PRINCIPLES OF OPTICS

B. K. MATHUR
M. Sc. (Phys. & Maths)
Ex-Associate Professor of Physics
D. A. V. College, Kanpur

Revised by

T. P. PANDYA
M. Sc., Ph. D. (Luck.)
Ph. D. (Lond.), D. I. C.
Reader in Physics
LUCKNOW UNIVERSITY

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CHAPTER 17

OPTICAL ACTIVITY

In the year 1811 *Arago*, while experimenting with a crystal of quartz (placed between two Nicols), discovered that when a beam of plane polarised light is directed through this crystal along its optic axis, the plane of vibration gradually undergoes rotation about the optic axis, as the beam penetrates deeper and deeper into the crystal. Finally, it emerges with its plane of vibration, in general, inclined to the plane of the incident vibrations. Obviously, the plane of polarisation also undergoes an equal rotation in the same direction—the phenomenon being termed as *rotatory polarisation* or more commonly, as ***optical activity***. It can be illustrated schematically by Fig. 17.1 where the plane of vibration of the plane polarised light before entering the crystal is in the plane *QQ* and on emergence the direction of vibration is in the plane *PP*. The angle of rotation of the plane of polarisation is obviously equal to that between *QQ* and *PP*.

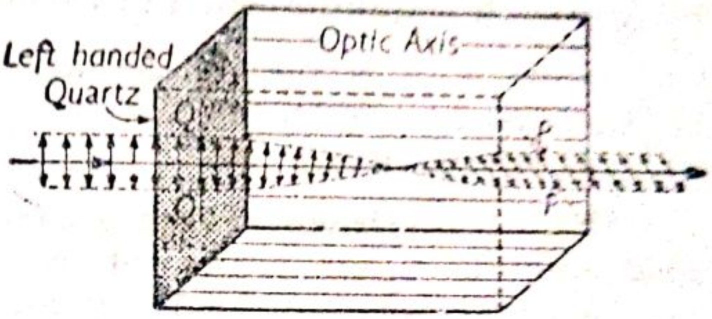


Fig. 17.1. Rotation of plane of vibration in optically active substance like quartz.

Many other crystal like sodium chlorate, sodium bromate and cinnabar exhibit the phenomenon of optical activity and such substances are said to be optically active. The angle of rotation of the plane of polarisation is found experimentally to be directly proportional to the thickness of the crystal section traversed by the plane polarised light. This fact brings into light the fact that the action occurs within the optically active medium and not at the surfaces. The angle of rotation is also found to depend upon the wavelength of the light employed and the nature of the optically active substance.

In addition to solids mentioned above, there are certain liquids *e g.*, turpentine, sugar solution, alcoholic solution of camphor etc. which are optically active. The optical rotation produced by liquids is however very small as compared to that produced by solids. Thus one millimetre thick quartz plate produces a rotation of about 18° in the red region of the spectrum while the same thickness of turpentine produces a rotation of only twenty five minutes. The amount of rotation produced by liquids is proportional to the following factors :

(*i*) The length of path into the liquid,

(*ii*) Inverse quareof wavelength (The law is approximate).

It was discovered by Biot that optically active liquid retains its property when it is dissolved in a solvent which does not react with it, The rotation produced by such solutions is proportional to the concentration. This property makes it possible to determine the concentration of an optically active solution by meassuring the rotation produced by a standard length of the solution.

An optically active liquid *e. g.*, turpentine ratains its property when it is transformed into vapour.

While in solids the optical activity is attributed to their crystalline structure, in the case of liquids it is attributable to the molecular structure itself.

17.1. Experimental Demonstration of Rotatory Polarisation. The phenomenon of rotatory polarisation can be experimentally demonstrated by an arrangement sketched in Fig. 17 2 where N_1 and N_2 are Nicol prisms mounted at a small distance apart and are capable of rotation about the common axis. In the crossed setting of the Nicols, the field of view is dark—the E vibrations from the polariser enter the analyser as

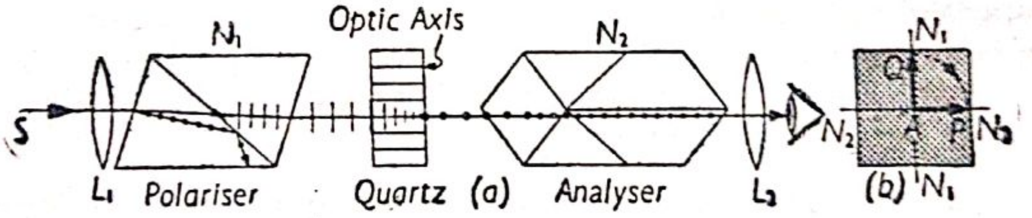


Fig. 17.2. Demonstrating the special case of rotation of plane of vibration through 90°.

O vibrations in this particular setting and hence are totally reflected within the analyser. However, on Inserting a plate of quartz (cut perpendicularly to the optic axis) between the crossed Nicols the field of view brightens *i. e.* some light is now transmitted by the combination. If the light is monochromatic (of single wavelength) then on rotating N_2 through a certain angle the light emerging from quartz can be once more completely extinguished. This shows that it is still plane polarised but the plane of vibration of the incident light has been rotated in passage through quatz by an angle through which N_2 has been rotated.

All this is more closely explained schematically in Fig. 17.3 where N_1N_1 represents the principal section of the polarising Nicol and therefore AQ represents the vibration incident on the quartz. This vibration is rotated from the plane AQ to AP in passing through the quartz and therefore AP represents the vibration emergent from quartz and incident on the analysing Nicol N_2, whose principal section is represented by N_2N_2 [17.3 (a) On entering the analyser, its component $AE = AP \sin\theta$ along N_2N_2 (plane of transmission in analyser) is transmitted as E vibration. On the other hand, the perpendicular component $AO = AP \cos\theta$ is totally reflected as O vibration within the analyser. This explains the brightening of the field of view on the insertion of quartz between the crossed Nicols. If now N_2 is rotated, then $N_2'N_3'$ is the required new position of its principal section, being perpendicular to AP, for complete extinction of AP. The angle of rotation of the plane of vibration due to quartz plate is, therefore, equal to the angle between N_2N_2 and $N_2'N_2'$ *i. e.* the angle through which the analysing Nicol has been rotated. Unfortunately, this is not the most sensitive and accurate method for measuring the angle of rotation.

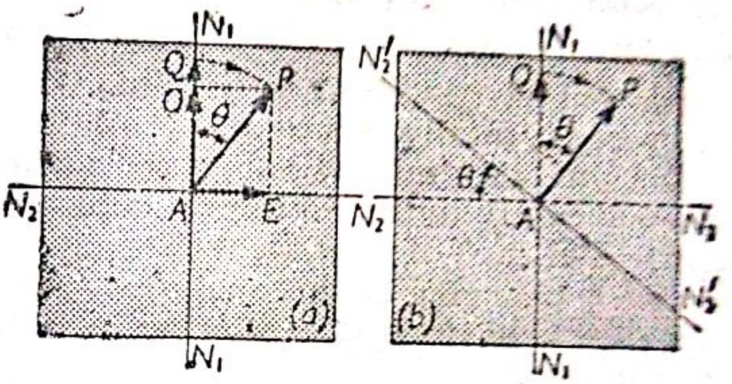


Fig. 17.3. Rotation of monochromatic light in a quartz plate mounted between crossed polarise and analyser.

