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(1) (b) ~~Designation of Bonds :-~~

Photochemistry ; T.D.C. Part III

The Absorption laws : Two laws

(i) Lambert's law (ii) Beer's law.

Lambert's law :- When a beam of monochromatic light (radiation) passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is directly proportional to the intensity of the incident radiation.

Mathematically, $$-\frac{dI}{dx} = KI$$

Where, I = Intensity of radiation after passing through a thickness, x, of the medium

dI = Infinitesimally small decrease in the intensity of radiation on passing through infinitesimally small thickness, dx of the medium.

$-\frac{dI}{dx}$ = rate of decrease of intensity of radiation with thickness of the absorbing medium,

K = Proportionality constant or absorption coefficient. Its value depends upon nature of absorbing medium

Let,

I_0 = Intensity of radiation before ~~entering~~ entering the absorbing medium ($x = 0$) & ~~then~~

Then, I, the intensity of radiation after passing through any thickness, say x of the medium calculated as:

$$\int_{I_0}^{I} \frac{dI}{I} = -\int_{x=0}^{x=x} K\,dx$$

or $\ln \frac{I}{I_0} = -Kx$ or $\frac{I}{I_0} = e^{-Kx}$

$$\therefore I = I_0 \cdot e^{-Kx}$$

The intensity of radiation absorbed, $I_{abs.}$ is given by

$$I_{abs.} = I_0 - I = I_0 - I_0 e^{-Kx} = I_0(1 - e^{-Kx})$$

$$I_{abs.} = I_0(1 - e^{-Kx})$$

The above Lambert's law equation can also be written by changing the natural logarithm ~~to~~ the base 10.

$$I = I_0 10^{-ax}$$

Where $a = \frac{K}{2.303}$ = extinction coefficient of the absorbing medium.

Beer's law :- When a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of absorbing solution is proportional to the intensity of incident radiation as well as concentration of the solution.

Mathematically,

$$-\frac{dI}{dx} = K'.IC$$

Where c = concentration of the solution in mol l⁻¹

K' = molar absorption coefficient and its value depends upon the nature of the absorbing substance.

Suppose I_0 be the intensity of radiation before entering the absorbing solution (when x = a), then the intensity of radiation, I after passing through the thickness x, of the medium can be calculated —

$$\int_{I_0}^{I} \frac{dI}{I} = -\int_{x=a}^{x=x} K'c\,dx$$

7) Photochemistry T.D.C. Part III

Vijay Kumar

Chemistry

$$\ln \frac{I}{I_0} = -k'cx \quad \text{or} \quad \frac{I}{I_0} = e^{-k'cx}$$

$$\boxed{I = I_0 e^{-k'cx}}$$

or

$$I = I_0 e^{-k'cx}$$

or

$$I = I_0 10^{-a'cx}$$

where $a' = \frac{k'}{2.303}$ = molar extinction coeff of the absorbing solut