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Instruction for practical physical chemistry

Semester- 6 (H), CC-14

Topic – Verification of Beer and Lambert's Law for $KMnO_4$ and $K_2Cr_2O_7$ solution

Volume of NH_4OH added

Titration of a strong acid against a weak base

1.11 Verification of Lambert-Beer's Law and to Determine the Concentration of a Given Solution

Theory: *It has been observed that when a beam of electromagnetic radiation is passed through a solution of an absorbing substance contained in a transparent cell the intensity of electromagnetic* radiation is reduced. Lambert and Beer independently investigated the nature of change of intensity of electromagnetic radiation and proposed two different laws.

(i) **Lambert's law:** According to Lambert's law, rate of decrease in intensity of radiation with space (path length) is proportional to the intensity of the incident radiation (light). This may be mathematically expressed as

$$\frac{-dI}{dx} \propto I, \qquad (1)$$

where I is the intensity of incident light, x is the path length through which light beam passes. Minus sign implies decrease in intensity.

(ii) **Beer's law:** Beer stated that the rate of decrease in intensity of electromagnetic radiation with space (path length) is proportional to the concentration of the solution through which the *radiation passes*. This may be expressed mathematically as

$$\frac{-dI}{dx} \propto c, \qquad (2)$$

where c is the molar concentration.

Combining the two laws (1) and (2), we get

$$\frac{-dI}{dx} \propto I.c. \qquad (3)$$

The expression (3) is known as Lambert-Beer's Law.

$$\text{or,} \quad \frac{-dI}{dx} = k.I.c.$$

or, $\frac{-dI}{I} = k.c.dx.$, where k is proportionality constant.

Integrating, we get

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

$$\text{or,} \quad \log \frac{I_0}{I} = k.c.x.$$

The proportionality constant k is generally denoted by ε and is known as molar absorption coefficient, which is constant at any given wavelength and is independent of concentration of the solution.

Thus, $\log \frac{I_0}{I} = \varepsilon.c.x.$ (4)

It may be mentioned that the space x is the size of cell in which the solution of absorbing substance is taken. It is usually taken one cubic centimetre, i.e., x =1.

Hence, $\log \frac{I_0}{I} = \varepsilon.c.$ (5)

The term $\log \frac{I_0}{I}$ is called absorbance and is generally indicated by A. Thus,

$$A = \varepsilon.c. \qquad (6)$$

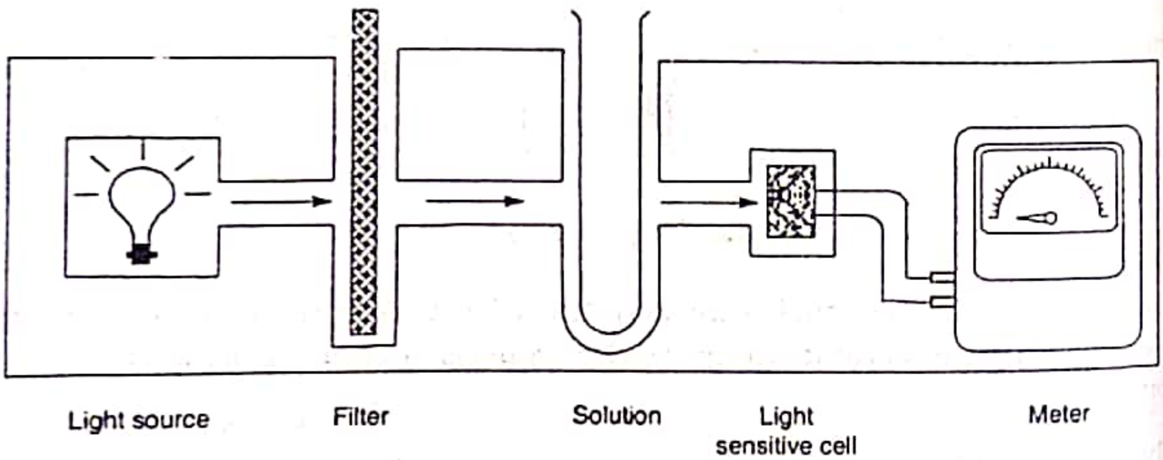
For the determination of concentration of the solution of absorbing substance wavelength of maximum absorption (usually denoted by λ_{max} where λ is the wavelength) for the compound is selected. Then the absorbances (A) of the solution of the substance are measured for different concentrations. Next the absorbances are plotted against concentration of the substance over a range of concentrations. If Lambert-Beer's law holds good a straight line should be obtained. This plot is used as a calibration curve for determining the unknown concentrations of a substance. The solution of unknown strength is taken in the uv-cell and its absorbance is measured. Corresponding to this absorbance the concentration of unknown solution can be calculated.