If, however, a plate of calcite, cut perpendicularly to the optic axis, be similarly inserted between the crossed. Nicols, the field of view remains dark, the plane polarised light from the first Nicol is transmitted by calcite without any modification and therefore, it is extinguished by the analyser. Thus, *calcite is an optically inactive crystal.*

17.2. Rotatory Dispersion. A careful study of optical activity would show that the planes of vibration of light of different wavelengths are rotated by different amounts in traversing the same thickness of quartz. The first accurate results in this direction are due to *Biot* who found that the angle of rotation is very nearly inversely proportional to the square of the wavelength—the light of wavelength in the violet region being rotated about four times more than the light of wavelength in the red region of the spectrum Therefore, if a plane polarised beam of white light be directed through quartz along its optic axis, the effect can be illustrated diagramtically as in Fig. 17.4 where QQ represents the direction of vibration in the polarised white light incident on the quartz. The waves of different wavelengths in the emergent beam will have different planes of vibration as shown in Fig. 17.4 (a), where AR is the plane of vibration of the wave of same particular wavelength in the red region and so on. *Consequently, when* emergent vibrations from quartz are analysed by the second Nicol with its principal section N_2N_2 (plane of trans mission), as shown in Fig. 17.4 (*b*), their components along N_2N_2 – from AE_R to AE_V – are transmitted as E vibrations while the perpendicular components – from AO_V to AO_R – are totally reflected as O vibrations within the analyser. Since $AE_V > AE_R$ the resultant transmitted colour will have violet tinge. What happens is that more of the red colour is totally reflected as O vibrations within the analyser. In fact, the resultant colour of the transmitted light is exactly complementary to the resultant colour of the totally reflected light. The field of view, therefore, appears coloured, the colours obviously changing as the analysing Nicol is rotated about its own axis, light never disappearing entirely for any one setting of the analyser.

Fig. 17.4. Rotation of white light in a quartz plate mounted between crossed polariser and analyser showing components of colours transmitted by the analyser.

The decomposition of white light into its constituent colours in the transmission of plane polarised white light through quartz, (along its optic axis) is termed as phenomenon of *rotatory dispersion.*

17.3. Two Samples of Quartz. There exist two kinds of quartz which are mirror images of each other even in their crystalline structure and form. The most peculiar thing about them is that their optical properties are also mirror images of each other. Thus, if one rotates the plane of vibration to the right, the other would rotate it to the left. Crystals belonging to the former class are called *dextro-rotatory* or simply *right-handed* while those belonging to the latter class are called *laevo-rotatory* or simply *left-handed.* The right-handed rotation means that the rotation of the plane of vibration occurs in the clock-wise direction with respect to

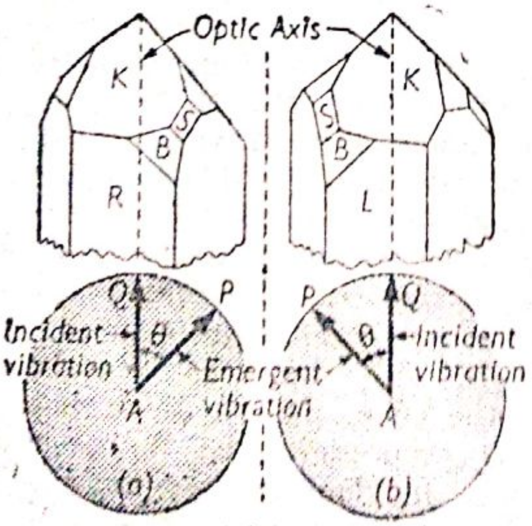


Fig. 17.5. Each quartz is a mirror image of the other.

an observer looking to-wards the oncoming beam of light. A left-handed crystal rotates the plane of vibration in the anti-clockwise direction.

A simple inspection of a quartz crystal enables one to ascertain its nature conclusively. The character of the crystal is determined by the relative positions of S and B with respect to K the surface of the hexagon which both touch. If S and B lie to the right of K, the crystal is a right-handed one; but if they are to the left it is a left handed variety.

17.4. Laws of Rotation of the Plane of Polarisation.

Shortly after the discovery of the phenomenon of rotatory polarisation by *Arago*, *Biot* in about 1815 made a detailed study of the phenomenon of rotatory polarisation with right handed as well as left-handed crystals and employing plane polarised light of different wavelengths. His conclusions are best expressed in the form of the following three laws :—

1. The angle of rotation of the plane of vibration, for any given wavelength, is directly proportional to the thickness of the optically active substance traversed by the incident light. In other words, the greater the thickness, the greater is the angle of rotation.

2. The rotation produced in transmission through two or more optically active substances is the algebraic sum of rotations which would be produced by these substances separately. In mathematical language we may express the resultant rotation θ due to a number of substances arranged one after another as

$$\theta=\theta_1-\theta_2+\theta_3-\theta_4+\theta_5-\theta_6+\ldots\ldots$$

when substances are alternately right-handed and left-handed varieties. *Therefore, a solution containing an equal number of right-handed and left-handed molecules is optically inactive.*

3. The angle of rotation is approximately inversely proportional to the square of the wavelength for a given thickness of the optically active substance

17.5. Fresnel's Explanation of Rotatory Polarisation.

The first explanation of the phenomenon of rotatory polarisation in optically active crystals like quartz was given by *Fresnel* on the supposition that the circularly polarised light is propagated along the optic axis without any modification. The theory is based on the elementary principle in dynamics that any rectilinear simple harmonic vibration may be regarded as resultant of the superposition of equal and oppositely described circular vibrations one clockwise and the other anti-clockwise—rotating with equal frequency. Analytically, the two circular vibrations may be represented by

$$\begin{matrix} x_1=a\cos\omega t \\ y_1=a\sin\omega t \end{matrix} \left[\begin{matrix}\text{Anti-clockwise}\\ \text{Motion}\end{matrix}\right] \quad\text{and}\quad \begin{matrix} x_2=-a\cos\omega t \\ y_2=a\sin\omega t \end{matrix} \left[\begin{matrix}\text{clockwise}\\ \text{Motion}\end{matrix}\right]$$

The *x* components of the circular vibrations, by the principle of superposition of wave motions cancel each other, leaving a linear polarised vibration

$$y = y_1 + y_2 = 2a \sin \omega t$$

This establishes the above stated dynamical principle.

