Lambert Beer's Law

This is an extension of Lambert's law put forward by Beer, so it is called Lambert Beer's law.

This law states that, *"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 the absorbing solution is proportional to the intensity of the incident* **as well as to the concentration of the solution."**

This law can be expressed mathematically as :

$$-\frac{dI}{dx} \propto cI$$

c = conc. of the solution in moles/litre

I = Intensity of the radiation

$$-\frac{dI}{dx} = K'cI,$$ where K′ is molar-absorption coefficient. Its value depends on the nature of absorbing solute and wavelength of light.

$$-\frac{dI}{I} = K'cdx$$

If I_0 is the intensity of the radiation before entering the absorbing solution *i.e.* when thickness of the medium $x = 0$, then the intensity of radiation, I_t after passing through the thickness x of the radiation can be calculated.

$$\int_{I_0}^{I_t} \frac{dI}{I} = -\int_{x=0}^{x=x} K'cdx$$

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$$\ln \frac{I_t}{I_0} = -K'cx$$

$$2.303 \log \frac{I_t}{I_0} = -K'cx$$

$$\log \frac{I_t}{I_0} = -\frac{K'}{2.303} cx$$

$$\frac{K'}{2.303} = a' \text{ or } \varepsilon$$

a' also be represented by ε *i.e.* Molar extinction coefficient of the absorbing medium.

$$\log \frac{I_t}{I_0} = -\varepsilon cx$$

$$\frac{I_t}{I_0} = 10^{-\varepsilon cx}$$

$$\boxed{I_t = I_0 10^{-\varepsilon cx}}$$

As $$\log \frac{I_t}{I_0} = -\varepsilon cx$$

$$\log \frac{I_0}{I_t} = \varepsilon cx$$

As $$\log \frac{I_0}{I_t} = A \quad \text{so} \quad \boxed{\varepsilon cx = A}$$

Or $$A = -\log \frac{I_t}{I_0}$$

$$= -\log T$$

$$A = -\log T$$

$$\boxed{A = \varepsilon cx = -\log T}$$

$$\boxed{\varepsilon = \frac{A}{cx}}$$

In SI units, c is expressed in mol m^{-3} and thickness in m, then units of molar absorption coefficient are m^2 mol^{-1}. Usually c is expressed in mol L^{-1} and x in cm, then molar absorption coefficient is expressed as L mol^{-1} cm^{-1} or M^{-1} cm^{-1}, where M is molarity.

Numericals on Absorption Laws

1. When an incident beam of wavelength 3000 Å was allowed to pass through 2 mm thick pyrex glass, the intensity of the radiation was reduced to one-tenth of its initial value. What part of the same radiation will be absorbed by 1 mm thick glass.

Solution. As
$$I_t = \frac{1}{10} \times I_0$$

$$\frac{I_t}{I_0} = \frac{1}{10} \qquad x = 2 \text{ mm} = 0.2 \text{ cm}$$

Applying Lambert's law,

$$\log \frac{I_t}{I_0} = -ax$$

$$\log \frac{1}{10} = -a\,(0.2)$$

$$a = \frac{1}{0.2} = 5$$

In the second case, $x = 1 \text{ mm} = 0.1 \text{ cm}$

as $a = 5$ applying Lambert's Law,

$$\log \frac{I_t}{I_0} = -a'x$$

$$\frac{I_t}{I_0} = \text{antilog}\,(-0.5) = 0.3162$$

$$I_t = 0.3162\, I_0$$
$$I_{abs} = I_0 - I_t$$
$$I_{abs} = I_0 - 0.3162\, I_0$$
$$= 0.6838\, I_0 = 68.38\% \text{ of the incident light}$$

2. Calculate the transmittance, absorbance and molar extinction coefficient of a solution which absorbs 90% of an incident radiation of a certain wavelength of light beam passed through a 1 cm cell containing 0.25 M solution.

Solution. 90% of incident radiation is absorbed *i.e.* $I_{abs} = 0.9\, I_0$

i.e.
$$I_{abs} = 0.9\, I_0$$
$$I_{abs} = I_0 - I_t$$
$$I_t = I_0 - I_{abs}$$
$$I_t = I_0 - 0.9\, I_0$$
$$I_t = 0.10\, I_0$$

$$\frac{I_t}{I_0} = 0.10$$

$$\therefore A = -\log(T) = -\log(0.1)$$

$$\log \frac{1}{0.1} = 1, \text{ so } A = 1$$

Applying Beer's law, we have

$$\log \frac{I}{I_0} = -\varepsilon cx$$

$$\log 0.10 = -\varepsilon \times 0.25 \times 1$$

$$-1 = -\varepsilon \times 0.25$$

$$\varepsilon = 4.0 \text{ L mol}^{-1} \text{ cm}^{-1}$$

Or

$$A = \varepsilon cx \qquad \varepsilon = \frac{A}{cx} = \frac{1}{0.25 \times 1} = 4 \text{ L mol}^{-1} \text{ cm}^{-1}$$

3. A substance when dissolved in water at 10^{-3} M concentration absorbs 10 percent of an incident radiation in a path of 1 cm length. What should be the concentration of the solution in order to absorb 90 per cent of the same radiation.

Ans. $c = 10^{-3}$

$$I_{abs} = \frac{10}{100} I_0$$

$$x = 1 \text{ cm}$$

$$I_{abs} = I_0 - I_t$$

$$I_o - I_t = \frac{1}{10} I_0$$

$$I_0 - \frac{1}{10} I_0 = I_t$$

$$0.9 = \frac{I_t}{I_0}$$

$$A = t c x$$

$$A = -\log T$$

$$A = -\log(0.9)$$

$$A = 0.045$$

$$\varepsilon \times 10^{-3} \times 1 = 0.045$$

$$\varepsilon = \frac{0.45}{10^{-3}} = 10^3 \times 0.45$$

Now $c = ?$

$$I_{abs} = \frac{90}{100} I_0$$

$$I_0 - I_t = \frac{9}{10} I_0$$

$$\frac{1}{10} I_0 = I_t$$

$$\frac{I_t}{I_0} = \frac{1}{10}$$

$$A = -\log T$$

$$A = -\log\left(\frac{1}{10}\right)$$

$$A = \log 10 = 1$$

$$A = \varepsilon c x$$

$$1 = 10^3 \times 0.45 \times 1 \times c$$

$$c = \frac{1}{0.45 \times 10^3} = \frac{1}{450}$$

$$= 0.0022 \text{ M} \quad \textbf{Ans.}$$

4. A solution shows a transmittance of 20% when taken in a cell of 2.5 m thickness. Calculate its concentration if molar absorption coefficient is 12,000 $dm^3\ mol^{-1}\ cm^{-1}$.

Solution.

$$T = 20\% = \frac{20}{100} = 0.2$$

$$A = -\log T, A = -\log (0.2)$$

$$A = \frac{20}{100}; c = \frac{A}{\varepsilon x}, x = 2.5 \text{ m} = 250 \text{ cm}$$

$$c = \frac{-\log 0.2}{12000\ dm^3\ mol^{-1}\ cm^{-1} \times 250\ cm}$$

$$= \frac{0.699}{12000 \times 250}$$

$$c = 2.33 \times 10^{-7} \text{ M}$$

6.9 EXPERIMENTAL TECHNIQUE

Absorption and emission spectroscopy gives the same information about the sample. But generally absorption spectroscopy is used as it is easy to interpret or read than emission spectroscopy. Hence absorption spectroscopy will be discussed.