CHAIN REACTION

Presented by :

<u>Arvind Singh Heer</u> <u>MSc-I</u> (Sem-II) <u>Inorganic Chemistry</u> <u>MITHIBAI COLLEGE</u>

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INTRODUCTION

- Defination:-A chemical or nuclear reaction which proceed through a sequence (chain) of self repeating steps initiated by a suitable primary process is called a chain reaction.
- Types of Chain Reactions:
 - Stationary Chain Reaction
 - Non-stationary Chain Reaction

CHAIN REACTION

■ Example : Reaction between hydrogen and bromine $H_2 + Br_2$ 2HBr The reaction follows simple elementary reaction. k_1

HBr +.H

HBr +

k₃

Initiation step: Br_2 .Br + .Br

k₂

Propagation step 1: .Br + H₂

Propagation step 2: .H + Br₂ .Br

- Inhibition step : .H + HBr H₂ +.Br
 k₅
 Termination step: 2.Br Br₂
- The steady-state hypothesis applied to the two intermediates Br & H, both of which are present at very low concentrations. The steady-state equation for H is

$$\frac{d[.H]}{dt} = \frac{k_2[.Br][H_2] - k_3[.H][Br_2] - k_3[.H][Br_2]}{k_4[.H][HBr]=0}$$
.....(1)

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

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Adding (1) & (2)

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

k_1 [Br_2] = k_5 [.Br]^2
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[.Br] = (k_1/k_5 [Br_2])^{1/2} .....(3)
from equation no. (1) ,we get
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k_{2} [.Br][H<sub>2</sub>] = K<sub>3</sub> [.H][Br<sub>2</sub>] + k<sub>4</sub> [.H][HBr]
k_{2} [.Br][H<sub>2</sub>] = [.H] (k<sub>3</sub>[Br<sub>2</sub>] + k<sub>4</sub> [HBr])
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$$[.H] = \frac{k_{2}[.Br][H_{2}]}{k_{3}[Br_{2}]+k_{4}[HBr]}$$

$$[.H] = k_{2} (k_{1}/k_{5})^{1/2} \frac{[H_{2}][Br_{2}]^{1/2}}{k_{3}[Br_{2}]+k_{4}[HBr]}.....(4)$$
HBr is formed in reaction (2) & disappears in reaction (3). The net rate of formation of HBr gives
,
$$\frac{1}{d[HBr]} = \frac{k_{2}[.Br][H_{2}] + k_{3}[.H][Br_{2}] - k_{4}[.H][HBr]}{k_{4}[.H][HBr]}(5)$$

from eq. (1) we know that, $k_3 [.H][Br_2] = k_2 [.Br][H_2] - k_4 [.H][HBr]$





Dividing both numerator & denominator of above equation by k₃[Br₂]

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

k_3[Br_2]

$$\frac{d[HBr]}{dt} = \frac{K [H_2][Br_2]^{1/2}}{1 + k'[HBr]/[Br_2]}$$
where K= 2k₂(k₁/k₅)^{1/2}
k'= k₄/k₃

In the initial state of the reaction order of reaction is 1.5 At the initial stage of the reaction HBr is negligibly small & hence

This is the rate law equation for given reaction.

REFERENCES

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