Accordingly, Fresnel's first assumption is that a plane polarised light (linear vibrations) just on entering any crystal along its optic axis is resolved into two equal and opposite circular motions, described with equal frequency, which may [Fig. 17.6 (*b*)] or may not [Fig. 17.6 (*e*) and (*h*)] be propagated with the same speed, depending upon the nature of the crystal. In crystals like calcite, since the spherical and the ellipsoidal wave surfaces actually touch each other at points where optic axis through the point of origin of light intersects them, the two circular components travel with the same speed ($V_L = V_R$) along the optic axis. Consequently, both arrive simultaneously at any point *B* along

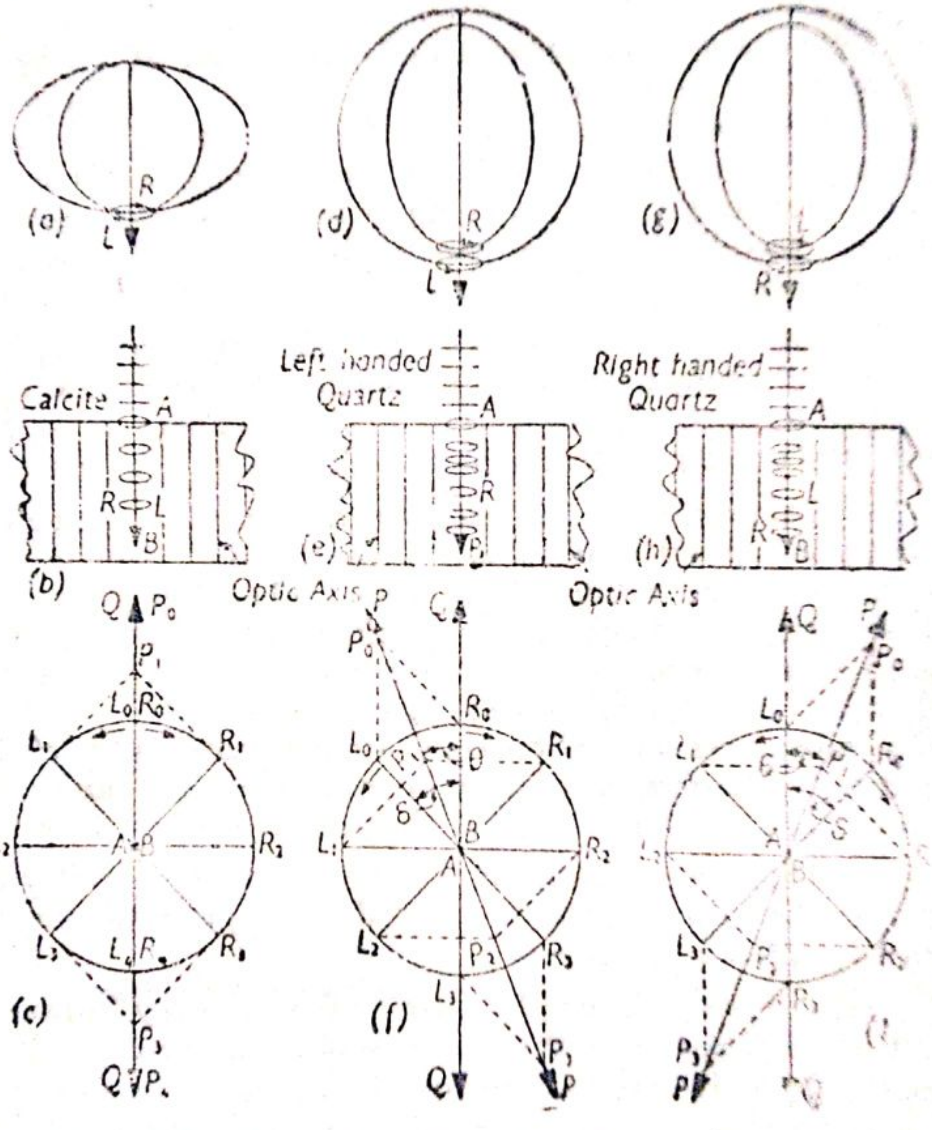


Fig. 17.6. Fresnel's explanation of optical rotation.

their path in the crystal, and as the wave travels on, due to equality of frequencies, the R and the L vectors rotate through equal angles in equal intervals of time—the R vector in the clockwise and the L vector in the anti-clockwise direction—both initially starting from the same point. For every simultaneous position of the R and the L vectors, as shown in Fig. 17.6 (e), their resultant lies along the direction BP_0, which is coincident with AQ, the vibration plane of the incident wave. Thus the light at the point B is still plane polarised and the plane of vibration is the same as that of the incident wave. Calcite, thus, does not exhibit the phenomenon of rotatory polarisation.

In an optically active crystal the two wave surfaces do not actually touch each other at points where the optic axis through the point of origin of the light intersects them. What would normally be the spherical surface, is distorted outwards by a small amount in the region of the axis, and the ellipsoidal surface is distorted inwards. Hence, circularly polarised components travel along the optic axis with slightly unequal speeds. In the right-handed quartz the clock-wise component travels *faster* [Fig. 17.6 (g)] while in the left handed quartz anti-clockwise component travels *faster* [Fig. 17.6 (d)]. Due to this inequality in their speeds a certain phase difference will be introduced between the two components in transmission through the quartz. As a result of this, as explained in the sequence, their resultant vibration will be inclined to the plane of vibration of the incident light and thus the rotation of the plane of polarisation will be accounted for.

Let us now consider more closely the rotation of the plane of vibration in the left-handed quartz. Let the light vector AQ in, the plane polarised light, incident normally on the crystal face be initially vertical. Since $V_L > V_R$, the L component arrives first at any point B along the path of propagation of light in the crystal, and as the wave travels on, the L vector continues to rotate (at B) in anticlockwise direction, having turned through an angle δ, say, before the R component arrives at B. This angle δ, therefore, is the phase difference between the L and the R components on reaching the point B. As this instant, which we call $t=0$, both circular components rotate in opposite directions the one starting at R_0 and the other at L_0, due to equality of frequencies tracing out equal angles in equal intervals of time. For every simultaneous position of R and L vectors, as shown in Fig. 17.6 (f), their resultant lies along the plane BP_e, which it is easy to see makes an angle $\frac{1}{2}\delta$ with the virbration plane of the incident wave. We, therefore, conclude that at point B light is still plane polarised but the plane of vibration has been rotated through an angle $\frac{1}{2}\delta$ in the anticlockwise direction in traversing the thickness AB of the crystal.

In the right handed quartz, the R component arrives first at B and when its vector has described an angle δ in the clockwise direction, the L component arrives at B. At this instant, $t=0$, both circular components rotate in opposite directions with equal frequency, the R vector starting at R_0 and the L vector at L_0. As shown in Fig. 17.6 (*i*), the point P executes linear vibrations along BP. Thus, in travelling, from A to B along the optic axis, the plane of vibration has been rotated through an angle $\frac{1}{2}\delta$ in the clock-wise direction. It is now obvious that the plane of vibration would rotate gradually as the light penetrates deeper and deeper into the crystal.

It may be remarked that Fresnel's explanation is quite satisfactory, as far as it goes, but it fails to give any plausible reason for the curious resolution of the plane polarised light into equal and opposite circularly polarised beams.

