Laws of Photochemistry

First law of photochemistry, known as Grotthus-Draper law:-

Only that light which is absorbed by a system can cause chemical change.

The probability or rate of absorption is given by the Lambert - Beer law.

The Lambert law states that the fraction of incident radiation absorbed by transparent medium is independent of the intensity of incident radiation, and that each successive layer of the medium absorbs an equal fraction of incident radiation.

Beer law states that the amount of radiation absorbed is proportional to the number of molecules absorbing the radiation, that is the concentration c of the absorbing species.

The two laws can be combined as

$$-\frac{dI}{I} = \alpha_v \, c\, dl \quad \text{—} (1)$$

α_v → proportionality constant

$c\,dl$ → measures the amount of solute per unit area of layer, dl being thickness of the layer, dl being thickness of the layer.

$$C = \frac{\text{mole}}{\text{volume}} = \frac{\text{mole}}{\text{area} \times \text{thickness}}$$

Therefore, $$C\,dl = \frac{\text{mole}}{\text{area}}$$

On integrating equation within the boundary conditions, we get

$I = I_0$

when $l = 0$

and $I = I$

and $l = l$

we have, $$\ln \frac{I_0}{I} = \alpha_\nu C l$$

$\alpha_\nu \rightarrow$ absorption coefficient, is a function of frequency or wave-length of radiation. The final form is expressed in the ~~deda~~ decadic logarithm.

$$\log \frac{I_0}{I} = \epsilon_\nu C l$$

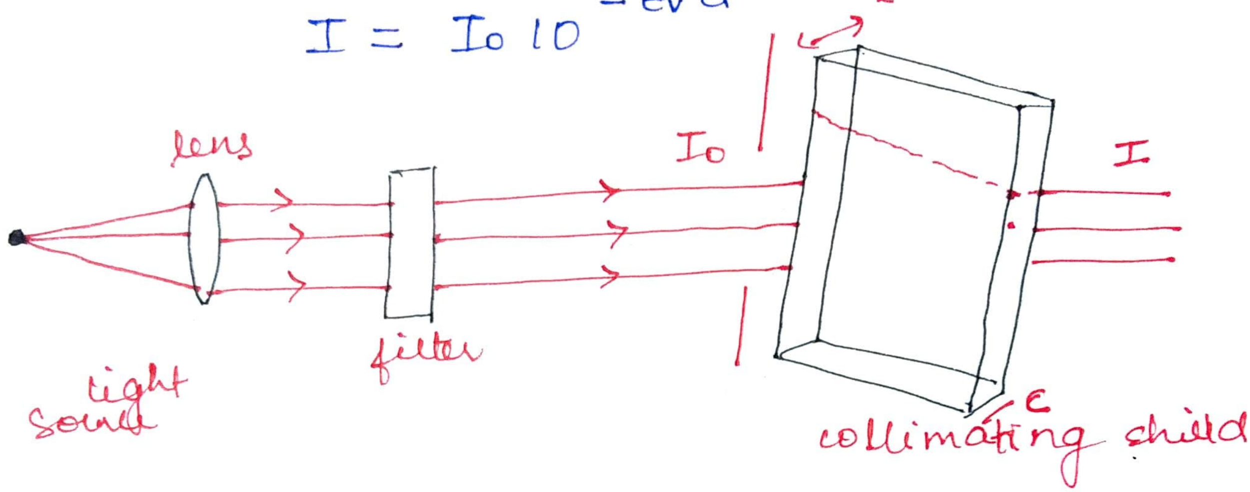
where $\epsilon_\nu = \frac{\alpha_\nu}{2.303}$ called molar extinction coefficient and is a function of frequency ν, the concentration is expressed in moles per litre and l is the optical path length in cm.

The SI unit of c, l and ϵ are $mol\,dm^{-3}$, m and $m^2\,mol^{-1}$ respectively.

I_0 and I are incident and transmitted intensity. The quantity $\log I/I_0$ is commonly known as the optical density OD or absorbance A.

Plot of ϵ_v (or its logarithm) vs wavelength or wave number gives rise to familiar absorption bands.

$$I = I_0 10^{-\epsilon_v c l}$$



The amount of light absorbed I_a

$$I_a = I_0 - I = I_0 - I_0 10^{-\epsilon_v c l}$$
$$= I_0 (1 - 10^{-\epsilon_v c l})$$

Second law of photochemistry :-

One quantum of light is absorbed ~~by~~ per molecule of absorbing and reacting substances that disappear.

Molecules which absorb photons become physically excited and this is much different from being chemically active.

Quantum efficiency (ϕ) which measures the efficiency of a photochemical reaction, is given by

$$\phi_{reaction} = \frac{\text{number of molecules decomposed or formed}}{\text{number of quanta absorbed}}$$

This term was introduced by Einstein.

→ when high intensity light sources as from flash lamps or lasers are used 'biphotonic' photochemical effects may occur which modify the application of Einstein law.

→ At high intensity, a molecule may absorb two photons simultaneously; a more common effect.

The concept of quantum yield can be extended to any act, physical or chemical, following light absorption.

$$\phi_{process} = \frac{\text{number of molecules undergoing that process}}{\text{number of quanta absorbed}}$$

$$= \frac{\text{rate of process}}{\text{rate of absorption}}$$