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Optical Rotatory Dispersion. Part I: The Natural and Magnetic Rotatory Dispersion in Quartz of Light in the Visible Region of the Spectrum

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IX. *Optical Rotatory Dispersion.—Part I. The Natural and Magnetic Rotatory Dispersion in Quartz of Light in the Visible Region of the Spectrum.*

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1. *Introduction.*

THE phenomena of rotatory dispersion are of special interest from two points of view. To the chemist they afford the most hopeful clue to the solution of the difficult and much discussed question as to why a particular substance possesses a given rotatory power. To the physicist, they contribute important data for the discussion of the mechanism involved in the propagation of light through matter, on the lines laid down by MAXWELL, in 1869, and extended by the subsequent work of SELLMEIER, VON HELMHOLTZ, LARMOR, DRUDE, and others. On the chemical side, progress depends mainly on the accumulation of data as to the rotatory dispersion of a large number of substances for a few selected wave-lengths; in particular also upon the development of simple and effective laboratory methods, permitting of the measurement of rotatory dispersion being made a part of the ordinary routine of every laboratory in which polarimetric studies are undertaken. Progress on the physical side demands that a few selected substances shall be examined with light of many

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wave-lengths, extending over the whole of the available range of the spectrum, and that the measurements shall be made with the highest degree of accuracy.

The present investigation of rotatory dispersion, which has been in progress continuously since 1905, is concerned with the natural rotatory power of crystals and of optically active liquids, and also with the rotatory power induced in them by a magnetic field. It was undertaken primarily from the chemical standpoint with a view to obtaining information as to the variations of rotatory power with wave-length in organic liquids. But it was soon found that the two lines of investigation indicated in the preceding paragraph were inseparable, since the only satisfactory way of establishing standard laboratory methods for everyday use was to make measurements of rotatory dispersion with light of every available wave-length and to strive persistently to increase the degree of accuracy attained. Only in this way could adequate experience be gained as to what was possible in work of this kind. Thus, after making observations with light of some thirty wave-lengths, it was found that measurements of the highest degree of accuracy could be made with twenty-four lines in the spectra of the elements Li, Na, Tl, Zn, Cd, Hg, Cu, Ag; nine of these were used in the earliest series of laboratory-measurements, but the number was soon reduced to seven and finally to four (or even two) lines, which were found to give an adequate representation of the rotatory dispersion of the simpler organic compounds.

The measurements which are now described of the rotatory power of quartz for twenty-four wave-lengths in the visible region of the spectrum were undertaken originally in order to test the methods which were being devised for general laboratory use. But it was soon apparent that measurements might be made which would be much more accurate than those that had been recorded hitherto, even including the measurements of SORET and SARASIN which have been accepted as standards during the past thirty years. The observations were therefore continued and extended in order to provide material which could be used in testing with the greatest stringency the relationships between rotatory power and wave-length which have been put forward by DRUDE and others. Measurements of magnetic rotatory dispersion in quartz were also made, in order to test, under more stringent conditions than those which have generally been adopted, the validity of G. WIEDEMANN'S Law of the proportionality of natural and magnetic rotatory dispersions.

Experiments are in progress to extend the measurements of the natural rotatory power of quartz in such a way as to cover the whole of the spectrum transmitted by the mineral. Up to the present, measurements have been made from λ 17000 to λ 2327; it is hoped that, by the adoption of new methods, it may be possible ultimately to carry the experiments into the unexplored regions lying beyond these limits, but this final extension will be accomplished only after overcoming a number of new and serious difficulties.

Measurements have also been made of natural and magnetic rotatory dispersion in some fifty or sixty paraffinoid compounds, including a series of twenty-three optically-active alcohols prepared by Dr. R. H. PICKARD; these will be described in a separate communication as soon as two series of active alcohols now under examination have been completed and tested.

2. *General Review of Previous Observations and Methods.*

Although much work has been done on the optical rotatory power of organic compounds, it is remarkable that almost the whole of the observations have been made with light of one colour—the yellow doublet of sodium. Observations have been made occasionally with light of other wave-lengths, usually by physicists who have proceeded from the study of quartz or of sodium chlorate to analogous observations on the rotatory dispersion of some optically active liquid such as turpentine or ethylic tartrate. But the measurement of rotatory dispersion has never become a part of the normal work of the chemical laboratory. Chemists have been content to devote their energies to the elucidation of the effect of solvents, of temperature and of chemical constitution on the rotatory power of substances for sodium light, usually without paying attention to the influence of the nature of the light on the property in question.* This limitation is the more remarkable since many of the substances selected for examination are known to exhibit anomalous rotatory dispersion, and cannot, therefore, be expected to exhibit any simple relationships until attention is directed to the whole course of the rotatory dispersion-curve rather than to any one arbitrarily selected point.

Measurements of magnetic rotatory dispersion have been even more uncommon. PERKIN made a few scattered observations with lithium and thallium in addition to sodium light; a few measurements have also been made in order to determine the form of the dispersion-curve or to test the validity of WIEDEMANN'S Law of the proportionality between natural and magnetic rotatory dispersion, but practically the whole of the literature of magnetic rotatory power, like that on natural optical rotation, is expressed in terms of the effects produced on yellow sodium light.

The influence of wave-length on the optical rotatory power of crystals has been studied much more fully than in the case of liquids. Of some thirty substances which show this property, about one-third have been examined with light of three or more wave-lengths. In the case of quartz and of sodium chlorate, the observations have been extended by SORET, SARASIN, and GUYE ('Geneva Archives,' 1882 [III.], vol. 8, 5–59, 98–132, 201–228; 1889 [III.] vol. 22, 130) from the visible to the ultra-violet region of the spectrum. Observations of the optical rotatory power of quartz in the infra-red region have been made by E. CARVALLO ('Comptes Rendus,' 1892, vol. 114, 288) and by R. DONGIER ('Comptes Rendus,' 1897, vol. 125, 228). As questions of solvent, concentration and chemical constitution enter scarcely at all into the study of the optical rotatory power of crystals, this property has been investigated mainly from the standpoint of crystallography or of pure physics. In addition to the influence of the wave-length of the light, the effect of temperature has been the problem mainly studied. In particular, the optical rotation produced by quartz plates has been measured over the range of temperature from +840° C. (JOUBERT, 'Comptes Rendus,' 1878, vol. 87, 497) to −190° C. (MOLBY and GIBBS, 'Phys. Rev.,' 1910, vol. 30, 77–91; vol. 31, 291–310).

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* See, for instance, Prof. FRANKLAND'S review of the subject in his Presidential Address to the Chemical Society, March 28, 1912.

NOTE.—It does not appear to be generally known that chemists and physicists have adopted different conventions as regards the sign of an optical rotation, so that dextro-quartz and dextro-camphor actually rotate the plane of polarisation in opposite directions. In the case of dextro-quartz the rotation is clockwise to an observer looking along the path of the light; in the case of dextro-camphor the rotation is clock-wise as viewed from the eye-piece of the polarimeter.

The methods used in measuring rotatory dispersion differ from one another mainly in two respects:—

1. As regards the source of light, which may give (*a*) a continuous spectrum or (*b*) a line-spectrum, either monochromatic or multichromatic;
2. As regards the methods used in selecting a line or portion of the spectrum, which may depend (*a*) upon a spectroscope whereby the light is resolved either before or after it passes through the polarimeter or (*b*) upon the use of absorption-screens.