Calculation of the Angle of Rotation. The angle of rotation of the plane of vibration in traversing a given thickness of quartz along the optic axis can be very easily expressed in terms of the refractive indices of quartz for propagation of the right and the left handed circular vibrations. The time difference between the two circular components in traversing the right-handed quartz is

$$\Delta t = t_L - t_R = (d/V_L) - (d/V_R)$$

and if c is the velocity of light in air, then

$$\text{Path difference} = c\Delta t = d[(c/V_L) - (c/V_R)$$
$$= d(\mu_L - \mu_R)$$

Hence, the phase difference between the two circular components is

$$\delta = \frac{2\pi}{\lambda} d\,(\mu_L - \mu_R)$$

Therefore, the angle of rotation of the plane of vibration is given by

$$\theta = \tfrac{1}{2}\delta = (\pi/\lambda)\, d\,(\mu_L - \mu_R)$$

where μ_L and μ_R are respectively the refractive indices of the right-handed quartz for the propagation along the optic axis of the L and the R circularly polarised components of the incident linear vibration.

Similary, the angle of rotation of the plane of vibration by the left handed quartz is expressed by

$$\theta = -\tfrac{1}{2}\delta = -(\pi/\lambda)\, d\, (\mu_R - \mu_L)$$

Refractive indices for the right-handed Quartz

Wavelength	μ_R	μ_L	μ_E	μ_o
7020 *A.*	1.53914	1.53920	1.54811	1.53917
3968 *A.*	1.55810	1.55821	1.56771	1.55815

17.6. Analytic treatment of Fresnel's Theory of Rotatory Polarisation. We may also explain, in keeping with Fresnel's principles, the phenomenon of rotatory polarisation by considering the equations of various vibrations. Let the vibration in the plane polarised light incident normally on a quartz plate, cut with faces perpendicularly to the optic axis, be represented by the equation of simple periodic motion, viz.

$$y = 2a \sin \frac{2\pi}{T} t$$

According to Fresnel's idea, this linear vibration is resolved, just on entering the crystal, into two equal and opposite circular motions, which may be represented by the equations of their components along two mutually perpendicular directions.

$$x_1 = -a \cos (2\pi/T)t \qquad \text{[\textit{Right-handed}}$$
$$y_1 = a \sin (2\pi/T)t \qquad \textit{circular motion}$$

and

$$x_2 = a \cos (2\pi/T)\, t \qquad \text{[\textit{Left-handed}}$$
$$y_2 = a \sin (2\pi/T)\, t \qquad \textit{circular motion} \text{]}$$

These circular motions travel along the optic axis of the quartz with slightly unequal velocities, say V_R and V_L, the velocities of the *right* and the *left-handed* motions respectively. The right handed motion, therefore traverses the thickness d of the crystal in the time interval

$$t_R = d/V_R$$

Hence in traversing the thickness d of the crystal, in each component of the R motion, the phase difference will have the value $\frac{2\pi}{T} t_R$ or $\frac{2\pi}{T} \times \frac{d}{V_R}$ (since in complete period T, the phase of the wave changes by 2π). The components of the right handed motion just on emerging from the crystal thickness d along the optic axis, may therefore, be represented by equations

$$x_1 = -a \cos \frac{2\pi}{T}\left(t - \frac{d}{V_R}\right) \qquad y_1 = a \sin \frac{2\pi}{T}\left(t - \frac{d}{V_R}\right)$$

Similarly, the left-handed motion on emergence from the crystal can be represented by the equations

$$x_2 = a \cos \frac{2\pi}{T}\left(t - \frac{d}{V_L}\right) \qquad y_2 = a \sin \frac{2\pi}{T}\left(t - \frac{d}{V_L}\right)$$

The resultant of the two emergent circular motions can be obtained, according to the principle of superposition of wave motions, by the algebraic summation of X and Y components individually. Then we get

$$\begin{aligned} x &= x_1 + x_2 \\ &= a\left[\cos \frac{2\pi}{T}\left(t - \frac{d}{V_L}\right) - \cos \frac{2\pi}{T}\left(t - \frac{d}{V_R}\right)\right] \\ &= 2a \sin \frac{\pi d}{T}\left(\frac{1}{V_L} - \frac{1}{V_R}\right) \sin \frac{2\pi}{T}\left[t - \frac{d}{2}\left(\frac{1}{V_R} + \frac{1}{V_L}\right)\right] \end{aligned}$$

and,
$$\begin{aligned} y &= y_1 + y_2 \\ &= a\left[\sin \frac{2\pi}{T}\left(t - \frac{d}{V_L}\right) + \sin \frac{2\pi}{T}\left(t - \frac{d}{V_R}\right)\right] \\ &= 2a \cos \frac{\pi d}{T}\left(\frac{1}{V_L} - \frac{1}{V_R}\right) \sin \frac{2\pi}{T}\left[t - \frac{d}{2}\left(\frac{1}{V_R} + \frac{1}{V_L}\right)\right] \end{aligned}$$

where, we have assumed $V_R > V_L$ i. e. the crystal is of the right handed variety

The resultant x and y motions, being in the same phase, compound into a rectilinear simple harmonic motion, viz.,

$$s = \sqrt{x^2 + y^2}$$

or
$$s = 2a \sin \frac{2\pi}{T}\left[t - \frac{d}{2}\left(\frac{1}{V_R} + \frac{1}{V_L}\right)\right]$$

Thus, the light emerging from the crystal is still plane polarised but the direction of vibrations is inclined to Y axis i. e. to the direction of vibrations in the incident light by an angle given by

$$\tan\theta = \frac{x}{y} = \tan \frac{\pi d}{T}\left(\frac{1}{V_L} - \frac{1}{V_R}\right)$$

Hence,
$$\theta = \frac{\pi d}{T}\left(\frac{1}{V_L} - \frac{1}{V_R}\right) = \pi d \frac{c}{\lambda}\left(\frac{1}{V_L} - \frac{1}{V_R}\right)$$

or
$$\theta = \frac{\pi d}{\lambda}(\mu_L - \mu_R) \text{ radians}$$

This angle is independent of t, which simply means that at each point of quartz the two circular vibrations combine into linear vibrations. However, θ is proportional to d, indicating that the plane of vibration rotates gradually in the clockwise direction as the plane polarised wave penetrates deeper and deeper into the right-handed quartz along its optic axis.

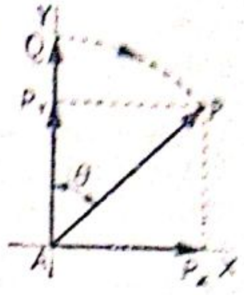


Fig. 17.7.

In the left-handed quartz, since $V_L > V_R$, the angle of rotation of the plane of vibration is given by

$$\theta = -(\pi d/\lambda)\ (\mu_R - \mu_L)$$

On the other hand, if the two circularly polarised components travel with the same speed, as in calcite crystal, then $\mu_L = \mu_R$ and hence $\theta = 0$. The plane polarised light is, therefore, propagated along the optic axis of such crystals with direction of vibrations unaffected. Thus, calcite does not exhibit the phenomenon of rotatory polarisation.

