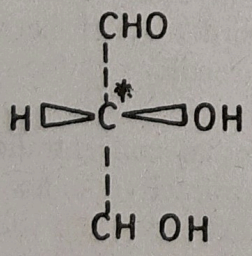
10

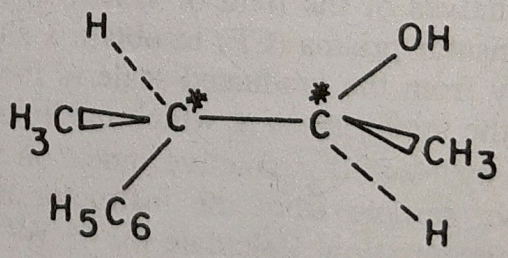
Polarimetry

10.1 General

There are many organic compounds which have ability to rotate the plane of polarized light. Such substances are called *optically active* or that they possess *optical rotary power*. The optical rotatory power arises due to the presence of structural asymmetry contained in any substance. This again may be because of symmetry of a plane or a centre of symmetry in the molecule, some examples of the origin of structural asymmetry inherent in the structure of molecules are (i) dextrose (ii) in the crystalline form like quartz but not in the liquid or gaseous state (iii) helical form of polypeptide. The other examples of asymmetrical molecules are; D + glyceraldehyde and 3–phenyl–2–butanol as shown below.



D+GLYCERALDEHYDE



3-PHENYL-2-BUTANOL

Further, substances can be classified as ''isotropic'' when radiation coming into contact with them is affected in the same way regardless of direction of vibration or direction of propagation. For example, gases, liquids in absence of orienting field, isometric crystals (NaCl). When one direction is not optically equivalent to the other because of differences in the numbers of each kind of atoms encountered or in the spacing of units in the lattice patterns, such substances are called ''anisotropic''. For example, uniaxial crystalline solids, tetragonal, hexagonal etc. Let us consider the resolution of an incident radiation falling on a uniaxial crystal containing a single optic axis. The crystal will resolve the radiation into 2 rays having mutually $\perp$ plane of vibration. One vibration will be in a principle plane i.e. plane formed by the optic axis and $\perp$ to the main faces of the crystal. The other vibration will be in the plane $\perp$ to the principal

axis. The ray along the optic axis will establish the ordinary index of refraction (n_o) and is called "Ordinary ray". It travels with vibrations $\perp$ to the principal plane at the same velocity. The other component i.e. ray with vibrations in the principal plane is called "extra ordinary ray". It has the index of refraction n_E and varies with the direction of propagation.

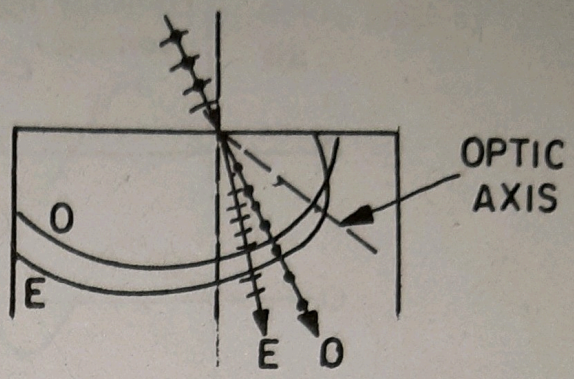


Fig. 10.1 Radiation falling on a uniaxial crystal

10.2 Theory

The subject of polarimetry involves the study of following two changes that may be produced in a polarized light when it interacts with an optically "anisotropic matters". (i) a change in the direction of vibration i.e. a rotation of a linear vibration perpendicular to the direction of propagation and (ii) a change in the state of vibration i.e. a transition of a linear vibration into an elliptic or circular vibration or vice-versa. Generally a change in the direction of vibration of linearly polarized light during passage through an anisotropic matter is called "optical rotation" i.e. when the effect is due to anisotropic refraction, but when effect is produced by anisotropic absorption or scattering it is called 'optical dichroism". Therefore, such substances which have an inherent ability to rotate the plane of polarized light are called "optically active."

Under normal conditions, the natural ordinary light is presumed to consist of a large number of electromagnetic waves vibrating in all possible directions around the direction of propagation. If from this natural wave front, only those rays vibrating in one particular plane are separated out by some means, it is called "plane polarized light". Similarly, a circularly polarized light would comprise a wave in which electrical component (also the magnetic component) would travel either clockwise (left handed) around the direction of propagation e.g. α, β — helix and screw nail etc.