BROCH'S *Method.*—The earliest measurements of rotatory dispersion were made on quartz with the help of sunlight falling upon a vertical slit; after passing through a simple polarimeter (consisting of movable polariser, quartz plate and analyser) the light was resolved by means of a single glass prism, without a telescope or eye-piece; the polariser was rotated until a dark extinction-band was superposed on one after another of the Fraunhofer lines from B to G (BROCH, 'Ann. Chim. Phys.,' 1852, vol. 34, 119–121; from 'Repertorium der Physik,' 1846, vol. 7, 113). The same method was suggested in general terms a year previously by FIZEAU and FOUCAULT ('Comptes Rendus,' 1845, vol. 21, 1157). This method was improved by G. WIEDEMANN ('Pogg. Ann.,' 1851, vol. 82, 215–232), who added a telescope to the refracting prism, and with this apparatus made the first exact observations of the natural rotatory dispersion of liquids (turpentine and lemon oil for the Fraunhofer lines B to G) and of their magnetic rotatory dispersion (carbon disulphide and turpentine for the Fraunhofer lines C to G), and discovered the proportionality of the two rotatory powers over a series of wave-lengths (turpentine for the Fraunhofer lines C, D, E, B, F gave the ratios 4·07, 4·12, 4·10, 4·14, 4·12). A. ARNDTSEN used a cross-wire in the telescope to locate the positions of the Fraunhofer lines and measured the rotatory dispersion of sugar, tartaric acid,* malic acid and camphor. J. STEFAN ('Wien. Ber.,' 1864 [II.], vol. 50, 88–124) developed this method of working into its final form by using, in series with a simple polarimeter, a complete spectroscope, with a prism of crown-glass, flint-glass, water or quartz, or a grating, to refract the light; he used an artificial source of light,† measured the positions of the extinction-bands on the circle of the goniometer (polariser and analyser fixed) and, after establishing a linear relationship between the rotatory power of the quartz and the refraction of the prism, calculated the rotatory power of the quartz for the seven Fraunhofer lines B to H. STEFAN showed that, whilst the rotatory dispersion could not be represented by BIOT'S formula $\alpha = k\lambda^{-2}$, a satisfactory concordance between theory and experiment could be obtained by using CAUCHY'S formula $\alpha = k_1 + k_2\lambda^{-2}$. STEFAN'S method† was used by V. VON LANG ('Wien. Ber.,' 1875 [II.], vol. 71, 707–714) in measuring the influence of temperature upon the optical rotatory power of quartz; he calibrated the spectroscope by means of lithium, sodium and thallium flames and brought the extinction-bands to these three positions by rotating the analysing Nicol prism. A complete spectroscope in series with a simple polarimeter was also used by SORET and SARASIN ('Geneva Archives,' 1882 [III.], vol. 8, 5–59, 98–132, 201–228) with solar light as illuminant and Fraunhofer lines as standards of wave-length in their measurements of optical rotation in quartz; the same arrangement was used by GUYE ('Geneva Archives,' 1889 [III.], vol. 22, 130) with artificial light in his measurements of optical rotation in sodium chlorate.

LIPPICH'S *Method.*—In order to read rotations which are too small in magnitude to give rise to narrow bands, LIPPICH ('Wien. Ber.,' 1885 [II.], vol. 91, 1070) passed the light through a spectroscope *before* it reached the polarimeter; the spectrum, instead of being received by an eye-piece, fell upon a second slit,

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* BIOT, who discovered the phenomenon of anomalous rotatory dispersion in tartaric acid ('Mem. Acad. Sci.,' 1838, vol. 15, 93; vol. 16, 229; 'Ann. Chim. Phys.,' 1844, (3), vol. 10, 5, 175, 307, 385; vol. 11, 82; 1850, vol. 28, 215, 351; vol. 29, 35, 341, 430), merely used blocks of the spectrum, in the red, yellow, green, &c., without attempting to locate accurately their positions in the spectrum.

† LANDOLT ('Optical Rotating Power,' 1902, p. 423) attributes to VON LANG the method described by STEFAN eleven years previously of using artificial light in place of sunlight.

which formed the source of light for the polarimeter. The difficulty of having to move the light-source, collimator and prism for every fresh colour is effectively overcome by using a constant-deviation prism (CHRISTIE, 'Roy. Soc. Proc.,' 1878, vol. 26, 8) mounted on a spectroscope in which both slits are fixed and the colour is varied by merely rotating the prism (see F. TWYMAN, 'Phil. Mag.,' 1907, vol. 13, 481). LIPPICH's method of working has the great advantage that it can be applied to his half-shadow instruments with a double or triple field.

LANDOLT'S *Method.*—Another method in which a continuous spectrum is used as a source of light is that of LANDOLT ('Sitz. Akad.,' Berlin, 1894, 323; 'Ber. Deut. Chem. Ges.,' 1894, vol. 27, 2872), in which five filters are used to separate light in the red, yellow, green, light blue and dark blue portions of the spectrum, the optical mass-centres of the transmitted light at wave-lengths 6659, 5919, 5330, 4885, and 4482 being near to those of the Fraunhofer lines C, D, E, F, G at 6563, 5893, 5270, 4861, and 4308 respectively. This method, which avoids the use of a spectroscope, is the only one that has been adopted widely in chemical laboratories (WINTHER, 'Zeit. Physikal. Chem.,' 1907, vol. 60, 563; WALDEN, 'Zeit. Physikal. Chem.,' 1906, vol. 55, 1; TSCHUGAEFF, 'Zeit. Physikal. Chem.,' 1911, vol. 76, 469; GROSSMANN, 'Zeit. Physikal. Chem.,' 1910, vol. 75, 129).

PERKIN'S *Method.*—The use of a small direct-vision spectroscope in front of the eye-piece of the polarimeter was introduced by Sir WILLIAM PERKIN as a method of purifying the flame-spectrum of sodium. But it is capable of a much wider application as affording the simplest and one of the most efficient means of measuring rotatory dispersion in ordinary laboratory practice. PERKIN used it in reading the magnetic rotation of red lithium and of green thallium light, salts of these metals being added to a platinum boat, already containing a sodium salt, heated by a jet of oxygen in the centre of the flame of a Bunsen burner. Used in conjunction with the lithium and sodium flames and the enclosed mercury arc, PERKIN'S method satisfies all the requirements of a standard laboratory method for modern use.

In reviewing the methods described above, it is necessary to emphasise the fundamental requirement for accurate polarimetric work, namely, that *the field of the polarimeter must be uniformly lighted with monochromatic light.* Of the methods in which a continuous source of light is used, BROCH'S method cannot be used to measure optical rotations of small magnitude and (as will be shown in a later paper) it can be improved considerably even in the case of large rotations by using a polarimeter with a triple field and replacing the continuous spectrum by a crowded line spectrum, such as that of the iron arc; LANDOLT'S method, on the other hand, breaks down completely in the case of rotations exceeding a very few degrees, the large blocks of spectrum employed giving no extinction at all with rotations of larger magnitude; the LIPPICH method is also unsatisfactory, especially in the case of large rotations, on account of stray light; this point is discussed in a later paragraph (p. 266). Of all the methods described above, the only one that is available for the accurate measurement of rotations, both of large and of small magnitude, is that of PERKIN, in which a light-source containing two or three strong spectrum lines is resolved by means of a direct-vision prism placed in front of the eye-piece of the polarimeter.

3. *New Methods and Devices for Measuring Rotatory Dispersion.*

PERKIN'S method gives excellent results when applied to light comprising only a few spectrum lines. It is very economical of light and, after repeated trials of other methods, has been found to be the best method now available for reading:—

The red lithium line	6708·2
The green thallium line	5350·65
The violet mercury line	4358·58.

It can also be used very satisfactorily to read :—

The green mercury line	5460·97
The yellow sodium doublet	{5890·19 5896·16}
The yellow mercury doublet . . .	{5769·16 5790·49}.

The two doublets are only available for reading small rotations and must be resolved into separate lines if large rotations are to be observed.

The flame spectra of lithium, sodium and thallium, and the arc spectrum of mercury (LANDOLT, p. 433; DISCH, 'Ann. Phys.,' 1903 (IV.), vol. 12, 1155; SCHÖNROCK, 'Zeit. Vereins Deutsch. Zuck.-Ind.,' Tech. Part, 1903, vol. 53, 652), giving the six colours shown above, were the only line spectra that had been effectively made use of in polarimetry* at the time when the present investigation was commenced. In order to increase the number of available light-sources, recourse was had to the brilliant line-spectra of the metallic arcs, as described in Section 4 of the paper. With these new light-sources PERKIN's method can no longer be used, the glare of adjacent lines being so great that it is impossible to take accurate readings of the line that is being brought to extinction. Under these conditions it is necessary to resolve the light spectroscopically before it enters the polarimeter. This was done by means of a constant-deviation spectroscope, the instrument being arranged so that an image of the slit fell upon the triple-field of a polarimeter in the position normally assigned to the eye-piece of the spectroscope; a wide slit opening symmetrically was inserted immediately in front of the triple-field and could be used to cut off the light from lines immediately adjacent to the one under observation.

