Chain transfer (The active particles is growing polymer chain to ~~activity in elementary step~~ form an inactive polymer whose growth is terminated

Termination (The active particles loses its activity in elementary step e.g. by recombination of two free radicals

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CHAIN LENGTH:

It is defined as the average number of times the propagation cycle is repeated and equals the overall reaction rate divided by the unit initiation rate.

Some chain reactions have complex rate equations with fractional order or mixed order kinetics.

Example 01

The reaction between Hydrogen and Bromine proceeds by the following mechanism.

$$H_2 + Br_2 \longrightarrow 2HBr$$

~~Initiation~~ ~~$H_2 + Br_2 \longrightarrow 2HBr$~~

Initiation

$$Br_2 \longrightarrow 2Br^{\bullet} \quad \text{(Thermal)}$$

or $$Br_2 + h\nu \longrightarrow 2Br^{\bullet} \quad \text{(photochemical)}$$

Each Br atom is a free radical and represented by the symbol ($\bullet$) which indicates an unpaired electron.

Propagation (cycle of two steps)

$$Br^{\bullet} + H_2 \longrightarrow HBr + H^{\bullet}$$

$$H^{\bullet} + Br_2 \longrightarrow HBr + Br^{\bullet}$$

Sum of these two steps corresponds to the overall reaction $H_2 + Br_2 \longrightarrow 2HBr$, with catalysis by $Br^{\bullet}$ which participates in the first step and regenerated in the second step

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