Let us consider a linearly polarized beam of monochromatic light travelling along the plane of this paper along the direction of arrow as shown in Fig. 10.2 and 10.3.

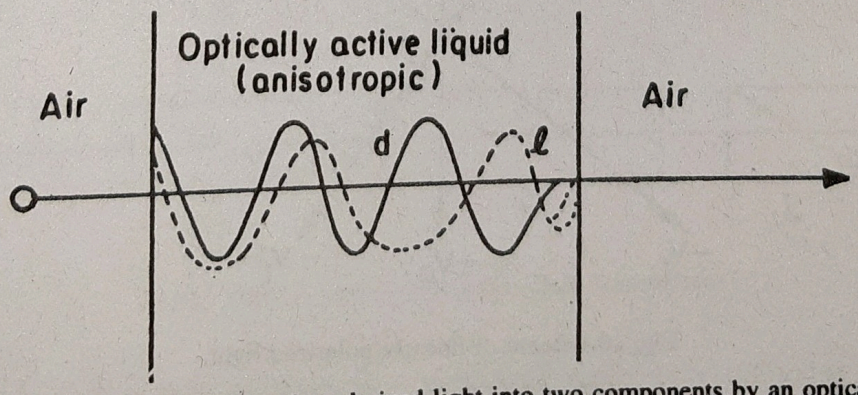


Fig. 10.2. Resolution of a beam of linearly polarized light into two components by an optically active liquid.

The beam is supposed to be resolved into two circular components around after it enters the liquid. The velocity of the two components in the liquid will be different from that of air. This is represented as follows :

$$V_d = V_1 = V_2 \text{ because } V_1 : V_2 = n_2 : n_1$$

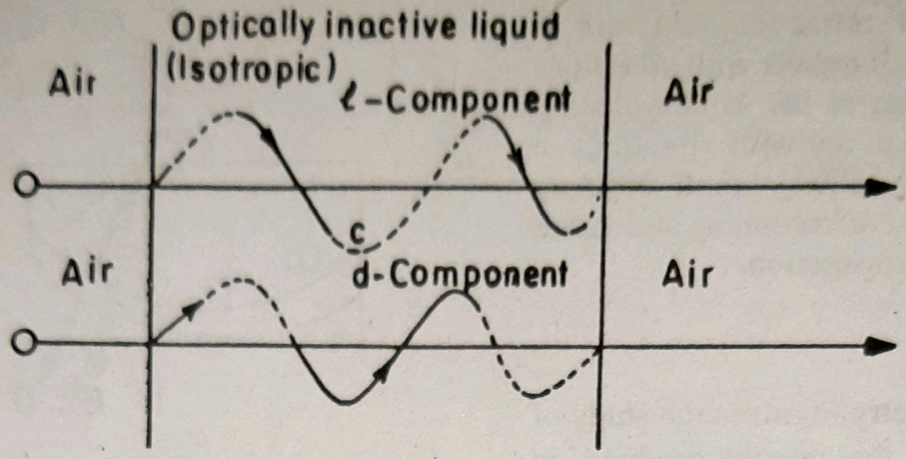


Fig. 10.3. Resolution of a beam of polurized light into two circular components by an isotropic liquid.

Where n_1 is the refractive index of air and n_2 is refractive index of liquid. V_2 is velocity in liquid and V_1 is velocity in air.

But refractive index $n = \frac{c}{v}$

Where c is velocity in vacuum, v is the frequency i.e. no of vibration per second (It is constant)

