B. Sc. Hons Part III

Paper : Physical Chemistry

Topic : Chemical Kinetics

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Examples of Chain Reactions :-

(i) A typical chain reaction is the "thermal reaction between hydrogen and bromine to form hydrogen bromide ($H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$). Linde and Bodenstein in 1906 established the following rate for this reaction :

$$\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1 + m[HBr]/[Br_2]} \quad — (1)$$

where k and m are constants.

The following mechanism has been proposed for this reaction :

1. Chain initiation $\quad Br_2 \xrightarrow{k_1} 2Br \quad$ (slow)

2. Chain propagation $\quad Br + H_2 \xrightarrow{k_2} HBr + H \quad$ (slow)

   $H + Br_2 \xrightarrow{k_3} HBr + Br \quad$ (fast)

3. Chain inhibition (or retardation) $\quad H + HBr \xrightarrow{k_4} H_2 + Br$

4. Chain termination (or breaking) $\quad Br + Br \xrightarrow{k_5} Br_2$

where k_1, k_2, k_3, k_4 and k_5 are the specific rates (i.e. rate constants) of all the five reactions respectively.

In this chain reaction, the reactive intermediate is consumed, the reactants are converted to products and the intermediate is regenerated. The regeneration of the intermediate allows the cycle to be repeated over and above again. Let us discuss the various steps briefly.

Step 1. Chain initiation: Bromine molecule acquires energy as a result of collision (with another bromine molecule or sometimes with a foreign molecule which may be present as an impurity to dissociate into two Br atoms. This is a chain initiation step since it produces the chain-carrying reactive (transient, short-lived) Br atoms.

Step 2. Chain propagation: Here there are two chain propagation steps. The chain consumes Br, converting H_2 and Br_2 into HBr and regenerating Br.

Step 3. Chain inhibition: In this step, the chain is inhibited by the destruction of product HBr thereby decreasing the rate of its formation.

Step 4. Chain termination: This step removes Br atoms converting them back to Br_2 molecules. This step is the reverse of the chain initiation step.

The reactive species H and Br, which are responsible for propagating the chain, are called chain carriers.

In this mechanism, the rate of formation of HBr is given by step 2. Hence

$$\frac{d[HBr]}{dt} = k_2[Br][H_2] + k_3[H][Br_2]$$

And the rate of decomposition of HBr is given by step 3. Hence

$$-\frac{d[HBr]}{dt} = k_4[H][HBr]$$

The overall rate of formation of HBr is

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

Applying steady state approximation concept for the intermediates H and Br atoms, we have equation

$$\frac{d[Br]}{dt} = k_1[Br_2] - k_2[Br][H_2] + k_3[H][Br_2] + k_4[H][HBr] - k_5[Br]^2 = 0 \quad \text{---} (3)$$

and

$$\frac{d[H]}{dt} = k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr] = 0 \quad \text{---} (4)$$

from equations (3) and (4), we get

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

$$\text{or,} \quad [Br] = \left(\frac{k_1}{k_5}[Br_2]\right)^{1/2} \quad \text{---} (5)$$

From equation (4), we have

$$[H] = \frac{k_2[Br][H_2]}{k_3[Br_2] + k_4[HBr]} \quad \text{---} (6)$$

Putting the value of [Br] from equation (5) in (6), we get

$$[H] = \frac{k_2 \cdot (k_1/k_5)^{1/2} \cdot [H_2][Br_2]^{1/2}}{k_3[Br_2] + k_4[HBr]} \quad \text{---} (7)$$

From equation (4) we have

$$k_2[Br][H_2] - k_3[H][Br_2] = k_4[H][HBr] \quad \text{---} (8)$$

And from equation (2) and (8), we get

$$\frac{d[HBr]}{dt} = 2k_3[H][Br_2] \quad \text{---} (9)$$

Putting the value of [H] from equation (7) in equation (9) we get

$$\frac{d[HBr]}{dt} = \frac{2k_3k_2(k_1/k_5)^{1/2}[H_2][Br_2]^{3/2}}{k_3[Br_2] + k_4[HBr]}$$

$$= \frac{2k_3 k_2 (k_1/k_5)^{1/2} [H_2][Br_2]^{3/2}}{k_3[Br_2]\left\{1 + \frac{k_4[HBr]}{k_3[Br_2]}\right\}}$$

or, $$\frac{d[HBr]}{dt} = \frac{2k_2(k_1/k_5)^{1/2}[H_2][Br_2]^{1/2}}{1 + \frac{k_4}{k_3}([HBr]/[Br_2])} \quad \text{—— (10)}$$

This equation is identical to equation (1) obtained by Linde and Bodenstein.

In the begining of reaction, i.e. when $t=0$, $[HBr]=0$, then the rate law equation (10) becomes

$$\frac{d[HBr]}{dt} = k[H_2][Br_2]^{1/2} \quad \text{—— (11)}$$

where $k = 2k_2(k_1/k_5)^{1/2}$ is the observed rate constant.

This equation gives order equal to 1.5 (i.e. 3/2). It means the overall order of reaction is 1.5. This is experimentally observed.

(ii) <u>Reaction between Chlorine and Hydrogen</u> :-

This reaction is initiated by chlorine atoms produced by photo dissociation or thermal dissociation or from the reaction between chlorine gas and the atomic sodium introduced in the reaction mixture. The probable mechanism is as follows :

(a) Chain Initiation :

(i) $Cl_2 + Na \longrightarrow NaCl + Cl$

(ii) $Cl_2 \xrightarrow{\Delta} 2Cl$

(iii) $Cl_2 \xrightarrow{h\nu} 2Cl$

(b) Chain Propagation :

(i) $Cl + H_2 \longrightarrow HCl + H$

(ii) $H + Cl_2 \longrightarrow HCl + Cl$

(c) Chain Inhibition :

(i) $H + HCl \longrightarrow H_2 + Cl$

(ii) $H + Cl \longrightarrow HCl$

(d) Chain Termination :

(i) $2H \longrightarrow H_2$

(ii) $2Cl \longrightarrow Cl_2$

(iii) $Cl + O_2 \longrightarrow ClO_2$

The thermal and photochemical reactions between hydrogen and chlorine show some resemblance to the hydrogen - bromine reactions, but the mechanisms are less straight forward.

The photochemical reaction of hydrogen and chlorine has a number of complicating experimental features although it is a little easier to understand than the thermal reaction between hydrogen and chlorine. Oxygen, even in minute amounts, has a profound effect on the rate. To a good approximation the rate of the reaction is inversely proportional to the concentration of oxygen, and as the gases are purified from oxygen the rate becomes extremely high.

A useful but slightly oversimplified expression for the rate of the photochemical reaction was given by Bodenstein and Unger

$$\frac{d[HCl]}{dt} = \frac{kI[H_2][Cl_2]}{m[Cl_2] + [O_2]([H_2] + n[Cl_2])}$$

where I is the intensity of light absorbed and m and n are constants.

The thermal reaction between hydrogen and chlorine has been investigated extensively and has some complicating features. To a useful approximation the rate may be expressed as

$$\frac{d[HCl]}{dt} = \frac{k'[H_2][Cl_2]^2}{m'[Cl_2] + [O_2]([H_2] + n'[Cl_2])}$$

Recommended Books :-

1. Principles of Physical Chemistry
   By Puri, Sharma, Pathania.

2. Advanced Physical Chemistry
   By Gurdeep Raj

3. Chemical Kinetics, 3rd Edition
   By K. J. Laidler

4. Advanced Physical Chemistry,
   By D. N. Bajpai

5. Essentials of Physical Chemistry
   By Bahl, Bahl, Tuli