- **Quantum yield:** To relate the number of photons (quanta) absorbed with the number of reacting molecules, a term called quantum efficiency or quantum yield $(\emptyset)$ has been introduced. It is expressed as –

$$\emptyset = \frac{Number\ of\ molecules\ reacting\ in\ a\ given\ time}{Number\ of\ quanta\ of\ light\ absorbed\ in\ same\ time}$$

$$= \frac{Number\ of\ molecules\ reacting\ in\ a\ given\ time}{Number\ of\ Einsteins\ of\ light\ absorbed\ in\ same\ time}$$

Hence quantum efficiency may be defined as the number of moles reacting per Einstein of the light absorbed.

- **State Stark – Einstein law of photochemical equivalence**: This law states that every atom or molecule that takes part in a photochemical reaction absorbs one quantum of the radiation to which the substance is exposed.

If υ is the frequency of the absorbed radiation, then the energy absorbed by each reacting atom or molecule is one quantum i.e. hυ where h is Planck's constant. The energy absorbed by one mole of the reacting molecules will be given by –

$$E = N_A hv = \frac{N_A hc}{\lambda(A^0)}$$

$$= \frac{(6.023 \times 10^{23} mol.^{-1})(6.626 \times 10^{-27} erg.\text{sec.})(3 \times 10^{10} cm.sec^{-1})}{(\lambda \times 10^{-8} cm.)}$$

$$= \left(\frac{1.197 \times 10^{16} erg.mol.^{-1}}{\lambda}\right)$$

We know quantum yield,

$$(\emptyset) = \frac{number\ of\ molecules\ reacting\ in\ a\ given\ time}{number\ of\ quanta\ of\ light\ absorbed\ in\ same\ time}$$

So, if Stark – Einstein law is strictly obeyed, $\emptyset$ should be equal to one. However, the law is applicable only to primary processes.

For eg., <u>decomposition of HI</u>:

(i) Primary process: One HI molecule absorbs a photon & dissociated to produce H & I.

$$HI \quad \rightarrow \quad H + I$$

So the primary reaction shows that one HI is composed for one photon, thus –

$$\emptyset = \frac{1}{1} = 1$$

(ii) Secondary process:

$$H + HI \rightarrow H_2 + I$$
$$I + I \rightarrow I_2$$
$$Overall\ reaction: 2HI \quad \rightarrow \quad H_2 + I_2$$

So, the overall reaction shows that the two HI are decomposed for one photon, so –

$$\emptyset = \frac{2}{1} = 2, i.e. \emptyset > 1.$$

Similarly for dimerization of anthracene,

$$2C_{14}H_{10} + hv \rightarrow C_{28}H_{20}$$

Thus quantum yield is 2 but actually it is found to be 0.5 for overall reaction because the above reaction is reversible –

$$C_{28}H_{20} \rightarrow 2C_{14}H_{10}\ (A_2 \rightarrow 2A)$$

But for primary process $A + hv \rightarrow A^*, \emptyset = 1$.
Hence Stark – Einstein's law is applicable for primary process where $\emptyset = 1$ always but for overall process $\emptyset$ may be greater than or less than one. So, the above statement does not violate the Stark – Einstein's law.

- **Grotthus – Draper principle**: When light falls on a body, a part of it is reflected, a part of it is transmitted & the rest of it is absorbed. It is only the absorbed light which is effective in bringing about a chemical reaction.
  However, the law does not imply that the absorbed light must always result into chemical reaction. The absorbed light may simply bring about phenomena such as fluorescence, phosphorescence etc. Similarly, the absorbed light energy may be simply converted into thermal energy, for eg. In case of $KMnO_4$ solution, the light energy is absorbed strongly but no chemical effect is produced. In some cases it is observed that light energy may not be absorbed by the reacting species directly but may be absorbed by some other substance present along with reacting substance which is known as photosensitization.
- **One Einstein**: The energy of one mole of photon is called one Einstein, i.e.

$$One\ Einstein\ (E) = E = N_A hv = \frac{N_A hc}{\lambda(A^0)}$$

$$= \frac{(6.023 \times 10^{23} mol.^{-1})(6.626 \times 10^{-27} erg.\text{sec.})(3 \times 10^{10} cm.sec^{-1})}{(\lambda \times 10^{-8} cm.)}$$

$$= \left(\frac{1.197 \times 10^{16} erg.mol.^{-1}}{\lambda}\right)$$

$$= \left(\frac{1.197 \times 10^{9} Joule.mol.^{-1}}{\lambda}\right)$$

$$= \left(\frac{1.197 \times 10^{9} Cal.mol.^{-1}}{4.18 \times \lambda}\right)$$

$$here\ \lambda\ is\ wave - length\ in\ A^0.$$

- **Photo-stationary state**: Absorption of radiation by reactants of a reaction at equilibrium increases the rate of forward reaction without directly affecting the rate of the reverse reaction. But the rate of the reverse reaction is increased due to the increase in the concentration of products. Thus a new state is reached when the increase in the rate of forward reaction due to the absorption of light (photochemical) becomes equal to the increase in the rate of reverse reaction due to the enhanced concentration of the products (thermal). This new state is called photo-stationary state & it is also known as photochemical equilibrium.

  For eg. Dimerization of anthracene.
- **Steady state or equilibrium state**: Photo-stationary state will have a composition different from that of the equilibrium state, because removal of the system from the surroundings (the radiation beam) will alter the properties of the system. In comparison the removal of the system from its surroundings causes no change in the properties of a system in equilibrium. Hence, photo-stationary state is a steady state not an equilibrium state.
- **Photosensitized reaction**: There are many substances which do not react directly when exposed to light. However, if another substance is added, the photochemical reaction starts. The substance thus added itself does not undergo any chemical change. It merely absorbs the light & then passes it on to one of the reactants.

  Such as substance which when added to a reaction mixture helps to start the photochemical reaction but itself does not undergo any chemical change is called photo-sensitizer & the process is called photosensitization. Thus a photo-sensitizer simply acts as a carrier of energy.

  Example: Photosynthesis is an example of photosensitized reaction.

  $$6CO_2 + 6H_2O \rightleftharpoons C_6H_{12}O_6 + 6O_2$$

  In this case neither CO_2 nor H_2O can absorb visible radiation. Initially radiation is absorbed by chlorophyll which acts as a photo-sensitizer.

- **Photo – inhibitors**: Presence of certain substances considerably reduces the quantum yield of some photochemical reaction; such substances are known as photo – inhibitors.

  For eg, in the photosynthesis of HCl, the presence of traces amount of oxygen, reduce the quantum yield of this reaction.