$$\therefore \quad n_1 = \frac{c}{v_1} \text{ and } n_2 = \frac{c}{v_2}$$

But $v = \frac{V}{\lambda}$

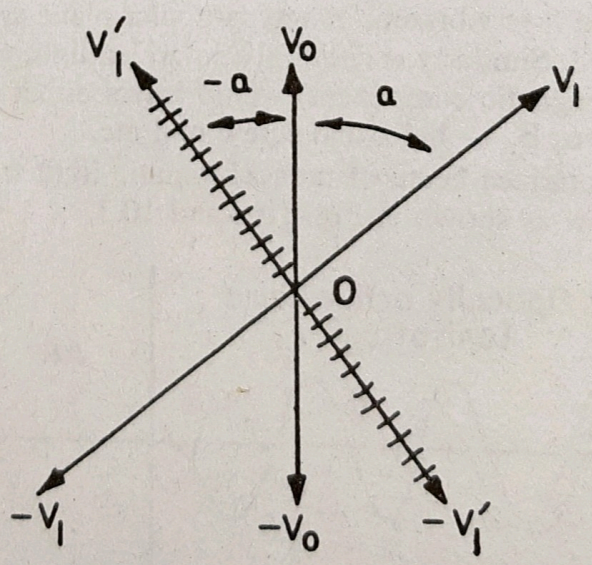


Fig. 10.4 Beam of linearly polarized light.

Further, $\lambda_1 : \lambda_2 = V_1 : V_2 = n_2 : n_1$ where λ_1 is wavelength in air and λ_2 is wavelength in the liquid, consequently light wave become contracted on entering in a liquid.

In figure 10.4. the beam of linearly polarized light is represented to intersect the plane at 0. Normally, the beam will vibrate along $- V_o O V_o$ but it will vibrate along $- V_1OV_1$ or $- V_1'OV_1'$ after traversing an optically active substance. Rotation α will be positive if the direction is clockwise (i.e. $- V_o OV_o \rightarrow - V_1OV_1$) and negative if the direction of vibration changes to $— V_1' O V_1'$. Substances that cause a positive rotation are termed *dextrorotatory* while that cause a negative rotation are termed *levorotartory*.

Let b be the length of the column of material travelled by the beam, λ the wavelength of light, υ is the velocity in vacuum, then the phase difference ϕ between the two rays will be given by :

$$\varphi = \frac{2\pi b \nu}{V_r} - \frac{2\pi b \nu}{V_l}$$

Where r and l are right and the left component of the plane polarized beam.

or $$\varphi = \frac{2\pi b \nu c}{V_r c} - \frac{2\pi b \nu c}{V_l c}$$

We know $$\nu = \frac{c}{\lambda} \quad \therefore \quad \frac{1}{\lambda} = \frac{\nu}{c}$$

Also $$n = \frac{c}{\nu} \quad \therefore \quad \bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

or $$= \varphi = \frac{2\pi b n_r}{\lambda} - \frac{2\pi b n_l}{\lambda}$$

$$\varphi = \frac{2\pi b}{\lambda}(n_r - n_l) \text{ or } \lambda = \frac{\pi b}{\lambda}(n_r - n_l)$$

Where α is the angle of rotation because α = 1/2 of phase difference.

10.3 Instrumentation Aspects

The main components of a polarimeter are : (i) The light source, (ii) a polarize, (iii) an analyzer, (iv) a graduated scale to measure the amount of rotation. (v) sample tubes. A block diagram of a manually polarimeter is given below. However, automatic digital type models are available in the market but are expensive.

A = Light source, B = Collimating lens, C = half-shadow prism D = Lever to adjust half-shadow angle,

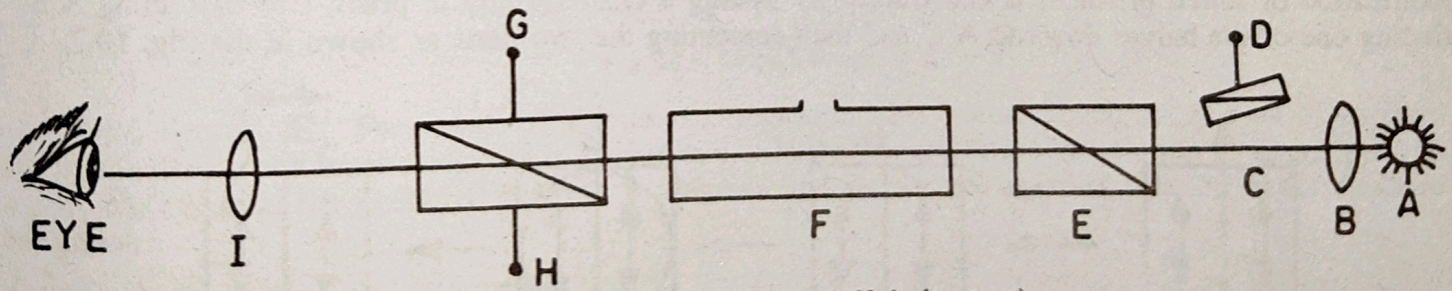


Fig. 10.5. A visual polarimeter (half shadow type)

E = Polarizing Prism, F = Sample tube, G = graduated scale, H = analyzing prism, I = eye piece.