17.7. Experimental Proof of Fresnel's Theory. The experimental proof of the curious resolution of plane polarised light into two circularly polarised components, in the manner described above, was also given by *Fresnel*. He reasoned that if there existed in reality two circular components, which travelled with unequal velocities, they should be refracted by different amounts into the air from an oblique surface of a quartz prism. But he failed to observe this separation, as the angular separation $i_L - i_R$) is too small to be observed. The increase in the angular separation between the two beams was, however, accomplished by him with the help of the ingenious device of employing a train of alternate right and left handed quartz prisms cut and arranged as shown in Fig. 17.8—the optic axis of each prism being in the same direction and perpendicular to the end faces.

The reason that the angular separation between the two beams, is increased at each oblique surface may be very easily explained. Since $V_R > V_L$ in the right handed quarts and in the

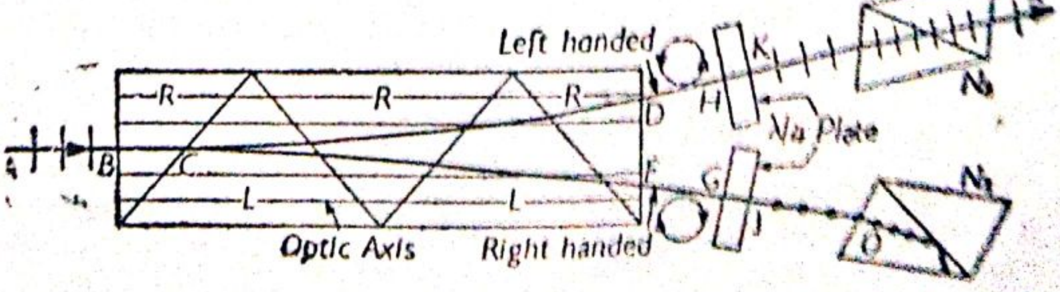


Fig. 17.8. *Fresnel multiple prism for demonstrating the circularly polarised components of plane polarised light.*

left-handed quartz, the circular components simply interchange their velocities i.e. $V_L > V_R$, it therefore follows that the *R* prisms act as the rarer media as compared to the *L* prisms so far as the propagation of the *R* motion is concerned. The reverse of this holds good for the propagation of the *L* motion. Keeping this fact is view, on the first oblique surface, since the *R* motion is passing from rarer (*R* prism) into a denser (*L* prism) medium it will be bent to-wards the boundary normal and hence turned downwards; the *L* motion is passing from a denser (*R* prism) into a rarer (*L* prism) medium; it will therefore be bent away from the normal and hence turned upwards. The reasoning along these lines shows that in passing the second oblique surface, the angular separation between the two beams is further increased. The net result is that the angular separation of the two rays increases at each successive refraction, the two rays finally emerging separated from each other.

The two images of the same source formed by the compound prism are examined by a Nicols prism. It would be observed that their intensities remain independent of the rotation of Nicol. This is also the characteristic of the ordinary unpolarised light when examined by the Nicol. But on introducing a $\lambda/4$ plate of mica, as shown in the figure, it is found that images are extinguished in succession as the Nicol is rotated – the $\lambda/4$ plate transforming the circularly polarised light into plane polarised light, the planes of vibration in the two beams being mutually perpendicular. This conclusively proves that the light emerging from the rectangular quartz block is circularly polarised in opposite directions.

17.8. Specific and Molecular Rotation. The dependence of the rotation produced by an optically active substance dissolved in a non-active solvent upon the concentration of the solution has led to a large number of applications *e.g.*, in the estimation and analysis of sugars. For a comparison of optical activity, therefore, a unit is adopted. This is called *specific rotation* and is defined by the following equation.

Specific rotation

$$= \frac{\text{Rotation produced by 10 cm. length of the solution}}{\text{Density of the solution in gms. per c c.}}$$

Thus if θ be the rotation produced by 'l' decimetres of the solution and ω be the amount of the optically active substance dissolved in one hundred c. cs. of the solvent then the specific rotation or the rotatory power α is given by

$$\alpha = \frac{100\,\theta}{l\omega} \text{ or } \theta = \frac{\omega\,\alpha\,l}{100}$$

The product of specific rotation and the molecular weight of the optically active substance is termed as *molecular rotation* or *molecular rotatory power*.

The specific rotation of an optically active liquid *e.g.* turpentine is the rotation produced by one decimetre column of liquid divided by its density. For a crystalline substance like quartz, the specific rotation is merely the angle of rotation produced by 1 mm. thickness of the crystal along the optic axis.

To distinguish between dextro and levo-rotatory substances the specific rotation of the former is written positive while for the latter it is written negative.

The specific rotations of a large number of substance dissolved in various non-active solvents have been measured. It has been found from these experiments that the specific rotation varies not only with the nature of the solvent but also with the concentration of the active substance present. Thus if P, Q and R are constants and C be the concentration of the active substance, the specific rotation is given by the equation

$$\alpha = P+QC+RC^2$$

The specific rotation of a substance also depends upon the temperature and the wavelength of light used and is usually written in the form $\left[\alpha\right]_t^D$ where 't' stands for the temperature and D for the D lines of sodium ($\lambda_1 = 5890°A$, $\lambda_2 = 5896°A$): Thus for quartz the specific rotation at any temperature t is given by

$$\left[\alpha\right]_t^D = 21.72\left\{1+0.000147\,(t-20)\right\}$$

In the case of sugar the variation of specific rotation with temperature is represented by

$$\left[\alpha\right]_t^D = 66.5-0.0184\,(t-20)$$

Thus the specific rotation of sugar at 20°C is 66.5°. The rotatory powers of a few substances are given in the following table :

$\lambda = 5893°A$

Active Substance	Solvent	$\left[\alpha\right]_D^{20°}$
Cane Sugar	Water	+66.5°
Glucose	Water	+52.5°
Fructose	Water	−91.5°
Turpentine	Pure	−37°
Nicotine	Pure	−162°
Camphor	Alcohol	+41°

17.9. Polarimeters. The famous scientist *Biot* discovered that a mixture of an optically active substance with an optically inactive one exhibits a rotatory power proportional to the concentration of the optically active compound present. This discovery has been applied in commerce and industry, for the estimation of the quantity of sugar in the presence of an optically inactive impurity. Consequently, a number of instruments called *polarimeters* have been designed for the accurate measurement of the angle of rotation. A polarimeter calibrated to read directly in percentage of cane sugar in the solution is known as *saccharimeter*.

The simplest form of polarimeter consists of two nicols N_1 and N_2, capable of rotation about a common axis and mounted a little distance apart. This simple arrangement, first employed by *Mitcherlich* and described in sec. 17.1, fails to help us in finding accurately the angle of rotation, owing to the difficulty in ascertaining one position of the analyser for complete extinction of the transmitted plane polarised light. This is due to the fact that the analyser can be rotated through an appreciable angle from its setting for complete extinction without allowing any appreciable amount of light to pass through it. Thus the field of view remains totally dark not for a single position but for a considerable range of the rotation of the analyser.

