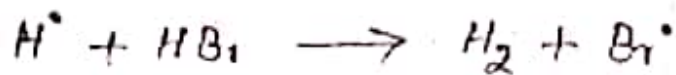


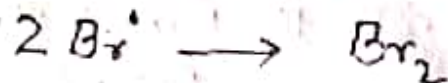
Retardation (Inhibition)

Page - 04



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

Termination



recombination of two radicals and corresponds to initiation in reverse.

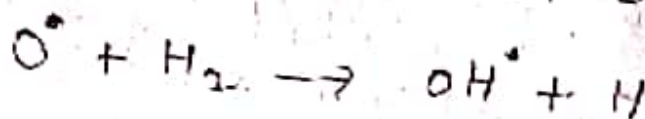
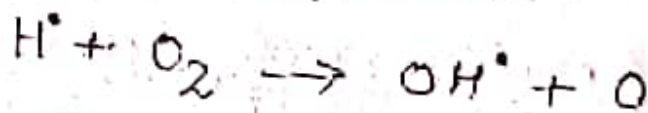
Using steady-state approximation, the thermal reaction has an initial rate of fractional-order ($3/2$) and a complete rate equation with a two-term denominator (Mixed order kinetics)

Example: 02

The reaction between $2 H_2 + O_2 \rightarrow 2 H_2O$

which provides the example of chain-branching.

The propagation is a sequence of two steps whose net effect is to replace one H-atom by other H-atom plus two OH radicals. Under certain conditions ~~this leads to an explosion~~ of temp^r and pressure this leads to an explosion.



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 triple for the 10° rise of temperature.

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

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

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

Date - 02.05.2020

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 elementary 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 and loses its ^{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)

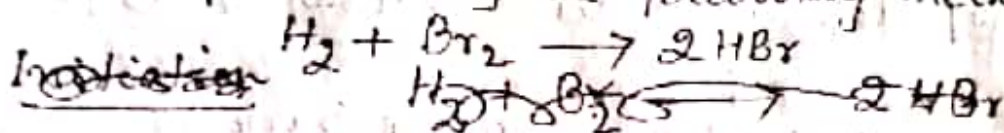
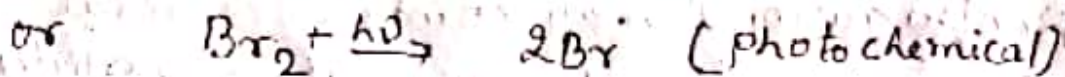
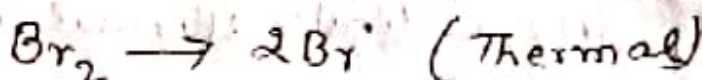
CHAIN LENGTH:

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

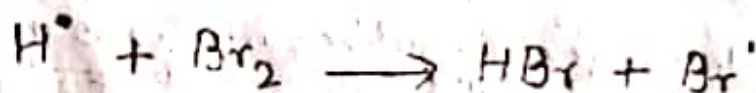
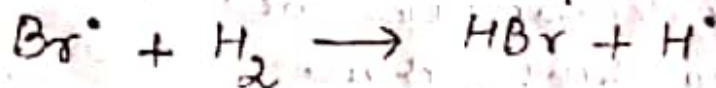
Some chain reactions have complex rate equations with fractional order or mixed order kinetics.

Example - 01

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

Initiation

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

Propagation (cycle of two steps)

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