The details concerning the main components are discussed below.

Light Source : The Common source of light used in polarimetry work are (i) sodium vapour lamp and (ii) mercury vapour lamps. The sodium vapour lamp emits light at wavelengths of 5890 A° and 5896 A°. The mercury vapour lamp emits light of wavelengths at 4358, 4916, 5461, 5770 and 5791 A°. Suitable type of filters can be used to isolate required lines.

Polarizer: Several different types of polarizing prisms are known. They differ in the angles of the

faces of the prism and of the cut diagonally through the prism. The Nicol prism and the Glau-Thompson prism are most commonly used polarizers. The Nicol prism is cheaper but not as good as the Glau-Thompson prism. The make up and mechanism of the Nicol prism is explained below :

Nicol prism is prepared from calcite crystals with a minimum of alteration of natural crystal faces.

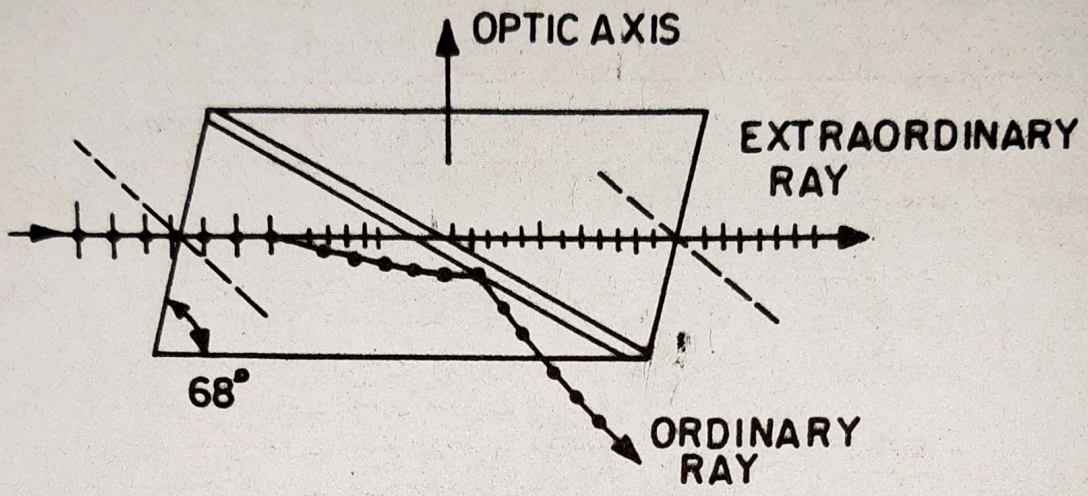


Fig. 10.6. Nicol Prism

The crystal is cut diagonally into two halves at such an angle so that one component of the light is totally reflected. The second component of the light passes through the second half of the crystal in the same direction as the original beam. The two halves of the crystal are cemented together by means of Canada balsom which has an index of refraction of 1.4865. The calcite is uniaxial crystal having n_e of 1.4865 and n_o of 1.6584. Thus the light emerging from the Nicol prism is displaced from the original and will revolve in a circle as the prism is rotated. Nicol prism can be used only in Visible range since Canada balsam is opaque to U.V. light. It also has certain other disadvantages like as dispersion and complete extinction cannot be obtained. The Glau-Thompson prism has many advantages over the Nicol prism and can also be used in UV region. The other polarising prisms available are Wollastan and Rochon prisms.

Analyzer : One of the simplest types of analyzers used in visual polarimeters is the Cornu modification of Jellett prism. It is constructed by sawing a Glau-Thompson prism into half along A B grinding one of the halves down to A C and then cementing the two parts as shown in the Fig. 10.7.