In order to increase the sensitiveness of the pair of crossed Nicols, polarimeters have been designed on what is known as *half shadow principle*. In these instruments, the field of view is divided into two halves, presented side by side. Consequently, the analyser can be set accurately for the equality of brightness of the two halves. It should be remarked that the eye is a better judge of equality of brightness than either the point of complete extinction or maximum brightness of the whole field of view.

17.10. Laurent half shade. Laurent removed the drawbacks of the simple polarimeter by interposing between the two nicols a device known as *Laurent half shade*. It consists of a semi-circular piece of quartz Q cut parallel to the optic axis (which is in turn parallel to CD). The thickness of the quartz plate is such that a phase difference of π is introduced between the E and O waves during their passage through it. In other words this semi-circular piece CAD is essentially a half wave plate made of quartz. To this piece, another semi-circular piece CBD of glass is joined along CD so as to make a composite circular plate $CADB$. The thickness of this glass half G is so adjusted that it transmits and absorbs the same amount of light as the quartz half Q does (Fig. 17.9).

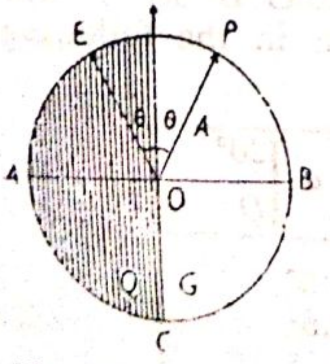


Fig. 17.9. Laurent's plate

This circular plate is known as a half shade and is placed just behind the polariser in such a manner that the quartz and glass halves both cover a semi-circle each of the field of view. Its action may be explained as follows ;

Let the vibration plane of the light incident on this glass quartz combination be parallel to *OP* inclined at an angle θ to the optic axis *CD* of the quartz half So far as the glass half is concerned the vibrations of light transmitted through it will remain in the same plane. But a change occurs in the quartz half.

To understand this change suppose that the vibrations incident upon the first face of the half shade are represented by

$$P_i = A \sin \omega t$$

where *A* is their amplitude and the subscript '*i*' stands for the incident wave. This amplitude can be resolved along the two principal directions of the quartz half *i. e.* along the optic axis (*Y* direction) and perpendicular to the optic axis (the *X* direction). The components of *A* along the *X* and *Y* directions are respectively *A* sin θ and *A* cos θ. Hence the incident plane polarised vibrations contained in the plane *OP* can be written as

$$x_i = A \sin \theta \sin \omega t \qquad [O\text{–wave}]$$

$$y_i = A \cos \theta \sin \omega t \qquad [E\text{–wave}]$$

These two mutually perpendicular vibrations travel with unequal speeds along the same direction perpendicular to both the *X* and *Y* directions defined above. Since the quartz half is essentially a half wave plate, the two vibrations which emerge out of the quartz half will be

$$x_e = A \sin \theta \sin (\omega t + \pi)$$

$$= -A \sin \theta \sin \omega t$$

$$y_e = A \cos \theta \sin \omega t$$

where the subscript '*e*' stands for the emergent beam. The resultant vibration wiil be given by

$$R = \sqrt{x_e^2 + y_e^2} = A \sin \omega t$$

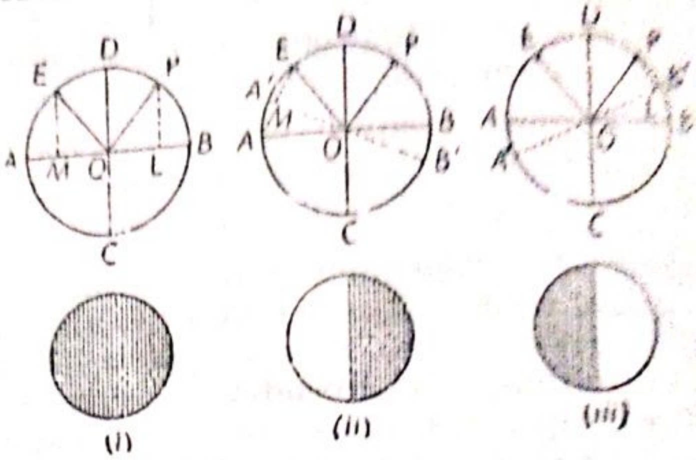
and the angle φ which the plane of *R* makes with the axis of *X* is given by

$$\tan \phi = y_e / x_e = -\cot \theta$$

$$\therefore \quad \phi = (\pi/2 + \theta)$$

It is, therefore, clear that the vibration plane of light emerging from glass half is *OP* while that of the light emerging from the quartz half is *OE* making the same angle θ with the optic axis as does *OP*.

The working of the half shade can now be understood with the help of Fig. 17.10. If the principal plane of the analyser is parallel to AOB, the components OL and OM of the vibrations emerging out of the two halves will be equal and therefore, they will appear equally bright [Fig. 17.10 (*i*)]. If the principal plane of the analyser is rotated by a small angle in the clockwise direction [Fig. 17.10 (*ii*)] the vibrations from the glass half will be completely cut off (provided OP is normal to $A'B'$) while a component OM of the vibrations emerging out of the quartz half will be transmitted. In general, the glass half in this case will be less bright as compared to the quartz half. If on the other hand the analyser is turned through a small angle in the anti-clockwise direction [Fig. 17.10 (*iii*)] the component of the vibrations emerging from glass half will increase while the component emerging from the quartz half will decrease and if OQ is normal to $A'B'$ the quartz half will be dark and the glass half will be bright. Thus the half shade serves the purpose of dividing the field of view in two halves. The device is so accurate that if the principal plane of the analyser is rotated through even a small angle with respect to AOB, a marked change in the intensity of the two halves is observed.



(*i*) (*ii*) (*iii*)

Fig. 17.10.
Principle of Half-shade Polarimeter.

The scheme of the polarimeter employing a half shade is shown in Fig. 17.11. Here S is a source of monochromatic light usually a sodium lamp. The lens L is employed to condense light on to the nicol prism P which serves as the polariser. Immediately behind the polariser the half shade plate H is kept. The optically active liquid is in the tube O provided with plane transparent glass windows at the ends. The analyser A is mounted coaxially

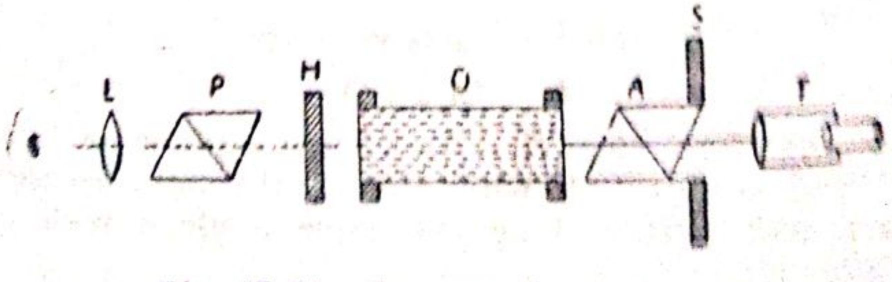


Fig. 17.11. Laurent Saccharimeter.

and at the same height as the polariser and the tube O. It can be rotated and its orientation read on the graduated scale S. (The polariser is also fitted with a similar device in order to change the half shadow angle θ). Lastly there is a short focus telescope T focussed on H and mounted in a manner similar to others.

