

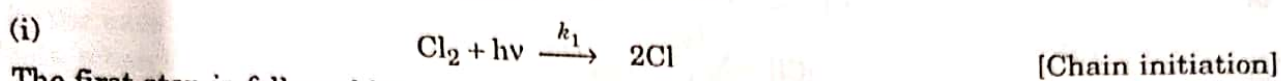
$$\text{Chain length} = k_2 \left(\frac{1}{k_1 k_4} \right)^{1/2} [\text{CH}_3\text{CHO}]^{1/2} \quad \dots (7)$$

and depends on the concentration of reactant.

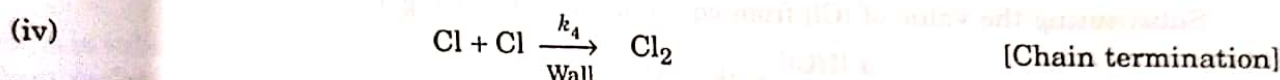
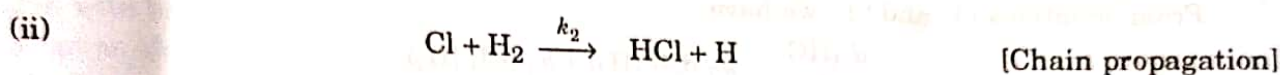
□ REACTION KINETICS OF PHOTOCHEMICAL HYDROGEN-CHLORINE REACTION

An interesting but perplexing photochemical process is afforded by the reaction between H_2 and Cl_2 . It was first observed by Cruickshank (1801) and studied in details by later workers such as Draper (1842), Bunsen and Roscoe (1857), Bodenstein (1916), but Nernst (1918) gave a mechanism for the reaction which is universally accepted.

According to Nernst, when exposed to light in the continuous region of chlorine spectrum ($\lambda = 4785 \text{ \AA}$), chlorine molecules dissociate into atoms as :



The first step is followed by,



In the reaction mechanism of $\text{H}_2 - \text{Cl}_2$ reaction as represented by the above equations, it has been shown that the cycle initiated by formation of chlorine atoms in step (i) is kept going by subsequent steps. The chain may be broken either by the combination of hydrogen and chlorine atoms to form hydrogen and chlorine molecules, respectively or on the walls of the vessel or by the union with some impurity, viz, NH_3 or O_2 which act as inhibitors.

The total rate of formation of hydrogen chloride is given by steps (ii) and (iii), and so

$$\frac{d[\text{HCl}]}{dt} = k_2 [\text{Cl}] [\text{H}_2] + k_3 [\text{H}] [\text{Cl}_2] \quad \dots(1)$$

The rate of formation of chlorine atoms is given by steps (i) and (iii), and so

$$\frac{d[\text{Cl}]}{dt} = k_1 I_{abs} + k_3 [\text{H}] [\text{Cl}_2] \quad \dots(2)$$

where I_{abs} = intensity of radiation.

The rate of removal of chlorine atoms is given by steps (ii) and (iv), and so

$$-\frac{d[\text{Cl}]}{dt} = k_2 [\text{Cl}] [\text{H}_2] + k_4 [\text{Cl}]^2$$

The net rate is given by,

$$\frac{d[\text{Cl}]}{dt} = k_1 I_{abs} + k_3 [\text{H}] [\text{Cl}_2] - k_2 [\text{Cl}] [\text{H}_2] - k_4 [\text{Cl}]^2$$

In the stationary state :

$$\frac{d[\text{Cl}]}{dt} = 0$$

$$\therefore k_1 I_{abs} + k_3 [H] [Cl_2] - k_2 [Cl] [H_2] - k_4 [Cl]^2 = 0$$

$$\text{or } k_1 I_{abs} + k_3 [H] [Cl_2] = k_2 [Cl] [H_2] + k_4 [Cl]^2 \quad \dots(3)$$