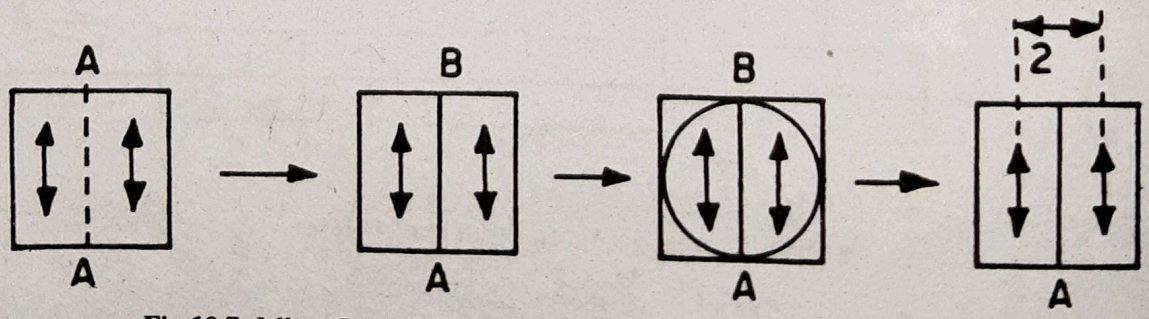


Fig 10.7. Jellett–Cornu Prism (arrows Indicate the direction of extinction).

When light passes through polarizing prism the two halves will produce polarized light beams tilted slightly with respect to each other. The rotation of the analyzer prism in front of such a polarizing prism would produce a complete extinction, first of one-half of the field and then the other-half. At some intermediate position, the two halves of the field would appear of equal brightness. This point is taken as the balance point (Fig. 10.8)

Lippich Prism : It is an another type of half-shadow device used for matching of two half-fields for a balance point. In this type of set up a small polarizing prism (A) precedes the large prism (B). With this kind of arrangement (Fig.10.9) one-half of the field can be rotated slightly with respect to other half. The analyzers must be at some intermediate position in order to achieve equal illumination of both halves of the field. The small prism is arranged in a slightly slanting position, (1 – 2°) in order to obtain a well illuminated and sharp dividing line of two fields. For this purpose, the faces of the small prism are corrected by 6-7°.

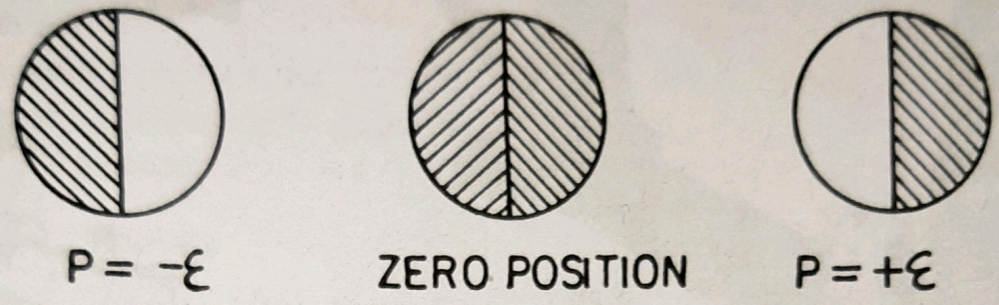


Fig 10.8. Fields of view (search for field intensity)

Polarimeter tubes : Two types and two sizes of polarimeter tubes including a jacked type for the purpose of cooling the sample are available. They are made of plane glass with a length of 1 dm or 2 dm and internal diameter 10 mm. Polarimeter tube is covered at both ends by plane parallel glass discs which are held in place by holders. For a tight, an elastic ring of rubber is inserted between the disc and the holder. The tube is placed in the light path normal to the beam.

