

**3. Chemical Reactions.** The activated molecule may also lose energy by undergoing chemical reaction. Since the molecule in singlet excited state returns quickly to the ground state, it gets no chance to react chemically. The molecule in a triplet excited state, however, returns to the ground state comparatively slowly, as explained above. This provides ample opportunity to the activated molecule to undergo chemical reaction. Thus, *the molecule which undergoes chemical reaction is the one which is previously in a triplet excited state.*

### Light Absorption by Solutions

The absorption of light in the visible and near ultraviolet regions by a solution is governed by a photophysical law, known as the Beer-Lambert law.

**The Beer-Lambert Law.** When a beam of monochromatic radiation of a suitable frequency passes through a solution, it is absorbed by the solution. As a result, the intensity of the light when it finally emerges from the solution, is considerably reduced. If  $I_0$  is the intensity of the incident beam and  $I_t$  is the intensity of the transmitted beam, then the intensity of the light absorbed,  $I_a$ , is given by

$$I_a = I_0 - I_t \quad \dots(1)$$

The intensity of the beam is defined as the energy falling on unit area perpendicular to the beam per unit time. It is proportional to the number of photons incident on unit area in unit time.

The probability that the photons of a beam of intensity  $I$  will be absorbed by the sample is directly proportional to the concentration and the thickness of the absorbing solution. Mathematically, we express it by writing

$$dI/I = -\alpha c dx \quad \dots(2)$$

where  $dI$  is the change in intensity produced by the absorption of radiation on passing through a thickness  $dx$  of the solution of concentration  $c$  and  $\alpha$  is the proportionality constant. The minus sign is introduced because there is reduction in intensity. Integration of Eq. 2 between the limits  $I=I_0$  at  $x=0$  and  $I=I$  at  $x=b$  gives

$$\int_{I_0}^I \frac{dI}{I} = -\alpha c \int_0^b dx \quad \dots(3)$$

or

$$\ln(I/I_0) = 2.303 \log(I/I_0) = -\alpha bc \quad \dots(4)$$

According to Eq. 4, *the intensity of a beam of monochromatic radiation decreases exponentially with increase in the thickness  $x$  and the concentration  $c$  of the absorbing medium.* This is **Beer-Lambert law.**

Putting  $\alpha/2.303 = \epsilon$  and defining  $\log(I_0/I)$  as the **absorbance,  $A$** , of the solution, we get

$$A = \log(I_0/I) = \epsilon bc \quad \dots(5)$$

In Eq. 5,  $\epsilon$  is called the absorption coefficient or extinction coefficient of the absorbing medium. It is characteristic of the solute and depends upon the nature of the solvent, temperature and the wave length of the radiation employed. If the concentration  $c$  is expressed in  $\text{mol dm}^{-3}$  and the path length  $b$  in cm, then  $\epsilon$  (expressed as  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) is referred to as **molar absorption coefficient** (formerly, and still widely, called the **molar extinction coefficient**).

The **transmittance,  $T$** , is defined as

$$T = I/I_0 \quad \dots(6)$$

Evidently, absorbance  $A$  and transmittance  $T$  are related as

$$A = -\log T$$

or

$$T = 10^{-A} = 10^{-\epsilon bc} \quad \dots(7)$$

The plots of  $T$  and  $A$  versus  $c$  are shown in Fig. 3. As can be seen, the plot of  $A$  versus  $c$  is a straight line passing through the origin. Hence,

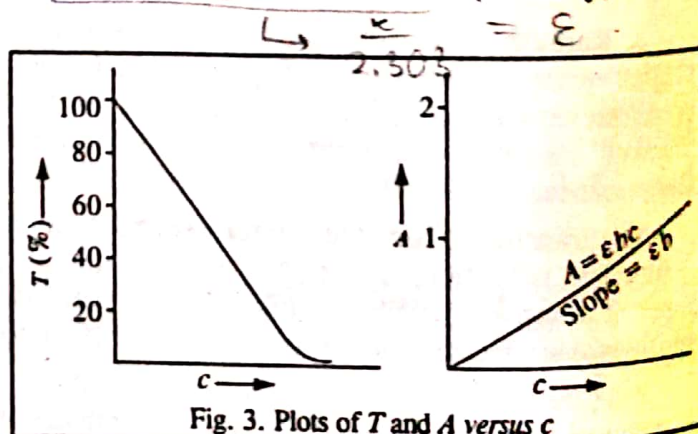


Fig. 3. Plots of  $T$  and  $A$  versus  $c$



this plot is more convenient to interpret than the plot of  $T$  versus  $c$ . The modern spectrophotometers are, therefore, calibrated to read absorbance although it is the transmitted light which is actually measured by the instrument.

