

• LAMBERT'S LAW:

'When a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of incident radiation.'

$$-\frac{dI}{dx} = kI$$

I = intensity of radiation after passing through thickness x , of medium.

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

k = absorption coefficient.

Let I_0 be intensity of radiation before entering the absorbing medium ($x=0$), and I be intensity of radiation after passing through thickness, x of medium.

$$-\frac{dI}{dx} = kI \Rightarrow \frac{dI}{I} = -k dx$$

$$\int_{I_0}^I \frac{dI}{I} = - \int_{x=0}^x k dx \Rightarrow \ln \frac{I}{I_0} = -kx \Rightarrow \frac{I}{I_0} = e^{-kx}$$

$$I = I_0 e^{-kx} \quad \text{--- (1)} \Rightarrow I = I_0 10^{-\frac{kx}{2.303}} \quad \left[\because \frac{k}{2.303} \right]$$

Intensity of radiation absorbed,

$$I_{abs} = I_0 - I = I_0 - I_0 e^{-kx} \quad (\text{By eqn (1)}) \\ = I_0 (1 - e^{-kx})$$

• BEER'S LAW:

"When a beam of monochromatic radiation is passed through a solⁿ of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solⁿ is proportional to the intensity of incident radiation as well as the concentration of the solⁿ."

$$-\frac{dI}{dx} = k' Ic$$

where c = conc. of solⁿ (moles/l)

k' = molar absorption coefficient
(depends upon nature of absorbing surface)

$$\int_{I_0}^I \frac{dI}{I} = - \int_{x=0}^{x=x} k' c dx$$

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

By changing the logarithm to base 10, $I = I_0 \cdot 10^{-a'cx}$

$$\frac{k'}{2.303} = a', \quad a' = \text{molar extinction coefficient of absorbing sol}^n$$

Beer's law can also be stated as:

When a monochromatic light is passed through a solⁿ of an absorbing substance, its absorption remain constant when the conc (c) and the thickness of the absorption layer (τ) are changed in the inverse ratio.

On combining the two laws, **Beer-Lambert Law**:

$$\log \frac{I_0}{I} = E.C.l = A$$

where,

I_0 = intensity of incident light

I = intensity of transmitted light

C = conc. of solⁿ (moles/l)

l = path length of the sample (usually cm)

E = molar absorptivity / molar extinction coefficient
($L/mol \cdot cm$)

A = Absorbance

Limitations of Beer Lambert Law - This law is not obeyed.

- i) In keto-enol tautomers
- ii) in fluorescent compounds
- iii) when solute and solvent form complexes.