At an early stage in the work it was discovered that, whilst this arrangement was fairly satisfactory for lines in the middle of the spectrum, it was seriously defective for lines in the red and blue, on account of stray light from the green and yellow lines. Thus readings of magnetic rotation in carbon disulphide were depressed from 70°·90 to 69°·33 in the case of the violet line Hg 4359 and from 58°·95 to 58°·28 in the case of the blue line Cd 4678 by stray light of longer wave-length. The readings, 40°·19, of the green line Hg 5461 were not affected by stray light; but the value for the yellow doublet Hg 5780 was raised from 35°·14 to 35°·19 and that for the red line Cd 6438 from 27°·52 to 27°·68 by stray light of shorter wave-length; the errors are here much less than in the case of the blue and violet lines but are sufficiently serious to destroy the value of the measurements as exact observations.

This fault, which does not appear to have been recognised previously, is inherent in all devices of the Lippich type, in which the light is resolved spectroscopically

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* DISCH had also taken readings with the red hydrogen line 6563·04 and with the mercury line 4916·41, but had been obliged to use half-shadow angles up to 30°.

before it enters the polarimeter. It was overcome by PERKIN's device of using a direct-vision prism in conjuction with the eye-piece to throw out the stray light. This prism forms an essential part of the apparatus and can only be dispensed with under exceptional circumstances some of which are discussed later in the paper. When the prism at the eye-piece was required to aid in the resolution of a close doublet or in the elimination of a satellite or to throw out stray light from a closely-adjacent line, direct-vision prisms were used which had been specially constructed with a centre-prism of glass of refractive index 1·92; three of these prisms were used for the red, green and blue portions of the spectrum respectively. A greatly-increased dispersion was secured with the help of two prisms, specially constructed from the same dense glass, of the Rutherford pattern (see fig. 1), in which the angle of the central prism is so great that light travelling parallel to the base would be totally reflected at an air-surface but is actually brought in and out of the prism at grazing incidence by prisms of light glass cemented to the dense prism. One of the Rutherford prisms transmitted the spectrum to about λ 4800; the violet lines were here lost by total reflection but were transmitted by a second prism constructed with a slightly smaller angle; the actual angles were :—

For red, yellow and green . . $\left\{\begin{matrix}\text{dense prism } 104^\circ \\ \text{light prisms } 8^\circ \text{ each}\end{matrix}\right\}$;

For blue and violet . . . . $\left\{\begin{matrix}\text{dense prism } 98^\circ \\ \text{light prisms } 10^\circ \text{ each}\end{matrix}\right\}$.

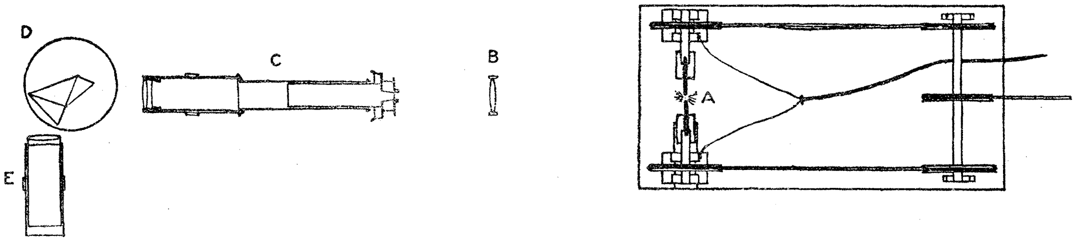
These prisms require more careful setting in front of the eye-piece than prisms of the ordinary direct-vision type and are more troublesome for the eye to find and to use; but their very high dispersion, combined with great economy of light, renders them of great value in cases where a system of specially high dispersive power is required.

The primary purpose of the prism in front of the eye-piece of the polarimeter is to eliminate stray light rather than to resolve the lines of the spectrum; this resolution must be effected mainly by the constant-deviation spectroscope, in order that adjacent lines and satellites may be blocked out by the polarimeter slit and so prevented from producing a distracting glare of light in the neighbourhood of the line under observation. A high resolution is of value, both in separating the lines of a doublet, such as the yellow doublet of mercury or of sodium, and in increasing the width of the lines that can be used without overlapping, so that in many cases it is possible to cover the whole width of the aperture of the polarimeter with a block of pure monochromatic light. But high resolution is usually gained at the cost of a serious sacrifice of light, and it was only when using bright arc-spectrum lines in the central part of the visible spectrum that the most dispersive systems could be used with advantage.

Successive increases in the dispersive power of the spectroscope were obtained in the following way :—

1. The 11-inch lens of the "eye-piece" tube of the spectroscope was replaced by an

achromatic lens of 22-inch focus, whereby the linear dimensions of the image were doubled, a slit 1 mm. in width now giving an image 2 mm. in width.



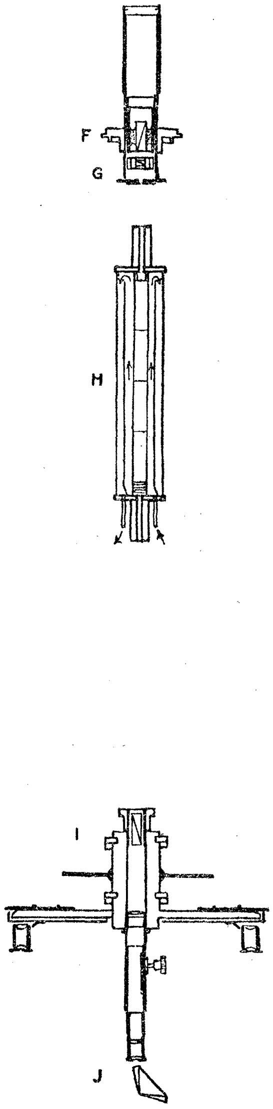


Fig. 1. General arrangement of apparatus for reading rotatory dispersion.

A. Rotating arc.
B. Condenser.
C. Collimator (11-inch focus).
D. Constant-deviation prism with grating replica on reflecting prism.
E. "Eye-piece tube" of constant-deviation spectroscope with lens of 22-inch focus.
F. Triple-field polariser.
G. Polarimeter slit.
H. Water-jacket with quartz cylinders.
I. Analyser.
J. Rutherford prism in front of eye-piece.

2. The light constant-deviation prism was replaced (a) by a dense prism of the same shape (b) by a pair of 30° prisms of the extra dense glass of refractive index 1·92 with a right-angle prism of light glass to act as reflector.

3. The right-angle prism was replaced by one bearing a Thorpe replica of a Rowland grating, placed so that the very bright first order diffraction spectrum on one side acted in co-operation with the two extra-dense 30° prisms to give the effect of a constant-deviation prism of exceptionally high dispersive power.

The resolution attained by these methods may be illustrated by giving the actual separation of the two mercury lines 5769·45 and 5790·49; these were used as test-lines during the early part of a series of experiments which had as their ultimate aim the effective resolution of the green silver doublet 5465·66 and 5471·73, and the yellow sodium doublet 5890·19 and 5896·16.

Actual Separation of Mercury Lines 5769 *and* 5790 *by Constant Deviation Spectroscope*:—

11-inch focus lens and light C.D. prism	0·1	mm.
22 ,, ,, ,, ,, ,, ,, ,, ...	0·2	,,
22 ,, ,, ,, ,, dense ,, ,, ...	0·3	,,
22 ,, ,, ,, ,, extra dense 30° prisms (1·92)	0·45	,,
22 ,, ,, ,, ,, grating replica	0·75	,,
22 ,, ,, ,, grating replica and extra dense 30° prisms . .	1·2	,,

Virtual Separation of Mercury Lines by Eye-piece Prisms:—

Ordinary D.V. prism	0·3	mm.
Extra dense (1·92) D.V. prism	0·4	,,
Rutherford prism	0·65	,,

The maximum separation was therefore 1·2+0·65 = 1·85 mm.