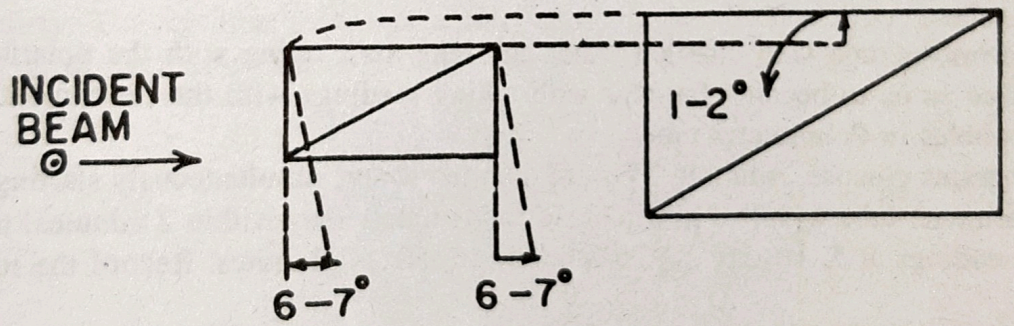


Fig. 10.9. Lippich Prism

10.4 Calculations : The results of polarimetric measurements are calculated under a set of standard conditions. If b is the layer thickness in decimeters, c is the concentration of solution in grams per 100 ml of solution α is the observed rotation in degrees and $[\alpha]_x^t$ is the specific rotation under standard conditions:

Thus $$[\alpha]_x^t = \frac{100\,\alpha}{bc}$$

Temperature is important, will cause contraction and expansion of the liquid.

Measurements of optical rotation are made with sodium D light (5890 A + 5896 A) at 25°. Temperature, solvent and concentration can have effect on the results.

EXERCISE 1. To investigate by half time method, the order of reaction of mutarotation of glucose using 5% and 10% solutions.

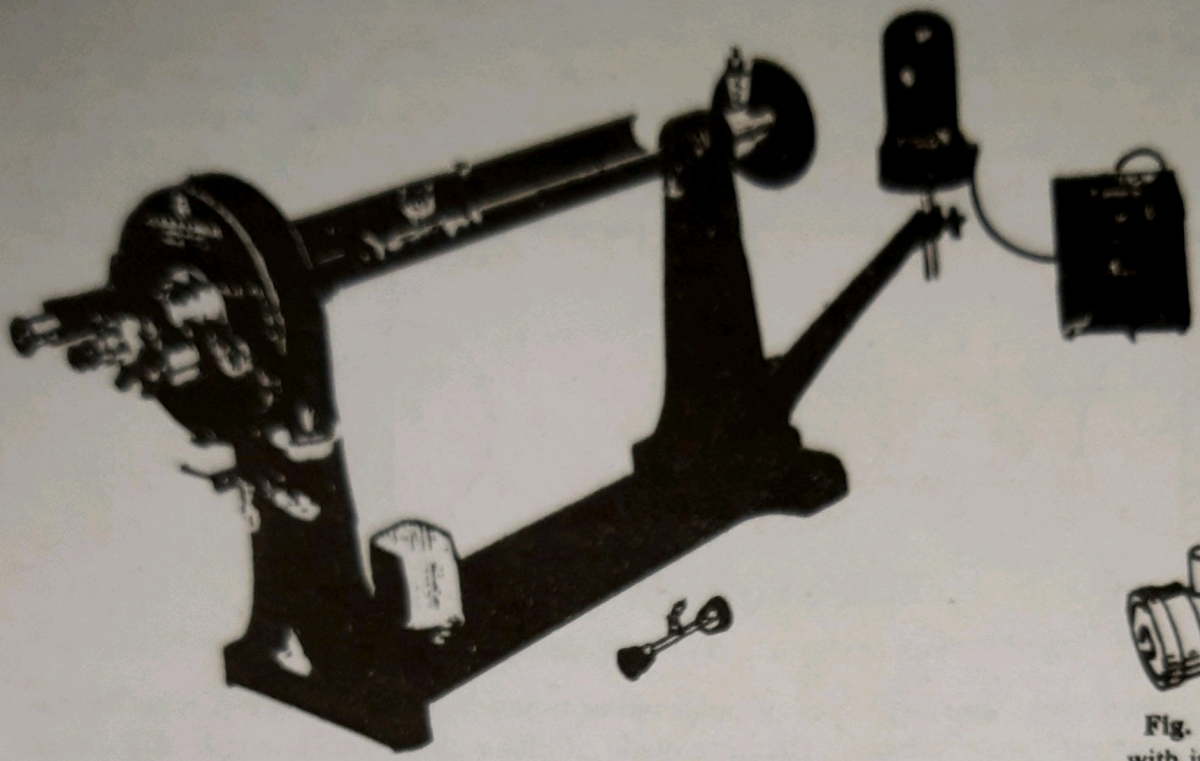


Fig. 10.10(a). Polarimeter (Rudolph)

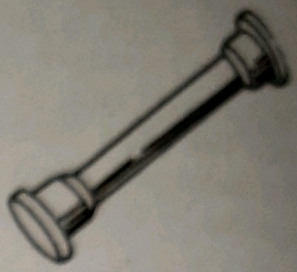


Fig. 10.10(b). Polariscope tube.