To measure the optical rotation of any solution the tube is first filled with the pure solvent and introduced at its position. The analyser A is turned to obtain the condition of equal brightness of the two halves of the field of view. This reading of the analyser is noted.

The solution having a known concentration of the solute is now filled in the tube and the process repeated thereby obtaining a second reading for the analyser. The difference in the two readings gives the rotation produced by the solution. Knowing the length of the tube the specific rotation can be calculated.

To obtain maximum accuracy with the instrument the half shadow angle θ [Fig. 17.9] is set at the proper angle by rotating the polariser. The accuracy depends upon this angle because of the simple reason that the components of the vibrations (emerging out of the two halves) transmitted through the analyser will depend upon it.

The device has, however, a disadvantage for it can be used only with a light source having the wavelength for which the quartz half serves as a half wave plate.

17.11. Biquartz. Another device which can be used instead of the half shade is the Biquartz. As the name suggests, it consists of two semi-circular pieces of the quartz NYN and $NY'N$ cut perpendicular to the optic axis and joined together along the diameter NN to make a composite circular plate (Fig. 17.12). One of these plates say $NY'N$ is dextrorotatory while the other is levorotatory. The thickness of these plates is so adjusted that the rotation introduced for the greenish yellow region of the spectrum is 90°. This thickness is 3.75 mm. for quartz.

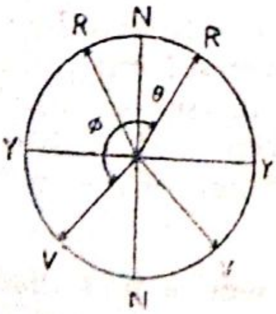


Fig. 17.12. Principle of Biquartz.

Since the plates are cut perpendicular to the optic axis light travels along the optic axis through these plates and therefore, the phenomenon of rotatory dispersion takes place. As a result of this the longer wavelengths have their planes of vibrations rotated through a smaller angle as compared to the shorter ones. Thus if the principal plane of the polariser is parallel to NN, the red region is rotated through an angle θ and the violet region through an angle ϕ in the two halves such that ϕ is greater than θ. The intermediate wavelengths will be rotated through angles intermediate between ϕ and θ.

If the principal plane of the analyser is parallel to NN [Fig. 17.13] the greenish yellow portion will not be transmitted through the analyser. Only the wavelength ranges at the two ends of the visible spectrum can be transmitted equally from the two halves. Their resultant colour in this case will be a mixture of red and blue namely greyish violet which is called the tint of passage.

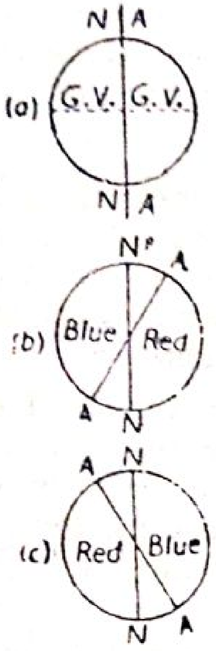


Fig. 17.13.

If the analyser is turned through a small angle in the clockwise direction [Fig 17.13 (b)] the longer wavelengths from the right half will be transmitted to a greater degree than the shorter ones. For the left half, however, just the reverse is the case—the shorter wavelengths are transmitted to a greater degree than the longer ones. In this particular setting, therefore, the right half will appear red while the left half will appear blue. If on the other hand the analyser is turned in the anticlockwise direction [Fig. 17.13 (c)] the left half will appear red while the right half will appear blue.

It is, therefore, obvious that the tint of passage is a very sensitive position. A slight rotation of the analyser with respect to this position makes one half of the field of view blue and the other half red and *vice versa*. This position is, therefore, employed for the accurate measurement of the angle of rotation. For this purpose, the biquartz is kept in the position occupied by the half shade [Fig. 17.11]. The tube is filled with the solvent and introduced in its position. The reading of the analyser for the tint of passage setting is noted. The process is repeated with the solution. The difference between the two readings of the analyser gives the rotation produced by the solution.

The biquartz possesses a great advantage over a half shade. It can be used with white light but the rotation is obtained for the wavelength which is quenched when the two nicols are parallel. This is usually the wavelength of sodium light $\lambda = 5893$°A.

The disadvantages of Biquartz polarimeter are as follows :—

(1) Even if colourless optically active substances are examined, it is practically impossible to achieve the accurate setting of the analyser for which the tint in both the halves of the prism is the same. This is due to the rotatory dispersion produced by the

optically active substance itself, and so some error is introduced in measuring the angle of rotation. This error is considerably increased when the optically active substance is coloured.

(2) It is impossible for a colour blind person to use this method, Even a man with normal vision will get widely different readings for the angle of rotation, as the relative sensibility curves of individual eyes (to light of different wavelengths) are not identical but show considerable variation.

17.12. Lippich's Two Prism Polariser. *Lippich's* polarimeter is also based on the half shadow principle and can be used with light of any wavelength The essential parts of this polarimeter are sketched in Fig. 17.14. The polarising system consists of a bigger Nicol prism N_1 followed by a smaller Nicol N_2 covering half the field. The principal sections of N_1 and N_2 are mutually inclined at a small angle 2ϕ, called the half shadow angle. The field of view as seen through the telescope and the analysing Nicol is, therefore, divided into two halves separated by a sharp line—the image of the near edge T of the prism N_2. One half of the field is illuminated by plane polarised light produced by the light which passes through N_1 and N_2 and hence the emerging light has vibrations in the principal section of N_2. The other half is illuminated by light which passes through N_1 only and hence the emerging light has vibrations in the principal section of N_1. Furthermore, the amp[itude of vibration in the plane polarised light from N_2 is slightly less than the amplitude of vibration of light emerging from N_1 only, because a small fraction of the later amplitude in the upper half of the beam emerging from N_1 is totally reflected as ordinary vibrations within the smaller Nicol N_2, while the amplitude of the lower half of the beam emerging from N_1 remains unchanged. (O rays are not shown in N_1.)

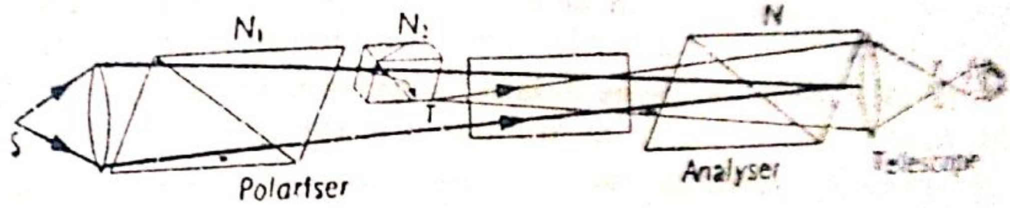


Fig. 17.14. Lippich's (two prism polariser) polorimeter.