**Limitations of the Beer-Lambert Law.** 1. The Beer-Lambert law is not obeyed if the radiation used is not monochromatic.

2. The law governs the absorption behaviour of *dilute solutions only*. At high solute concentrations, the ions of a solute, if it is an electrolyte, are close enough to disturb the charge distribution of their neighbours. The interionic interaction can drastically alter the ability of the solute to absorb a given wave length of the incident radiation. Thus, the relationship between  $A$  and  $c$  is no longer linear. Hence, at higher concentrations there are distinct deviations from linearity, as shown in Fig. 4.

At higher concentrations, the refractive index ( $n$ ) of the solution also changes. It has been found that in the Beer-Lambert law, it is the quantity  $[n/(n+2)^2]\epsilon$ , rather than  $\epsilon$ , which remains constant. Hence, severe deviations from the Beer-Lambert law will be observed when the factor  $n/(n+2)^2$  changes with change in concentration.

The temperature of the system should not be allowed to vary to a large extent. This is because the increase in temperature has a bathochromic effect on ions in solution, i.e., the absorption bands shift towards longer wave length.

**Example 1.** A monochromatic radiation is incident on a solution of 0.05 molar concentration of an absorbing substance. The intensity of the radiation is reduced to one-fourth of the initial value after passing through 10 cm length of the solution. Calculate the molar extinction coefficient of the substance.

**Solution.** According to the Beer-Lambert law,

$$\log I_0/I = \epsilon bc \quad (\text{Eq. 5})$$

In this case,

$$I/I_0 = 0.25 = 25\%, \text{ i.e., } I_0/I = 100/25$$

$$\therefore \log (100/25) = \epsilon \times 10 \text{ cm} \times 0.05 \text{ mol dm}^{-3}$$

$$\therefore \epsilon = 1.204 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$$

**Example 2.** A substance when dissolved in water at  $10^{-3}$  M concentration absorbs 10 per cent 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?

$$\text{Solution : } A = \log (I_0/I) = \epsilon bc \quad (\text{Eq. 5})$$

In the first case,

$$A = 10\% \text{ so that } T = I/I_0 = 90\%$$

$$b = 1 \text{ cm}, c_1 = 10^{-3} \text{ mol dm}^{-3}$$

$\therefore$

$$\log (100/90) = \epsilon bc_1 \quad \dots(i)$$

In the second case,

$$A = 90\% \text{ so that } T = I/I_0 = 10\%, b = 1 \text{ cm}$$

Let  $c_2$  be the concentration in the second case.

$$\log (100/10) = \epsilon bc_2 \quad \dots(ii)$$

From Eqs (i) and (ii),

$$\frac{\log (100/90)}{\log 10} = \frac{c_1}{c_2} = \frac{0.001 \text{ mol dm}^{-3}}{c_2}$$

$$c_2 = 0.0218 \text{ mol dm}^{-3}$$

**Example 3.** In a Beer-Lambert law cell, the aqueous solution of a substance of known concentration absorbs 10 per cent of the incident light. What fraction of the incident light will be absorbed by the same solution in a cell five times as long?

**Solution :**

In the first case,

$$A_1 = \log (I_0/I)_1 = \epsilon b_1 c$$

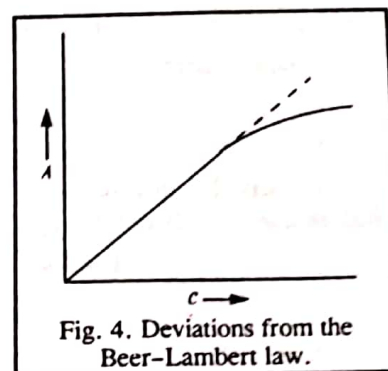


Fig. 4. Deviations from the Beer-Lambert law.