The complete apparatus as used in resolving the green silver doublet is shown in fig. 1.

A photographic method of measuring rotatory dispersion, which is specially valuable in the ultra-violet region of the spectrum, will be described in a later paper; the methods used in the red and infra-red regions will also be described later.

4. *Light Sources.*

The principal light sources used in measuring the rotatory dispersion of quartz were:—

(1) The flame spectra of lithium and thallium;
(2) The mercury arc enclosed in glass and in silica;
(3) The spectrum of sodium in a carbon arc;
(4) The open arc spectra of silver, copper, cadmium, and zinc.

In almost every case it was necessary to produce a light of the greatest possible intensity: only in this way was it possible to make use of a dispersive system of sufficient power to guarantee the effective purification of the light. Even when light-sources of the highest intensity were used, it was often found to be desirable to work with a system of lower dispersive power (using narrower slits and a narrower line in the field of the polarimeter) in order to maintain sufficient brightness to render possible the use of a small half-shadow angle; this factor is specially important in the case of the open-arc spectra, which are difficult to maintain in a condition to produce steady illumination.

(1) *Lithium.* 6708·2.

The flame spectrum of lithium is of such low optical intensity that even under the most favourable conditions it could not be read with a half-shadow angle of less than 7°. In order to economise light, the red lithium line was read with a direct-vision prism in front of the eye-piece as the only dispersive system. As PERKIN'S arrangement of the lithium flame did not give sufficient light, the arrangement shown in fig. 2A was used, a long, narrow globule of lithium carbonate being supported on a bundle of platinum wire over a jet of oxygen led by a platinum tube through the grid of a "Mecker" burner.

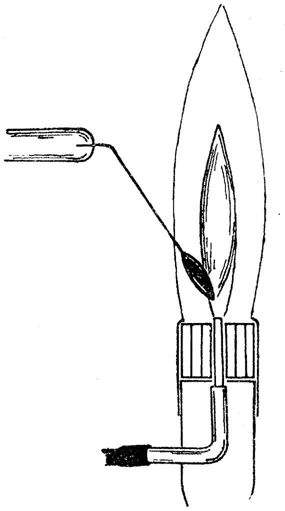


Fig. 2A. Lithium flame.

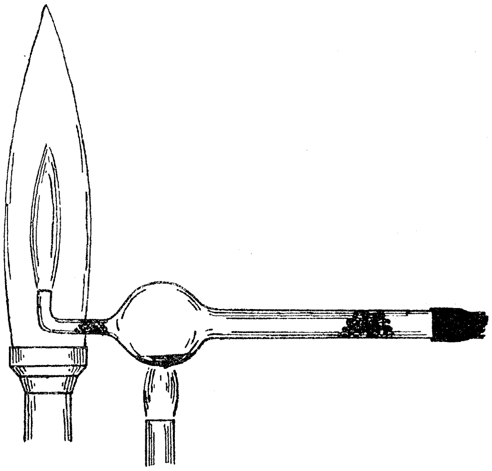


Fig. 2B. Thallium flame.

(2) *Thallium.* 5350·65.

Although the flame spectrum of thallium gives a very bright and pure monochromatic green light, its use was attended with very great difficulty on account of the extreme volatility of the chloride and the transient character of the light obtained by the ordinary methods of procedure. After many unsuccessful efforts, a steady light was finally obtained by the method shown in fig. 2B, the chloride being vaporised in a silica bulb and carried into the flame through a silica jet by a current of oxygen. With this arrangement, a very bright and steady illumination can be maintained during a period of several hours; the discovery of an equally efficient method for producing a steady lithium flame would be a very great convenience. The readings were taken with a dense direct-vision prism as the only dispersive system and a half-shadow angle of 5°.

(3) *Sodium.* 5896·16 and 5890·19.

The lines of the sodium doublet were by far the most difficult to read of the series now described. They could only be separated by using the highest available dispersion on the constant-deviation spectroscope, when the actual separation of the centres of the lines amounted to $\frac{1}{4}$ mm. Under these conditions the flame spectrum, even with the help of oxygen, was quite inadequate as a source of light. The actual readings were taken from a carbon arc with a thread of glass in the hollow core of the upper carbon. The main trouble was the reversal of the lines, which frequently appeared as a yellow band crossed by two very narrow black Fraunhofer lines. These reversed lines were admirably adapted for setting the spectroscope, the best possible adjustment being obtained when a black Fraunhofer line could be seen down the centre of the slit of the polarimeter, this slit being narrowed to about $\frac{1}{4}$ mm. in order to cut out the other line of the doublet; they were, however, quite useless for taking the actual readings. The device finally used to secure trustworthy observations consisted in levering open the jaws of the slit to see the character of the lines and releasing the jaws in order to take readings when the lines were seen to be narrow and luminous (without reversal). This condition could sometimes be maintained during several minutes but was never quite to be relied on; the reversal of the line could usually be detected even without opening the jaws of the slit, by the loss of sharpness of the extinction and a sudden change of perhaps 2° in the readings as the neighbouring line broadened and spread into the field of view; this effect was particularly troublesome in the case of the less refrangible line. The sodium lines were read without any prism on the eye-piece, as the half-shadow angle could be reduced from 10° to 5° by removing this prism; this exceptional course was justified (*a*) by the small amount of the stray light in the grating spectrum (*b*) by the fact that the stray light would be practically a continuous spectrum crossed by some scores of extinction bands and would not be likely to deflect the extinction more in one direction than in the other; the eye-piece would not in any case have been adequate to throw out stray light from the other sodium line.

A very promising method of producing a bright sodium spectrum *without reversal* consisted in adding sodium salts to a silver arc. But owing to the relative feebleness of the light and the extremely trying character of the work of taking readings, the attempt to utilise this method was finally abandoned.

(4) *Mercury.* 5790·49, 5769·45, 5460·97, 4358·58.

The mercury arcs used in these experiments included—

(*a*) *A Bastian lamp.* The arc is here formed in a zigzag glass tube 11 inches long and 3/16th inch diameter; this tube, which is normally in a horizontal plane, was tilted into a vertical plane for use with the polarimeter, one of the straight portions of the tube being focussed on the slit of the constant-deviation spectroscope. A long, straight arc of uniform luminosity, which can be focussed directly upon the slit, is an ideal source of light for work of this kind, as the uniform illumination of the triple field follows automatically without the careful adjustment that is necessary in the case of a spherical source of light. The Bastian lamp, taking a current of less than an ampere and capable of being connected directly to the ordinary lighting circuit, is the most convenient mercury lamp that has yet been devised and it is a matter for regret that it is no longer manufactured commercially.

(*b*) *An end-on mercury lamp* and

(*c*) *A vertical "Quartzlite" lamp*, both made of silica and taking a current of 3·5 amperes. These lamps were specially constructed for use with the polarimeter and have been described and figured in the 'Trans. Faraday Soc.,' 1912, vol. 7, 267.

(4) (A) *Mercury Green.* Hg 5460·97.

In reading rotations of large magnitude it is impossible to use sodium light as a standard, owing to the fact that the lines D_1 and D_2 are not extinguished together, the difference amounting in the experiments now described to 8° for the dextro-quartz and 11° for the lævo-quartz column. It was, therefore, necessary to adopt some other light for the purpose of making stringent tests on the quartz blocks before attempting measurements of rotatory dispersion. For this purpose the green mercury line was selected. The choice has been fully justified by practical experience during several subsequent years. Not only is the line one of the easiest to produce and read but it is the only line of the 24 which can be read as easily and as sharply to 0°·01 on a rotation of 12,000° as on one of 5°. Most of the measurements were made with the glass Bastian lamp as a source of light, a dense prism on the constant-deviation spectroscope and a dense direct-vision prism on the eye-piece. Although the line can be resolved on the *echelon* spectroscope, its spectral purity is incomparably greater than that of sodium (NUTTING, 'Bureau of Standards Bulletin,' 1906 [II.], 249), and it is undoubtedly the best line to use for standard measurements of natural and magnetic rotation, at least until the manufacture of enclosed cadmium arcs has been sufficiently perfected and simplified to render the green line Cd 5085·8240 available for general use. The green mercury line has the further advantage that it can be separated readily from the other lines of the spectrum by a direct-vision prism of low dispersive power and can, therefore, be used in everyday polarimetric work without an auxiliary spectroscope.