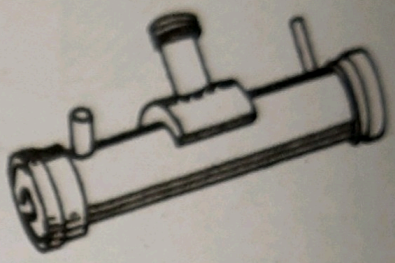


Fig. 10.10(c). Polariscope tube with jacket and thermometer well for constant-temperature.

PROCEDURE

1. Check the zero setting of the instrument by taking the reading of the polarimeter without the polarimeter tube.
2. Fill the polarimeter tube with distilled water and take the reading with the polarimeter. Repeat it twice or thrice so as to become familiar with taking readings with the instrument. See that there are no air bubbles in Polarimeter tube.
3. Weigh 2.50 grams glucose. Add it to 25 ml of distilled water, simultaneously starting the stop-clock. Fill the polarimeter tube with this solution and immediately (say within 2 minutes) take the reading. Repeat the readings at 5, 10, 15, 20, 25, 30, 35, 40, 50, 60 minutes. Record the readings on your notebook.
4. Weight 1.25 grams of glucose, Add it to 25 ml of distilled water, simultaneously starting the stopclock. Fill the polarimeter tube with this solution first rinsing it carefully with the solution. Take the reading immediately (say within 2 minutes). Repeat the readings at 5, 10, 15, 20, 25, 30, 35, 40, 50, and 60 minutes. Record the readings in your notebook.

S.No.	Time	Rotation

5. Draw a graph between time and angular rotation for both the solution using the same scale on the

same graph sheet. Extrapolate to zero time. Half of the difference of zero and infinity reading in each case gives the value of glucose half reacted and corresponding time for both solutions is noted. Record them in your notebook.

6. Verify your result using the equation:

$$\frac{t_1}{t_2} = \left(\frac{r_2}{r_1}\right)^{n-1}$$

where

r_1 = rotation at halftime t_1 for 5% solution.

r_2 = rotation at halftime t_2 for 10% solution.

n = order of reaction.

Interpretation of Results

The times of or half inversion of glucose for both 5% and 10% solutions should be same, as the reaction is of first order.

Precautions

1. Do not move the source when it is hot.
2. When filling the polarimeter tube, see that there are no air bubbles in it .
3. While using the instrument, see that the lenses are clean. Do not unnecessarily touch them with your hands. Clean them with tissue paper only. See that the glass covers of the polarimeter tubes are not dirty. The slightest strains on optical glass will hamper accurate readings.

EXERCISE 2. Determination of specific Rotation of Rochelle salt (Potassium sodium tartrate)

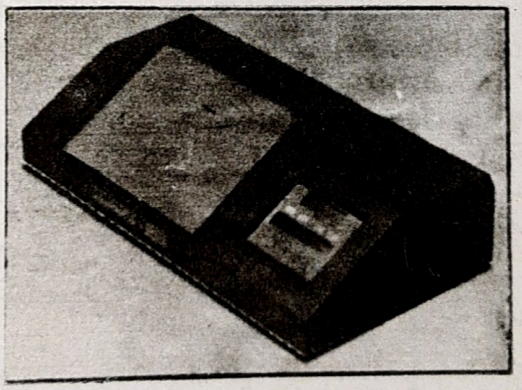


Fig. 10.11. The ADP-220 Polarimeter (Courtesy of Bellingham Stanley Ltd.)

Method: 1. Set up the polarimeter as per instructions of the instructor or as per instruction manual. 2. Prepare a standard solution of the given sample by dissolving 30.0 gm in 70 ml of water. 3. Place distilled water in the polarimeter tube and obtain a zero reading. 4. Replace the water in the polarimeter tube and measure the angle of rotation for the standard salt solution. 5. Calculate the specific rotation for this compound. 6. Now, obtain a solution of the *unknown* concentration from the instructor and measure its optical rotation obtained previously, calculate the concentration of the *unknown.*