B.Sc. (Honours) Part-III

Paper-VA

Topic: Photochemistry-Lambert-Beer Law

UG

Subject-Chemistry

Dr. Laxman Singh

Asst. Professor

Department of Chemistry

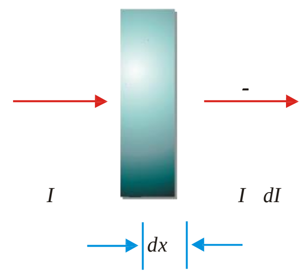
R.R.S. College (PPU)

(Mokama, Patna)

Lambert-Beer Law

LIGHT ABSORPTION

When light is passed through a medium, a part of it is absorbed. It is this absorbed portion of light which causes photochemical reactions. Let a beam of monochromatic light pass through a thickness *dx* of the medium. The intensity of radiation reduces from *I* and *I-dI.*



As a beam of intensity *I* passes through a medium of thickness *dx*, the intensity of the beam is reduced to *I* - *dI*.

The intensity of radiation can be defined as the number of photons that pass across a unit area in unit time.

Let us denote the number of incident photons by *N* and the number absorbed in thickness *dx* by *dN*. The fraction of photons absorbed is then *dN*/*N* which is proportional to thickness *dx*. That is,

$$\frac{dN}{N} = b\,dx = \mathbf{l}\,\frac{dI}{I}$$

where b is proportionality constant called **absorption coefficient.**

Let us set $I = I_0$ at $x = 0$ and integrate. This gives

$$I = I_0\,(-\,bx)$$

or $$\text{In}\left(\frac{I}{I_0}\right) = \text{l}\;bx \qquad \text{...(1)}$$

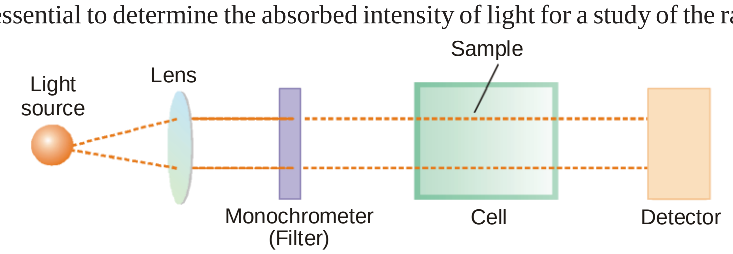
Lambert first derived equation (1) and it is known as **Lambert Law.** Beer extended this relation to solutions of compounds in transparent solvents. The equation (1) then takes the form (2).

$$\text{In}\left(\frac{I}{I_0}\right) = \text{l}\;\text{E}\,C\,x \qquad \text{...(2)}$$

where C = molar concentration; E is a constant characteristic of the solute called the *molar absorption coefficient.* The relation (2) is known as the **Lambert-Beer Law.** This law forms the basis of spectrophotometric methods of chemical analysis.

DETERMINATION OF ABSORBED INTENSITY

A photochemical reaction occurs by the absorption of photons of light by the molecules. Therefore, it is essential to determine the absorbed intensity of light for a study of the rate of reaction.



Schematic diagram of the apparatus used for measurement of light intensity.

An experimental arrangement for the purpose is illustrated in Fig. 3O.3.

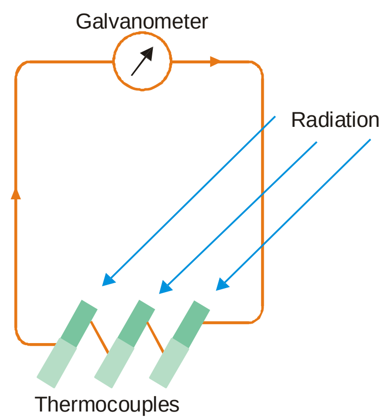
Light beam from a suitable source (tungsten filament or mercury vapour lamp) is rendered parallel by the lens. The beam then passes through a 'filter' or monochrometer which yields light of one wavelength only. The monochromatic light enters the reaction cell made of quartz. The part of light that is not absorbed strikes the *detector.* Thus the intensity of light is measured first with the empty cell and then the cell filled with the reaction sample. The first reading gives the incident intensity, I_0, and the second gives the transmitted intensity, I. The difference, $I_0 - I = I_a$, is the absorbed intensity.

The detector generally used for the measurement of intensity of transmitted light is :

(*a*) a thermopile (*b*) photoelectric cell (*c*) a chemical actinometer.

Thermopile

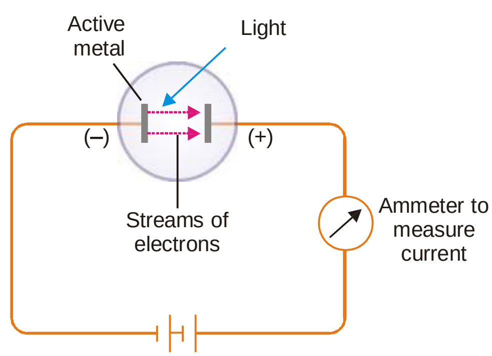
It is made of a series of thermocouples in which unlike metals such as bismuth and silver are joined together. One end of the couple is blackened with lamp black and the other end is left as such. When the radiation strikes the black end it absorbs energy and is heated up. The temperature difference between the two ends causes a current to flow in the circuit as indicated by the galvanometer. **The current is proportional to intensity of radiation.** The thermopile is previously calibrated against a standard source of light.



A thermopile.

Photoelectric Cell

A photoelectric cell (Fig. 30.5) can be conveniently used for measuring intensity of light. The light striking the active metal electrode (cesium, sodium or potassium) causes the emission of electrons. A current flows through the circuit which can be measured with an ammeter. The intensity of light is proportional to the current.



A photoelectric cell (illustration).

Chemical Actinometer

A chemical actinometer uses a chemical reaction whose rate can be determined easily. One such simple device is **Uranyl oxalate actinometer.** It contains 0.05 M oxalic acid and 0.01 M uranyl sulphate in water. When it is exposed to radiation, oxalic acid is decomposed to CO_2, CO and H_2O.

$$UO_2^{2+} + h\nu \longrightarrow (UO_2^{2+})^*$$

$$(UO_2^{2+})^* + \underset{\text{oxalic acid}}{\begin{array}{c}COOH\\ |\\ COOH\end{array}} \longrightarrow UO_2^{2+} + CO_2 + CO + H_2O$$

The concentration of oxalic acid that remains can be found by titration with standard $KMnO_4$ solution. The used up concentration of oxalic acid is a measure of the intensity of radiation.