Similarly, for hydrogen atoms in the stationary state, we have

$$\frac{d[H]}{dt} = 0 = k_2 [Cl] [H_2] - k_3 [H] [Cl_2]$$

$$\text{or } k_2 [Cl] [H_2] = k_3 [H] [Cl_2] \quad \dots(4)$$

Substituting the value of $k_2 [Cl] [H_2]$ from equation (4) in (3), we get

$$k_1 I_{abs} + k_3 [H] [Cl_2] = k_3 [H] [Cl_2] + k_4 [Cl]^2$$

$$\text{or } k_1 I_{abs} = k_4 [Cl]^2$$

$$\text{or } [Cl] = \sqrt{\frac{k_1}{k_4}} \cdot I_{abs}^{1/2} \quad \dots(5)$$

From equations (1) and (4), we have

$$\frac{d[HCl]}{dt} = k_2 [Cl] [H_2] + k_2 [Cl] [H_2]$$

$$= 2k_2 [Cl] [H_2] \quad \dots(6)$$

Substituting the value of $[Cl]$ from equation (5) in (6), we get

$$\frac{d[HCl]}{dt} = 2k_2 \cdot \sqrt{\frac{k_1}{k_4}} \cdot I_{abs}^{1/2} [H_2] \quad \dots(7)$$

Expression (7) is in perfect agreement with the experimental data.

The chain length is given by the expression,

$$\text{Chain length} = \frac{\text{Rate of the overall reaction}}{\text{Rate of the initiation reaction}}$$

$$= \frac{2k_2 \sqrt{\frac{k_1}{k_4}} \cdot I_{abs}^{1/2} [H_2]}{k_1 I_{abs}} = \frac{2k_2 [H_2]}{\sqrt{k_1 k_4} \cdot I_{abs}^{1/2}}$$

In presence of high chlorine content, step (iv) is replaced by rather complicated steps, viz.,



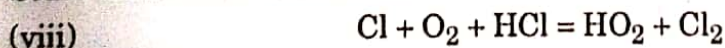
From steps (v) and (vi) the rate expression as given by (7) becomes very complex.

In presence of oxygen as impurity, steps (i), (ii) and (iii) are followed by



which is a chain terminating step.

Some chains are terminated as :



In presence of oxygen, it is assumed that removal of hydrogen atoms determines the kinetics of the reaction to a great extent, but in the absence of oxygen, the chains are supposed to be broken by the removal of chlorine atoms.

From steps (i), (ii), (iii) and (iv), we get

$$\frac{d[\text{HCl}]}{dt} = \frac{k_1 \cdot I_{\text{abs}} [\text{Cl}_2]}{[\text{O}_2]} \quad \dots(8)$$

The rate of reaction in presence of oxygen is directly proportional to the intensity of light radiation. But the inhibiting action of oxygen is approximately proportional to its own concentration as given by equation (8).

□ KINETICS OF HOMOGENEOUS CATALYSIS

Many homogeneous catalysed reactions have been studied in the liquid phase as well as gas phase. The reaction rates in such catalysed reactions are found to be proportional to the concentration of the catalyst.

In the case of a catalyst forming an intermediate compound with the reactant, we get the products, when this intermediate compound either gets decomposed or reacts with the remaining reactants. The reactant with which the catalyst combines is known as **substrate**. The catalyst provides, with lesser energy of activation, an alternative path for the reaction in which the rate is dependent on the concentration of the catalyst. Therefore,



where, A is substrate, X is catalyst, P is product and AX is the intermediate compound B is another reactant molecule. The reaction (ii) is slow and is the rate determining step.

$$\therefore \quad \text{Rate of reaction} = k_3 [AX] [B] \quad \dots (1)$$

If we use the steady state concept for the intermediate compound AX, then

$$\frac{d[AX]}{dt} = k_1 [A] [X] - k_2 [AX] - k_3 [AX] [B] = 0$$

$$\text{or} \quad k_1 [A] [X] = k_2 [AX] + k_3 [AX] [B]$$

$$\text{or} \quad [AX] = \frac{k_1 [A] [X]}{k_2 + k_3 [B]}$$

Substituting this value of [AX] in equation (1), we get

$$\text{Rate of reaction} = \frac{k_1 k_3 [A] [X] [B]}{k_2 + k_3 [B]} \quad \dots (2)$$

From equation (2), two cases may arise :

(i) If $k_2 \ll k_3 [B]$, then equation (2) becomes

$$\text{Rate of reaction} = \frac{k_1 k_3 [A] [X] [B]}{k_3 [B]} = k_1 [A] [X] \quad \dots (3)$$

(ii) If $k_2 \gg k_3 [B]$, then equation (2) becomes

$$\text{Rate of reaction} = k_1 k_3 \frac{[A] [X] [B]}{k_2} \quad \dots (4)$$

From equations (3) and (4), it follows that the rate of reactions depends on the concentration of catalyst, although it is neither consumed nor produced in the reaction.