Apparatus required: Colorimeter as shown in the figure.

Reagents required:

1. Absorbing substance $KMNO_4$ or $K_2Cr_2O_7$ solutions of the order M/50
2. Dilute H_2SO_4 (1N).

Procedure: A solution of known concentration is prepared and from this solution, by the method of dilution other solutions of different strength are prepared. Generally, M/50 and less concentrated solutions are prepared. In the case of $KMnO_4$ aqueous solution is used but in the case of $K_2Cr_2O_7$ dilute H_2SO_4 (1N) solution is used. For each solution of known strength absorbance is measured. Finally absorbance for solution of unknown strength is also measured. A plot of conductance against absorbance is drawn when a straight line is obtained. From this graph, concentration of unknown solution is measured. It may be mentioned that suitable filter (monochromator) is to be used in the colorimeter to adjust the required wavelength. Filter of 475 nm for $K_2Cr_2O_7$ and 530 nm for $KMnO_4$ solutions are to be used.



Colorimeter

Preparation of solutions of different strengths: Solutions of different strengths are prepared by mixing different volumes of solution of absorbing substence (N/50) and solvent according to the table given below:

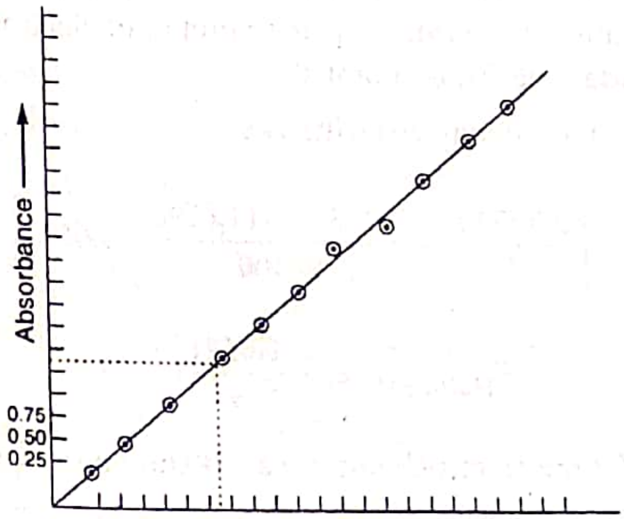
Volume of $KMnO_4$ or $K_2Cr_2O_7$ solution (M/50) (ml)	Volume of solvent (water for $KMnO_4$ and (1N) H_2SO_4 for $K_2Cr_2O_7$ ml	Serial number of solutions
1	9	1
2	8	2
3	7	3
4	6	4
5	5	5
6	4	6
7	3	7
8	2	8
9	1	9

Results

(i) Wavelength (filter) .... nm

Observation Solution No.	Absorbances
1	
2	
3	
⋮	
unknown solution	

A graph is drawn by plotting absorbance against concentration. The linearity of the graph proves the validity of Lambert-Beer's law. From the graph, the concentration of unknown solution is found to .... *a* molar.



Graph showing the relationship between absorbance and concentration