The yellow, green and violet mercury lines can also be separated by means of gelatine screens. This modification of LANDOLT's method is far more convenient than the original form in which absorbent solutions were used; it has the further advantage that it lends itself to accurate work, since the portions of the spectrum which are picked out are, except in the case of the yellow doublet, really monochromatic. But in spite of these merits this method of working has no advantage over the use of a direct-vision prism, which gives an even more efficient separation at about the same cost ; the economy of light, as compared with the absorbent screens, more than compensates for the glare of the adjacent lines.*

(4) (B) *Mercury Yellow.* Hg 5790·49, Hg 5769·45.

The yellow doublet of the mercury spectrum can be resolved with the utmost ease by the apparatus described above, giving wide blocks of pure monochromatic light in the field of the polarimeter. Unfortunately, the vertical silica lamp, which was required to illuminate the field with the system of highest dispersive power, was found to yield appreciable quantities of continuous light in this part of the spectrum ; the actual measurements were therefore made with the extra dense prisms (but no grating) on the spectroscope, and a Rutherford prism on the eye-piece, using a glass Bastian lamp and a half-shadow angle of 5°. For small rotations the two lines can be read as one, but there is no advantage in this, as so many purer light-sources are now available.

(4) (C) *Mercury Violet.* Hg 4358·58.

Owing to the weak visual intensity of the blue and violet portions of the spectrum, economy of light is of the utmost importance ; thus, in spite of its extreme brightness, the violet mercury line must be read with a prism at the eye-piece as the only dispersive system. The line is accompanied by two more refrangible satellites 4348·0. and 4341·0 ; these are not usually seen in the polarimeter, but become important when using a silica lamp as a source of light for reading optical rotations of several thousand degrees.

The Rutherford prism, which had been constructed for these measurements, could not be used, as the violet line was covered by a strong glare of green stray light. The observations were therefore made with a dense direct-vision prism, the slit in front of the triple field being narrowed until the line was completely separated from the two satellites. In order to make the line *at extinction* of about the same intensity as the unextinguished satellites, it was necessary to increase the half-shadow angle to 7°, when an excellent series of readings was obtained.

(4) (D) *Optical Mass-centre of the Violet Mercury Line.*

On account of its extreme brightness and the ease with which it can be produced,

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[* *Note added August* 6, 1912.—In the case of the violet line, Dr. MEES has suggested to me that a screen of pure xylene red may be used with a direct-vision spectroscope to reduce the glare of the green. Although it would not, if used alone, give a pure monochromatic light, it absorbs much less of the violet light and is therefore much more suitable for the present purpose than a screen of density sufficient to absorb completely all the other lines of the mercury spectrum.]

the violet mercury line occupies the same dominant position for polarimetric work in the violet that the green line holds for work in the brighter portions of the spectrum. No other line in the blue or violet can be read with the same ease and accuracy, and no other line in this region is available for general laboratory use. For all ordinary purposes it is sufficient to separate the line from the light blue (4916·41) and violet (4078·03 and 4046·78) lines without attempting to resolve the satellites (4348·0 and 4341·0); this can be done with an ordinary direct-vision prism on the eye-piece, and no further elaboration is necessary or desirable for readings of less than 1000°. With this simple arrangement and a vertical silica mercury lamp, readings can be taken with a half-shadow angle of 4° and with an accuracy but little inferior to that obtained in reading the green. These readings are of very great importance in measuring dispersion, as it is only on this line that the smaller differences of dispersive power can be perceived; the variations at the red end of the spectrum are much smaller and much more difficult to detect with certainty. In a later paper it will be shown that the measurement of the ratio $\alpha_{4359}/\alpha_{5461}$ affords the best method at present available for characterising the rotatory dispersion of a substance.

In order to ascertain the effect on the readings of including or excluding the two satellites, the following experiments were made. After having established the ratio of the violet and green rotations to be 1·62700 for long columns of quartz, a further series of measurements was taken with a short rod 25·902 mm. in length, the slit of the polarimeter being opened widely so that there was no separation of the satellites from the chief line. The readings were as follows:—

	Rotation.	Ratio.
Mercury green	661°·47	1·00000
Mercury violet (current 3 amperes) . . .	1076°·33	1·62717
,, ,, ,, 4 ,, ...	1076°·45	1·62729
,, ,, ,, 5 ,, ...	1076°·52	1·62747

These observations show that with a current of 3 amperes, the error produced by including the satellites amounts only to 1 part in 10,000 and would be inappreciable in readings of less than two right angles. In all ordinary polarimetric work involving readings of a few degrees only, the larger currents, giving an error of 1 part in 5,000 at 4 amperes and an error of 1 part in 3,000 at 5 amperes, may be used without hesitation, if desired.

(5) *Silver.* 5471·72, 5465·66, 5209·25.

Of all the open metallic arcs, the silver arc is that which is most readily adapted to polarimetric work. The chief features of the spectrum are the dark green line 5209·25 and the bright green doublet, 5471·72 and 5465·66, the more refrangible component of which approaches very closely to the green mercury line 5460·97. The dark and bright green lines could easily have been separated by a single direct-vision prism, but in practice all the open-arc spectra were resolved by means of the constant deviation spectroscope, the slit of which was adjacent to a small draught-hood in which the arc was placed.

The rotating arc shown in fig. 1 was a modification of that described by Baly ('Spectroscopy,' 1912, p. 391). Silver rods $1\frac{1}{4}$-inch long and $\frac{1}{4}$-inch in diameter were screwed into copper cylinders 1-inch long and $\frac{5}{8}$-inch diameter, which served to cool as well as hold the rods. The copper cylinders in their turn were screwed on to $\frac{3}{8}$-inch iron spindles which were rotated in opposite directions by means of pulley-wheels driven by belts from a small power shaft at the back of the machine, this shaft being run from a fan-motor in series with an adjustable resistance. One of the spindles was mounted on a pedestal provided with a slide, so that it could be moved inwards as the electrodes were burned away. In order to maintain a steady arc, free from serious flickering, it was necessary to exercise some care in centering the silver electrodes and also to run the machine at the highest convenient speed. A current of 5 amperes was usually employed but there is little doubt that in the case of the silver arc a heavier current up to 10 amperes might have been used.

(5) (A) *Silver Dark Green.* Ag 5209·25.

This line was read with the extra dense prisms on the constant deviation spectroscope but no grating and with a Rutherford prism in front of the eye-piece. The half-shadow angle was very small, about 3°, and the readings were amongst the easiest of those taken with the rotating arc.

(5) (B) *Silver Light Green.* Ag 5471·72 and Ag 5465·66.

This doublet, separated only by 6·06 units as compared with 5·97 units for the sodium doublet, was read quite easily with the system of highest dispersion, including the extra dense 30° prisms, grating, and Rutherford prism. The intensity of the light was so great that even in the case of the less refrangible weaker component, a half-shadow angle of only 5° could be used; the readings were among the most concordant of the whole series.

(6) *Cadmium.* 6438·4722, 5085·8240, 4799·9107, 4678·37.

Although an enclosed arc would undoubtedly be the ideal source of cadmium light, a very efficient substitute is afforded by an open arc with electrodes of a cadmium silver alloy (Lowry, 'Phil. Mag.,' 1909, vol. 18, 320). This can be run very satisfactorily during about an hour with a current of 4 amperes, the current being adjusted so that the cadmium distils out from the end of one of the electrodes, occasionally in such a way as to leave a considerable cavity in the interior of the rod. Before starting up again it is necessary to file away the tip of the electrode in order to bring to the surface a fresh supply of cadmium.

(6) (A) *Cadmium Red.* Cd 6438·4722.

