5.1.5 H_2 and Cl_2 Reaction

The quantum yield of H_2-Cl_2 combination is exceptionally high; it varies with the experimental conditions but is found to be between 10^4 and 10^6 in absence of O_2 with light of wavelength 4800 Å. The process occurs in the range 5460 to 4800 Å with an apparently lower efficiency because only a small proportion of light absorbed is capable of dissociating Cl_2 molecule. The mechanism can be proposed as

$$Cl_2 + h\nu \xrightarrow{k_1} 2Cl \qquad 1^{st} \text{ stage} \qquad \text{(i)}$$

$$\left.\begin{array}{l} Cl + H_2 \xrightarrow{k_2} HCl + H \\ H + Cl_2 \xrightarrow{k_3} HCl + Cl \end{array}\right] \text{chain reaction} \qquad \text{(ii, iii)}$$

$$Cl + \text{Wall} \xrightarrow{k_3} 1/2Cl_2 \qquad \text{termination} \qquad \text{(iv)}$$

Reaction (ii) between chlorine atom and hydrogen molecule is very rapid, since it is an exothermic process and has low energy of activation whereas corresponding reaction with bromine atom is very slow at ordinary temperature.

Applying the steady state treatment with respect to chlorine atom, we can get

$$k_1 I_{abs} + k_3[H][Cl_2] = k_2[Cl][H_2] + k_4\,[Cl] \qquad \text{(a)}$$

assuming that reaction (iv) is a first order reaction. Similarly, considering steady-state treatment with respect to hydrogen atom, we get

$$k_2[Cl][H_2] = k_3[H][Cl_2] \qquad \text{(b)}$$

Hence, from (a) and (b)

$$k_1 I_{abs} = k_4[Cl]$$

or

$$[Cl] = (k_1/k_4)\, I_{abs} \qquad \text{(c)}$$

The rate of formation of HCl is given as

$$\frac{d[HCl]}{dt} = k_2\,[Cl][H_2] + k_3\,[H][Cl_2]$$

$$= 2k_2[Cl][H_2] \text{ (from equation (b))}$$

Substituting the value of [Cl] from equation (c), we get

$$\boxed{\frac{d[HCl]}{dt} = \frac{2k_1 k_2}{k_4}\, I_{abs}\,[H_2]} \qquad (5.6)$$