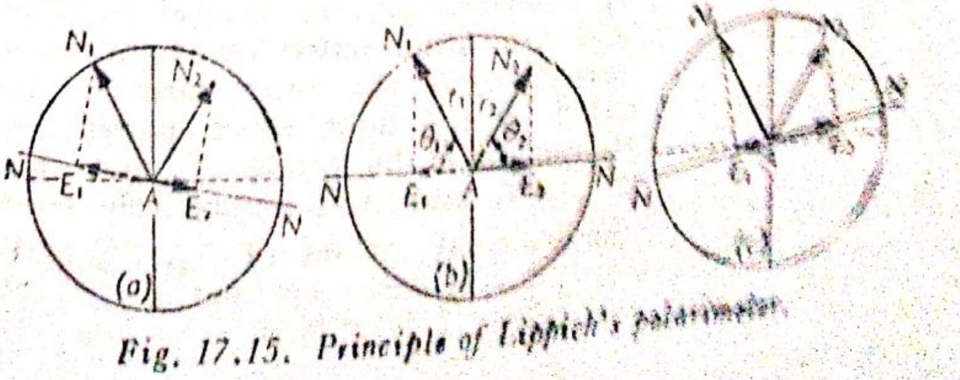


Fig. 17.15. Principle of Lippich's polarimeter.

Let the principal sections of N_1 and N_2 be represented by AN_1 and AN_2. Accordingly, if the principal section of the analyser is at right angle to AN_2 one half of the field is obviously dark; but if it is at right angle to AN_1, the other half is dark. Consequently, for an intermediate position, show in Fig. 17.15 (*b*) by NN, so that the relation

$$r_1 \cos \theta_1 = r_2 \cos \theta_2$$

is satisfied, the two halves of the field are equally bright. A slight rotation of the analyser from this setting in either direction causes the transmitted component of one vibration to increase rapidly and that of the other to decrease rapidly, thereby causing the intensities of corresponding halves of the field to increase and decrease rapidly. The analyser can be, therefore, very easily set for the position of equality of brightness of the two halves of the field. Thus, Lippich's polarimeter employing two Nicol prisms as polariser is exactly similar in action to Laurent's half shade polarimeter. It has a distinct advantage over the latter in as much as light of any wavelength can be employed while working with it which is, however, not possible in using Laurent's polarimeter.

17.13. Lippich's Three Prism Polariser. In modern polarimeters, the accuracy in the measurement of the angle of rotation is increased by dividing the field of view into three parts. The two outer parts are equally illuminated for every setting of the analyser while the central portion which may be illuminated differently from the adjacent parts, has to be adjusted for the same intensity (as that of outer parts) by the help of the analysing Nicol. In modern polarimeter this is achieved by employing a polarising system consisting of three Nicols N_1, N_2 and N_3 arranged as shown in Fig. 17.16. The principal sections of N_2 and N_3 are mutually parallel but slightly inclined to that of the bigger Nicol N_1. Accordingly, the central parts of the field are illuminated by light emerging from N_1 while the outer parts are illuminated by the light which passes through N_1 and one of the prisms N_2 and N_3. Let AN_1 AN_2 and AN_3 respectively represent the principal sections of N_1, N_2 and N_3. Consequently, AN_1, AN_2 and AN_3 also represent the vibrations incident on the analysing Nicol. If the analyser is set in a position

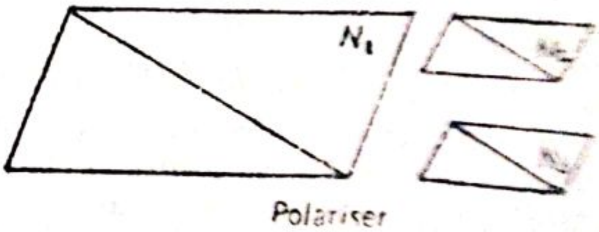


Fig. 17.16. Lippich's three prism Polariser.

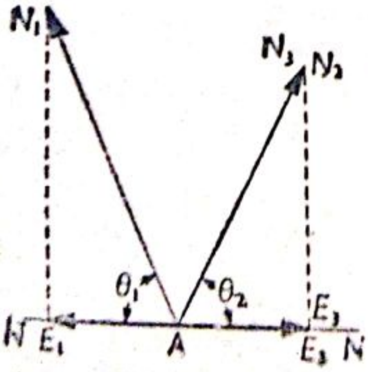


Fig. 17 17.

so that its principal section occupies the position *NN* satisfying the relation

$$AN_1 \cos \theta_1 = AN_2 \cos \theta_2 = AN_3 \cos \theta_3$$

the three parts of the field will be uniformly illuminated. A slight rotation of the analyser from this setting in either direction causes the intensity of the central portion of the field to be markedly different from that of the two outer portions and so the accurate setting of the analyser for uniform illumination of the field can be very easily accomplished.

This polarimeter is used for most accurate work. In the half shadow instrument we may match the two halves at a wrong setting of the analyser. This error is not possible with the polarimeter employing three prism polarising system, for a slight displacement of the eye from the axis would cause the side to-wards which the eye is displaced, to appear too bright as compared to the other side. Hence, the experimenter would immediately adjust his eye on this axis. Owing to the same reason, the experimenter can correct any slight error in the alignment of the light source with the optical axis of the polarimeter.

Problems—Chapter 17

1. State the laws of rotatory polarisation. Give Fresnel's hypothesis for rotatory polarisation and derive the formula for the rotation produced by quartz. Give the experimental verification of this formula

2. Discuss the phenomenon of rotation of the plane of polarisation of light by optically active materials. Give the necessary theory.

Show that the rotation of the plane of vibration is given by

$$(\pi d/\lambda)\,(n_A = n_C)$$

where n_A and n_C are respectively the refractive indices of the crystal in the direction of the optic axis for anti-clockwise and clockwise circularly polarised light and '*d*' is the thickness of the crystal plate.

3. What is specific rotation ?

Give with full details the construction and working of a Laurent's half shade polarimeter. Explain how you would use it to determine the specific rotation of sugar.

4. Describe briefly the various methods that may be used to increase the sensitivity of a pair of crossed nicols in polarimetry.

5. What is optical rotation ? Describe a polarimeter using a biquartz plate and explain how you would use it to find the specific rotation of an optically active substance.

Discuss the relative merits of biquartz and half-shade polarimeters.

6. Calculate the specific rotation of sugar solution from the following data :

Length of tube containing solution = 11 cm.
Volume of solution = 44 c.c.
Amount of sugar in solution = 8 gm.
Angle of rotation = 4°07′

7. A tube 20 cm. long, filled with a solution of 15 gm. of cane sugar in 100 c.c. of water is placed in the path of polarised light. Find the angle of rotation of the plane of polarisation if the specific rotation of cane sugar is 66°. [*Kanpur, 1971*]

8. A 20 cm. long tube containing sugar solution is placed between crossed nicols and illuminated by light of wavelength 6×10^{-5} cm. If the specific rotation of sugar is 60° and the optical rotation produced is 12°, what is the percentage of sugar in the solution ?

9. A solution of camphor in alcohol in a tube 20 cm. long is found to rotate the plane of vibration of light by 27°. What is the mass of camphor in unit volume of the solution ? The specific rotation of camphor is + 54°.