On account of the presence of continuous red light, this line is not easy to read when working with rotations of 3,000° to 4,000°; a specially narrow slit was used in conjunction with a Rutherford eye-piece and extra dense 30° prisms (without the grating) on the constant-deviation spectroscope. The half-shadow angle was 4°.

(6) (B) *Cadmium Green.* Cd 5085·8240.

This magnificent line, if more easily produced, would be the most suitable for use in place of the green mercury line as principal standard in polarimetric and refractometric work. It was read with the same dispersing system as the preceding line but with a half-shadow angle of only 3°.

(6) (C) *Cadmium Light Blue.* Cd 4799·9107.

This line was read with the same dispersive system but with the half-shadow angle increased to 5° or 6°.

(6) (D) *Cadmium Dark Blue.* Cd 4678·37.

This line is difficult to read on account of its smaller intensity and diminished visual efficiency; the presence of the silver line Ag 4668·70 presents a further difficulty in the case of large rotations, as it acts as a somewhat close satellite. The line was read with considerable difficulty, using the ordinary dense constant-deviation prism on the spectroscope, a dense direct-vision prism on the eye-piece and a half-shadow angle of 8°.

(7) *Zinc.* 6363·7, 4810·71, 4722·26, 4680·38.

The methods used to read the zinc lines were similar to those followed in the case of cadmium. Two alloys were used, a silver-zinc alloy and a brass specially prepared from pure zinc and electrolytic copper; the latter alloy was the easier to burn; it gave the best results with a small current of about 3 amperes.

(7) (A) *Zinc Red.* Zn 6363·7.

This line was more difficult to read than the corresponding cadmium line on account of the greater amount of continuous light in the spectrum—an unimportant factor with readings of ordinary magnitude but of vital importance when reading large rotations. It was finally read with the ordinary dense constant-deviation prism, Rutherford prism, specially narrow slit and a half-shadow angle of 7°.

(7) (B) *Zinc Blue.* Zn 4810·71, Zn 4722·26, Zn 4680·38.

These lines were read under the same conditions as the blue cadmium lines. The third zinc blue line presents practically the same difficulties as the second cadmium blue line, from which it is separated by only two Ångstrom units; it was read with brass electrodes, thus eliminating the silver line, and a half-shadow angle of 6°. The extreme difficulty of reading these lines serves to emphasise the extraordinary value of the violet mercury line, which is 320 units further on in the violet region and yet can be read with greater ease than even the least refrangible of the bright blue zinc and cadmium lines.

(8) *Copper.* 5782·30, 5700·39, 5218·45, 5153·33, 5105·75.

Unlike the alloys used to produce the spectra of cadmium and zinc, the copper arc can be used with heavy currents up to about 10 amperes, although the highest current used in the present experiments did not exceed 5 or 6 amperes. The spectrum is much more complex than those of the preceding metals and some care is needed to ensure spectral purity. Values are now given for the two yellow and three green lines but occasional readings have been made with four of the blue lines (4705, 4651, 4587·19, 4378·40), and by using a heavy current there is little doubt that some at least of these could be added to the list of 24 wave-lengths tabulated below.

(8) (A) *Copper Yellow.* Cu 5782·30, Cu 5700·39.

The yellow copper lines are of good spectral purity and are easy to read, specially so in the case of the less refrangible line. They were read with the extra dense 30° prisms on the spectroscope (without a grating), a Rutherford prism at the eye-piece and a half-shadow angle of only 4°.

(8) (B) *Copper Green.* Cu 5218·45, Cu 5153·33, Cu 5105·75.

The two more refrangible lines were read without difficulty under the same conditions as the yellow lines. In spite of the presence of two satellites, 5158·53 and 5144·35, the central line proved to be the best of the three copper greens; it may be noted that these satellites are of weak intensity and lie one on either side, so that even if they were not completely eliminated by the dispersive system they would probably have very little influence on the optical mass-centre of the line. The least refrangible line has a strong satellite at 5220·25; when using the system of highest dispersion it could be seen distinctly, although separated by only 1·80 Ångstrom units; but as it could not be eliminated by the methods then available, a direct-vision prism was substituted for the Rutherford prism and the readings were taken with line and satellite superposed; this is the only case in the whole series in which a line with a visible satellite was used as if it were a single line.

5. *Quartz.*

With the exception of sodium and thallium, complete series of readings of all the lines referred to in the preceding section had been taken as long ago as the spring of 1908. The delay of four years in the completion of the work may be traced almost entirely to the extreme difficulty of securing quartz of sufficiently high quality to withstand the more and more stringent tests that were found to be necessary in the course of the work. Much time and many thousands of readings might have been saved if these new tests had been discovered before the work of measuring the rotatory dispersion of the specimens was commenced.

The commonest type of flaw in quartz is that due to the "twinning" of the dextro- and lævo-rotatory varieties. When the intermingling is close the quartz becomes "feathery," and presents the striated appearance seen in an ascending current of hot air; when viewed through a Nicol prism, with light partially polarised by reflection from a glass surface, the striæ are coloured and can be seen without difficulty. It is scarcely necessary to add that this fault, and other obvious flaws, were carefully avoided in selecting plates for the investigation.

Plates 25 mm. in thickness were first cut from blocks of dextro- and lævo-quartz, and from each plate four cylinders 15 mm. in diameter were cut. On taking readings of the optical rotatory power of these cylinders with green mercury light, the whole of the four lævo-cylinders were rejected, some because striæ revealed by the monochromatic illumination rendered it impossible to take satisfactory readings, others because the readings of the cylinders (all cut from the same plate and accurately equal in length) not only differed from cylinder to cylinder, but also when the same cylinder was rotated about its own axis. The best of the four lævo-cylinders gave the readings:—

L_3	613°·17	613°·17	613°·30	613°·58.	Mean 613°·30.

Of the four dextro-cylinders, one gave readings ranging over 4° and the other three gave:—

R_1	613·14	613·16	613·08	613·03.	Mean 613·10.
R_2	613·02	613·38	613·28	613·02.	,, 613·17.
R_4	613·09	613·11	613·08	613·16.	,, 613·11.

As a result of these tests, the first and last of the dextro-cylinders, which differed only by 0°·01, were selected as satisfactory, the two other cylinders for which figures are given were rejected as doubtful, the remaining four were thrown out as obviously faulty.

Additional plates of dextro- and lævo-quartz were then cut to about the same thickness and cylinders cut and tested in the same way by reading each in four positions. The figures were:—

R_{10}	636·80	636·79	636·87	636·79.	Mean 636·81.
R_{20}	637·16	636·97	636·80	636·16.	,, 637·02.
R_{30}	636·81	636·76	636·75	636·76.	,, 636·77.
R_{40}	636·79	636·75	636·76	636·76.	,, 636·77.
L_{10}	640·27½	640·24	640·27	640·33.	,, 640·28.
L_{20}	640·27	640·25	640·29	640·31.	,, 640·29.
L_{30}	640·43	640·21	640·23	640·27.	,, 640·29.
L_{40}	640·24	640·21	640·22	640·26.	,, 640·23.
L_{50}	640·34	640·26	640·21	640·24.	,, 640·26.
L_{60}	Bad extinctions.				
L_{70}	640·19	640·21	640·19	640·14.	,, 640·18.
L_{80}	640·21	640·22	640·23	640·31.	,, 640·24.

After rejecting R_{20} and L_{60}, these cylinders with R_1 and R_4 were used for several complete series of measurements with light of all the available wave-lengths. As the whole of these readings, covering a period of nearly three years, were subsequently rejected, they need not be referred to in detail, except in the case of the mercury green readings which are of importance as bearing on the tests by which the validity of the values finally given was established.

After a number of preliminary experiments, the two groups of cylinders, each cemented into a rod, were found to give the following values (*a*) by setting to the position of minimum rotation (*b*) by setting with the help of a reflecting eye-piece :—

$$7\ \textit{L Cylinders}\ .\ .\ .\ .\ \left\{\begin{array}{ll}(a) & 4481^{\circ}{\cdot}78\\ (b) & 4481{\cdot}79\end{array}\right\}.\quad \text{Rotation per millimetre } 25^{\circ}{\cdot}5350.$$

5 *R Cylinders* . . . . 3136·51. ,, ,, ,, 25·5342.

