Determination of Equilibrium Constant

$$AB_n \rightleftharpoons A + nB$$

A wavelength is chosen where only the complex absorbs appreciable. Therefore,

$$A = \{l \cdot \varepsilon(AB_n)\}[AB_n]$$

The value of the expression within the bracket can be determined by taking a known concentration of A (say, c) to which a very large excess of B is added so that the equilibrium is shifted to left and thus

$$[AB_n] \simeq [A]$$

For the above solution, A_{max} is determined experimentally and thus, we have

$$\{l \cdot \varepsilon(AB_n)\} = \frac{A_{max}}{c}$$

*Physical Chemistry by KL Kapoor (Vol. 5)

Now the absorbance of a solution containing, respectively, the concentrations c and nc of A and B, is determined. Let it be represented by A_s. At these concentrations, the concentrations of various species at equilibrium are

$$[A] = \alpha c$$
$$[B] = n\alpha c$$
$$[AB_n] = (1 - \alpha)\, c$$

Thus $\quad A_s = \{l \cdot \varepsilon(AB_n)\}(1 - \alpha)\, c = \dfrac{A_{max}}{c}\,(1 - \alpha)\, c = A_{max}\,(1 - \alpha)$

Hence, $\quad \alpha = \dfrac{A_{max} - A_s}{A_{max}}$

Knowing α, K_c can be determined from the expression

$$K_c = \frac{[A][B]^n}{[AB_n]} = \frac{(\alpha c)(n\alpha c)^n}{(1 - \alpha)c}$$

Quantum Yield

$$\Phi(\lambda) = \frac{\text{amount of reactant consumed or product formed}}{\text{number of photons absorbed}}$$

$$= \frac{\text{amount of reactant consumed or product formed per unit time}}{\text{amount of radiation absorbed per unit time}}$$

$$= \frac{-\mathrm{d[R]/dt}}{\mathrm{I_{abs}}}$$

- Always 1 for primary processes (law of photochemical equivalence)
- Overall quantum yield can be greater than or less than 1, depending on the nature of secondary processes.

Low Quantum Yield ($\phi < 1$): When the number of molecules decomposed is less than one per photon.

High Quantum Yield ($\phi > 1$): When two or more molecules are decomposed per photon.

Reasons for low quantum yield:

1. The excited molecule is deactivated through fluorescence or phosphorescence.
2. The excited molecule is deactivated by converting its energy into the kinetic energy of other molecules (heating effects are produced).
3. The secondary process may involve a step which produces the reactant molecule as one of the products.
4. The energy absorbed might not be sufficient to cause any fruitful excitation of the molecule.

Reason for high quantum yield:

Atoms or radicals generated in the primary process may initiate chain reactions.

*Physical Chemistry by KL Kapoor (Vol. 5)

Reaction	Quantum Yield
$H_2 + Cl_2 \rightarrow 2HCl$	up to 10^6
$H_2 + Br_2 \rightarrow 2HBr$	0.01

Why?

Kinetics of Photochemical Reactions

1. Mechanism of photochemical decomposition of HI

$$HI \xrightarrow{h\nu} H + I$$

$$H + HI \xrightarrow{k_2} H_2 + I$$

$$I + I \xrightarrow{k_3} I_2$$

*Physical Chemistry by KL Kapoor (Vol. 5)

The rate of disappearance of HI

$$-\frac{d[HI]}{dt} = I_{abs} + k_2 [\dot{H}] [HI] \tag{1}$$

Applying the steady-state approximation to hydrogen atoms, we get

$$\frac{d[H]}{dt} = 0 = I_{abs} - k_2 [H] [HI]$$

Hence, $\quad k_2 [H] [HI] = I_{abs}$ **(2)**

Substituting Eq. (2) in Eq. (1),

$$-\frac{d[HI]}{dt} = 2I_{abs} \tag{3}$$

The quantum efficiency is

$$\Phi = \frac{\text{Rate of disappearance of HI}}{\text{Rate at which light is absorbed}} = \frac{-d[HI]/dt}{I_{abs}}$$

$$= \frac{2I_{abs}}{I_{abs}} = 2$$

Quantum efficiency decreases as the reaction proceeds due to accumulation of iodine and hence the following thermal reaction which becomes appreciable:

$$H + I_2 \xrightarrow{k_4} HI + I$$

The steady state approximation as applied to H atom,

$$\frac{d[H]}{dt} = 0 = I_{abs} - k_2 [H][HI] - k_4 [H][I_2]$$

Hence, $$[H] = \frac{I_{abs}}{k_2[HI] + k_4[I_2]}$$

Substituting this in the expression

$$-\frac{d[HI]}{dt} = I_{abs} + k_2[H][HI] - k_4[H][I_2]$$

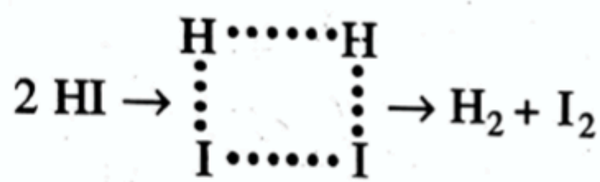
we get $$-\frac{d[HI]}{dt} = I_{abs} + (k_2[HI] - k_4[I_2]) \frac{I_{abs}}{k_2[HI] + k_4[I_2]}$$

or $$-\frac{d[HI]}{dt} = I_{abs}\left(\frac{2}{1 + \{k_4[I_2]/k_2[HI]}\right)$$

$$\Phi = \frac{2}{1 + \{k_4\,[I_2]/k_2[HI]}$$

As the concentration of I_2 increases and that of HI decreases, quantum yield decreases from its original value of 2.

Mechanism of thermal decomposition of HI:



Rate law,

$$-\frac{1}{2}\,\frac{d[HI]}{dt} = k\,[HI]^2$$

2. Mechanism of photochemical reaction between H_2 and Br_2

$$Br_2 \xrightarrow{h\nu} 2Br$$

$$Br + H_2 \xrightarrow{k_2} HBr + H$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br$$

$$H + HBr \xrightarrow{k_4} H_2 + Br$$

$$Br + Br \xrightarrow{k_5} Br_2$$

1. **Determine the expression for quantum yield of the reaction.**
2. **Prove that the rate formation of HBr is twice the rate of decomposition of Br_2**