Example 5.3: If the transmittance of a solution is 19.4%, what is its absorbance or optical density?

$$\%T = 19.4;\ T = 0.194$$

$$\text{Absorbance } A = -\log_{10} T = \log_{10} 1/T$$

$$= \log_{10} 1/0.194 = 0.712$$

Example 5.4: The transmittance of a 2×10^{-4} *M* solution of a substance was found to be 76.2% at a wave length of 350 mμ, when placed in a cell of 1 cm length. Calculate (*i*) the absorbance (*ii*) molar absorptivity and (*iii*) the percent transmittance, if the cell length is 2.0 cm.

(*i*) $T = 0.762$

$$A = -\log_{10} T = \log_{10} 1/0.762 = 0.118$$

(*ii*) $A = \varepsilon bc$

$$\varepsilon = \frac{A}{bc}$$

$$= \frac{0.118}{1 \times 2 \times 10^{-4}}$$

$$= 5.9 \times 10^{2}\ \text{dm}^{3}\ \text{mol}^{-1}.\ \text{cm}^{-1}$$

(*iii*) $-\log_{10} T = \varepsilon bc$

i.e., $\log_{10} 1/T = 5.9 \times 10^{2} \times 2 \times 2 \times 10^{-4} = 0.236$

$$1/T = 1.722;\ \text{and } T = 0.581$$

$$\%T = 58.1$$

Example 5.5: The molar absorptivity of a substance in solution is $4.65 \times 10^{3}\ \text{dm}^{3}\ \text{mol}^{-1}.\ \text{cm}^{-1}$ at a wave length of 375 mm. If the transmittance of this solution in a cell of 1 cm length is 0.67, calculate (*i*) the concentration of the solution and (*ii*) the concentration of the solution that will give a transmittance of 0.78 when placed in the same cell at the same wave length.

(*i*) $A = \log_{10} 1/T = \varepsilon bc$

$$= \log_{10} 1/T = \log_{10} 1/0.67 = 0.1739$$

$$c = \frac{0.1739}{4.65 \times 10^{3} \times 1} = 3.74 \times 10^{-5}\ M$$

(*ii*) $A = \log_{10} 1/T = \log_{10} 1/0.78 = 0.1079$

$$c = \frac{0.1079}{4.65 \times 10^{3} \times 1} = 2.32 \times 10^{-5}\ M$$

Example 5.6: A solution containing 4.48 ppm of $KMnO_4$ (Mol. wt – 158.04) was found to have transmittance of 0.309, when measured in a 1 cm cell at a wave length of 250 nm. Calculate the molar absorptivity of the $KMnO_4$ solution.

$$1 \text{ ppm} = 1 \text{mg per dm}^3$$

The given solution contains 4.48 ppm of $KMnO_4$ =

$$4.48 \text{ mg } KMnO_4 \text{ per dm}^3 = 4.48 \times 10^{-3} \text{ g. dm}^{-3}$$

Molarity of the solution $= 4.48 \times 10^{-3}/158.04$

$$= 2.84 \times 10^{-5}$$

$$A = -\log_{10} T = \log_{10} 1/0.309 = 0.51$$

$$A = \varepsilon bc$$

$$\therefore \varepsilon = A/bc$$

$$= \frac{0.51}{1 \times 2.84 \times 10^{-5}}$$

$$= 1.796 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}. \text{ cm}^{-1}$$

Example 5.7: The molar absorptivity of a solute is 1.4×10^4 dm^3. mol^{-1}. cm^{-1}. If a solution of the substance has an absorbance of 0.85, in a 1 cm light path cell, calculate (*i*) the transmittance and (*ii*) the concentration of the solution.

(*i*) $$\log_{10} 1/T = A = 0.85$$

$$\therefore 1/T = 7.079 \text{ and } T = 0.1413$$

(*ii*) $$A = \varepsilon bc$$

$$\therefore c = \frac{A}{\varepsilon b} = \frac{0.85}{1.4 \times 10^4 \times 1}$$

$$= 6.07 \times 10^{-5} M$$

Example 5.8: An aqueous solution which is 10^{-3} *M* absorbs 10% of the incident radiation in a path length of 1 *cm*. Calculate the concentration of a solution of the same substance that will absorb 90% of the same incident radiation in the same cell.

Since the solution absorbs 10% of the incident radiation, its transmittance is 90%.

$$\therefore T = 0.9$$

$$A = \log_{10} \frac{1}{T} = \log_{10} \frac{1}{0.9} = 0.0458$$

$$A = \varepsilon bc$$

$$\therefore \varepsilon = \frac{A}{bc} = \frac{0.0458}{1 \times 10^{-3}} = 45.8 \text{ dm}^3. \text{ mol}^{-1}. \text{ cm}^{-1}$$

When 90% light has to be absorbed, the transmittance, T will be 10%.

$T = 0.1$ and for this solution $A = 1$

$$c = \frac{A}{\varepsilon b} = \frac{1}{45.8 \times 1} = 2.18 \times 10^{-2}\, M$$

Example 5.9: The absorbance of a solution containing 5×10^{-3} g. dm^{-3} of a solute in a 1 cm cell is 1.0. Calculate (*i*) the absorptivity and (*ii*) molar absorptivity of the solution. The molecular weight of the solute is 125.

$$A = abc$$

$$\therefore a = \frac{1}{1 \times 5 \times 10^{-3}}$$

$$a = 2 \times 10^{2}\ \text{dm}^3.\text{g}^{-1}.\text{cm}^{-1}$$

A = εbc

$$\varepsilon = a \times M$$

$$= 2 \times 10^{2} \times 125$$

$$\varepsilon = 2.5 \times 10^{4}\ \text{dm}^3.\text{mol}^{-1}.\text{cm}^{-1}$$

Example 5.10: Over what concentration range could analysis be performed for an Fe (III) complex which possesses a molar absorptivity of 12,000 dm^3 mol^{-1} cm^{-1} if it is desired to confine transmittance reading to within the range 0.4 and 0.85? Assume optical path length of 1 cm

$$A_1 = \log_{10} \frac{1}{0.4} = 0.3979$$

$$A_2 = \log_{10} \frac{1}{0.85} = 0.0706$$

$$A_1 = \varepsilon b c_1$$

$$\therefore C_1 = \frac{A_1}{\varepsilon b}$$

$$= \frac{0.3979}{12000 \times 1}$$

$$= 3.32 \times 10^{-5}\, M$$

$$C_2 = \frac{A_2}{\varepsilon b} = \frac{0.0706}{12000 \times 1}$$

$$= 5.88 \times 10^{-6}\, M$$

$\therefore$ The concentration range is $3.32 \times 10^{-5}\, M$ to $5.88 \times 10^{-6}\, M$.