After re-cementing, somewhat lower values were obtained :—

7 *L Cylinders* . . . . 4481·61. Rotation per millimetre 25·5340.

5 *R Cylinders* . . . . 3136·41. ,, ,, ,, 25·5336.

In trying to determine the effects of the satellites upon the reading of the violet mercury line, the mechanical arrangement of the polariser was modified so that the half-shadow angle could be thrown either to the left or to the right. This was found to have a marked effect on the readings, which was subsequently recognised as occurring even in the case of the very pure mercury green line which gave :—

$$7\ \textit{L Cylinders}\ .\ .\ .\ \left\{\begin{array}{ll}\text{H.S.}+ & 4481{\cdot}61\\ \text{H.S.}- & 4481{\cdot}53\end{array}\right\}\ 4481^{\circ}{\cdot}57 = 25^{\circ}{\cdot}5338 \text{ per mm.}$$

$$5\ \textit{R Cylinders}\ .\ .\ .\ \left\{\begin{array}{ll}\text{H.S.}+ & 3136{\cdot}41\\ \text{H.S.}- & 3136{\cdot}53\end{array}\right\}\ 3136{\cdot}47 = 25{\cdot}5338 \text{ per mm.}$$

The method of reading with both positive and negative half-shadow angles had thus brought the values of the dextro- and lævo-cylinders into complete agreement and appeared to have provided the last device needed to ensure accurate readings. With the experience gained during the two preceding years, yet another series of readings was undertaken, therefore, in which every line was read with both a positive and a negative half-shadow angle. These readings, which were practically complete when the quartz was discarded, are referred to later as proving that faulty quartz gives incorrect figures for rotatory dispersion even when allowance has been made for errors in the absolute values.

At the close of this series, the cement was found to have been separated a little in some of the joints ; it was therefore all cleaned off and the cylinders were put together in optical contact, giving a greatly improved parallelism to the end faces of the column. After this alteration the cylinders were retested by setting each group in eight or more different positions and reading with both positive and negative half-shadow angles. The results were remarkable :—

7L	H.S. +	4481·78	1·37	1·58	1·53	1·50	1·41	1·54	1·57
	H.S. –	4481·88	2·34	2·07	1·89	1·76	2·01	1·98	1·99
Mean . . .		4481·83	1·85	1·83	1·71	1·63	1·71	1·76	1·78
Difference.		0·10	0·97	0·49	0·36	0·26	0·60	0·44	0·42

Mean of all readings = 4481·76.

5R	H.S. +	3136·07	6·27	6·24	6·57	6·32	6·21	6·37	6·55	6·60	6·67	6·66	6·49
	H.S. –	3137·00	6·85	6·55	6·49	6·72	6·74	6·53	6·53	6·53	6·51	6·50	6·71
Mean . . .		3136·53	6·56	6·40	6·53	6·52	6·47	6·45	6·54	6·56	6·59	6·57	6·60
Difference.		+0·93	+0·58	+0·31	–0·08	+0·40	+0·53	+0·16	–0·02	–0·07	–0·16	–0·16	+0·22

Mean of all readings = 3136·53.

It was evident that the difference between the values for the two half-shadow angles might be very serious, amounting to as much as 0°·97 in the lævo- and 0°·93 in the dextro-cylinders, but that positions might be picked out in which the discrepancy was very small; further, the average value for each position was seen to be almost independent of the variations produced by reversing the half-shadow angle. It was hoped that by placing the quartz columns in suitable positions satisfactory results might still be obtained, though the differences between the average values for the cemented cylinders and for the cylinders in optical contact could not lightly be set aside.

In seeking for the origin of the anomaly, the conclusion was reached that it might be accounted for by the presence of patches of material which failed to give a proper extinction, *e.g.*, because they produced elliptical or circular polarisation. Such a bright patch, if occurring in the centre of the field, would require to be compensated by bringing the analysing Nicol more nearly perpendicular to the main polarising Nicol; this would mean moving the analyser to the left or to the right according as the polarising Nicol had been turned to the left or to the right relatively to the smaller fixed Nicols used to produce the "half-shadow" effect; the presence of a non-extinguishing patch would therefore raise or lower the observed rotation and by approximately equal amounts according as the half-shadow angle was positive or negative, whilst the average rotation would be substantially the same as if the patch were absent.

As it seemed possible that a non-extinguishing film or patch might have been produced by the optical contact, the cylinders were separated and examined in groups and finally in units but still showed the same phenomena. Finally, the existence of actual flaws was detected in at least 10 of the 12 cylinders by viewing the quartz with monochromatic green mercury light, with a zero half-shadow angle, the eye-piece being drawn right out of the telescope of the polarimeter, so that it was possible for the first time to focus upon the interior of the quartz specimens, instead of looking through them to the Nicols of the triple field. Black and green bands, resembling interference fringes, were then seen, some of the specimens showing two series of bands running in directions inclined to one another.

As showing the extreme difficulty of procuring satisfactory material it may be mentioned that a pair of plates of dextro- and lævo-quartz to take the place of the defective cylinders was procured from a Continental firm under a guarantee that the specimens should be absolutely free from flaw when tested in the most stringent way; although each plate had an area of 25 sq. cm., the utmost that could possibly have been done with them would have been to drill out a single cylinder from one plate and possibly four or five of smaller diameter from the other, the whole of the rest of the material being shown to be grossly defective when viewed in the way described above.

Finally, Messrs. A. Hilger and Co. were able to provide a plate of dextro-quartz, 51 mm. in thickness after grinding and polishing, which showed some feathery patches and also groups of acicular crystals running through the block; but by careful examination, it was possible to pick out four 15 mm. circles which showed no flaw of any description. Two of these, unfortunately, were splintered in drilling and had to be reduced to about 40 mm. in length. Each of the four cylinders satisfied the following tests:—

(1) No flaw or irregularity could be seen on viewing the crystal between crossed Nicols with monochromatic green light.

(2) No differences could be detected between the optical rotations with positive and negative half-shadow angles; of fifty pairs of readings, taken without special precautions, only two pairs showed a difference greater than 0·05° and these were not confirmed on repetition.

(3) No differences greater than 0°·05 were found when the cylinders were rotated about their axes, each cylinder being set with the reflecting eye-piece and tested in six different positions.

(4) No differences could be detected in the rotatory powers of the four cylinders beyond those which might be ascribed to variations of temperature due to imperfect jacketing. The actual values at *about* 20° were:—

R_1 . . 25·5366, R_2 . . 25·5369, R_3 . . 25·5368, R_4 . . 25°·5365 per mm.

In order to increase the length of the quartz column, which had been reduced some 20 mm. by breakages, a bridge-piece, R_5, separating two of the cylinders in the block, was tested and cut. Examined in three positions, with positive and negative half-shadow angles, it showed an extreme variation of only 0°·03. But the rotation per millimetre was higher, at 25°·5378, a relative difference that was confirmed after regrinding; the piece (which had a clear aperture of only about 8 mm. instead of 15 mm.) was not used, therefore, in the final series of observations.

As the dextro-quartz, although withstanding all the new tests that had been devised during four years of continuous work, had been cut from the immediate neighbourhood of material that was obviously faulty, it was felt that some uncertainty might still attach to the absolute value of the observations made with it. Great importance, therefore, was attached to the discovery in Messrs. Hilger's stock of a large block of lævo-quartz in the form of a plate 58 mm. in thickness; this was badly cracked in places but showed no trace whatever of any optical flaw in a mass which must have weighed at least 6 pounds. The block was so large that the central part was reserved for a 30° Cornu prism 5 inches in height, only the outer portions being used in the present investigation. These outer portions were submitted to a further careful examination without revealing any flaw, after which nine 15 mm. cylinders were drilled out, one being broken in drilling and reground to two lengths of 22·2 and 25·9 mm. respectively. The eight complete cylinders were then tested by every available method and found to be optically perfect in every respect; the rotations at *about* 20° C. were:—

L_1 . . 25·5365	L_2 . . 25·5372	L_3 length not measured	L_4 . . 25°·5362 per mm.
L_5 . . 25·5365	L_6 . . 25·5368	L_8 . . 25·5372	L_9 . . 25°·5372 per mm.

The separate values recorded above were found to be influenced by the air-temperature and, therefore, are only approximate. This objection does not apply to the group measurements which gave:

R_{12345} . . .	$l = 233·5716$	$\alpha = 5964°·51$	$\alpha/l =$ **25°·5361** per mm.
L_{1456} . . .	$l = 231·4212$	$\alpha = 5909°·78$	$\alpha/l =$ **25°·5369** per mm.

During the drilling of the cylinders many of the surfaces were scratched by the emery and subsequently re-polished to unequal lengths. The optical contacts were found to be so weak and unsatisfactory that the cylinders were cemented together in groups and reground to exact parallelism and equal lengths.

The final figures after regrinding were as follows:—

	l_{20}.	α_{20}.	α_{20}/l_{20}.
R_1	38·4634	982·20	25·5360
R_2	41·6118	1062·60	25·5360
R_3	50·6814	1294·22	25·5364
R_4	50·6811	1294·22	25·5364
R_5	50·6809	1294·26	25·5373
L_1	56·5920	1445·21	25·5373$_5$
L_2	56·5915	1445·20½	25·5375
L_3	56·5910	1445·19	25·5374$_5$
L_4	56·5915	1445·20	25·5374
L_5	56·5914	1445·19½	25·5373$_5$
L_6	56·5921	1445·19½	25·5370$_5$
L_8	56·5911	1445·18½	25·5373
L_9	56·5918	1445·21	25·5376

The group figures were

R_{12345}	232·1194	5927·46	25·5363
R_{1234}	181·4382	4633·21	25·5360
L_{1256}	226·3670	5780·76	25·5371
L_{3489}	226·3654	5780·76	25·5373

The tests of the separate cylinders were exceedingly satisfactory. Thus, the extreme difference in 40 pairs of readings for positive and negative half-shadow angles in the case of the eight lævo-cylinders, was only 0°·04; the extreme range of variation in the average values for the eight cylinders was only 0°·02; the extreme variation in length after regrinding amounted only to 0·0011 mm. and the extreme variation of rotatory power per millimetre to 0°·0006 per mm.

The final values for the optical rotation of the quartz were

	Lævo.	Dextro.
Before regrinding	25·5369	25·5361
After ,, ...	25·5371	25·5363
,, ,, ...	25·5373	25·5360
	25·5371	25·5361

In view of the much more favourable conditions prevailing in the measurements of the lævo-cylinders, it was decided that these must be made the basis of the values finally taken, the dextro-cylinders being used mainly to balance the lævo-cylinders in measurements of rotatory dispersion. The value adopted for the rotatory power of quartz at 20° C. for Hg 5461 is therefore

25·5371 degrees per millimetre.

The sixth figure has been used and is of importance in connection with the column of relative values given in a subsequent table for twenty-four wave-lengths in the visible region of the spectrum; but it is impossible to regard it as having any absolute value until other equally good crystals of quartz have been found and tested and examined in the same way. When, however, it is noticed that the value 25°·5338 per mm. given by the faulty specimens used in the earlier part of the work differs only by 0°·003 per mm. from the value finally adopted and that the dextro-cylinders (selected with some difficulty from the only sound portions of a faulty block) gave a value 25°·5361 per mm., only 0°·001 below the final figure, there can be little doubt that the fifth figure in the value 25°·5371 per mm., given by the optically-perfect lævo-quartz crystal, may be regarded as correct.

6. *Experimental Methods.*

1. The *polarimeter*, a triple-field instrument of the Lippich pattern, made by the Cambridge Scientific Instrument Company, was graduated to read by means of a vernier to 0°·002; but in practice readings were usually taken only to 0°·01, without using the vernier. Whilst it may be possible under some conditions to read a polarimeter to the third decimal of a degree, it is only very rarely that such readings have any absolute value; in the present investigation the policy was deliberately adopted of making the readings so large that any impurities in the light or faults in the material should obtrude themselves to such an extent as to make the reading of the rotations impossible; relative values based upon minute readings of smaller rotations would have been of much less value, since most of the sources of error would have been overlooked. The aperture of the triple field was 6 mm., the main polarising and analysing Nicols being 10 × 10 × 30 mm.

2. The *spectroscopes* and *prisms* were by Hilger and need not be described in detail. The slits were arranged to open symmetrically; the slit of the spectroscope could be opened to a width of 3 mm. giving an image 6 mm. in width; the slit of the polarimeter could be opened to the full width (6 mm.) of the aperture in front of the triple field. The constant-deviation spectroscope was provided with a drum which could be calibrated in wave-lengths, so as to illuminate the polarimeter with light of any desired colour selected from a continuous spectrum; but it is impossible to recommend the use of such a method, as the wave-length of the light actually delivered to the slit of the polarimeter was found to be seriously affected when the half-shadow angle was altered. This displacement had not been anticipated when using flat-ended Nicols prisms but is a necessary consequence of the method followed in constructing them; it was discovered when using narrow lines to illuminate a narrow slit, by noticing that the line was displaced and partially obliterated on changing the sign of the half-shadow angle. This observation was regarded as a further justification of the policy of using monochromatic or multichromatic, instead of continuous, sources of light; the only effect of the displacement was then a slight narrowing of the line, which could be overcome by readjusting the drum of the spectroscope; with a continuous spectrum, the wave-length of the light would be altered and the readings would be rendered uncertain from a cause that would not easily have been detected or traced.

3. The *setting* of the quartz was effected with the help of a reflecting eye-piece. The pointer of the eye-piece was brought to coincide with the centre of the image of the slit of the spectroscope; the telescope was then racked in till focussed for infinity and the bright image of the pointer, reflected from the surface of the quartz, was brought point to point with the dark image of the pointer itself. The setting was effected in a very simple way: the water-jacket containing the quartz cylinders rested in a rectangular trough; by placing thin cards on one side or other of the trough, the quartz could be tilted in two planes at right angles to one another; the cards were

placed at one end or the other of the water-jacket, according as the quartz required to be tilted forward or backward. By means of the reflecting eye-piece, it would have been easy to set the quartz within a fraction of the thickness of a card but this was not required, as it was necessary to insert or remove some half-dozen cards before the readings were altered by more than 0°·01. The appearance of the reflected image was the best test of the optical contact of the cylinders; if these came apart (as always happened if water was spilled into the jacket) a series of widely separated images was seen; but if the optical contact held, the grinding was so perfect that it was barely possible to recognise the double character of the image reflected from the ends of the column of quartz, the error in parallelism being probably only a fraction of a minute of arc.

4. The *axis* of the quartz, which in the earlier plates had been located in the ordinary way by means of the interference rings, was set much more carefully in the later plates, using the very sensitive method described by J. Walker ('Phil. Mag.,' 1909, vol. 18, 195). The error in setting the axis normal to the surfaces was estimated not to exceed 5 minutes of arc. As the cylinders could be tilted more than this without increasing the readings, there was no reason to suppose that the setting was not sufficiently accurate, even when taking readings to 0°·0001 per mm. This conclusion is all the more reasonable in view of the fact that readings concordant within about 0°·001 per mm. have been obtained by a number of different workers for the optical rotations of sodium light in thin plates of quartz, set to axis by the rougher methods generally in use.

5. The *temperature* was maintained at 20° C. by means of a generous flow of water at constant temperature. The spiral gas-regulator used in the thermostat was of the pattern designed in 1905 ('Trans. Chem. Soc.,' 1905, vol. 87, 1030–1034) and was capable of maintaining the temperature of the well-stirred bath, over long periods, within 0°·01 of the desired temperature. The water was drawn out of the bath and through the jackets by means of an Albany pump of $\frac{1}{2}$-inch bore, the arrangements being in other respects very similar to those described and figured in an earlier paper ('Trans. Faraday Soc.,' 1907, vol. 3, 119). As the pump works best with an ample flow of water, the water jackets were always arranged in parallel, thus avoiding the obvious drawbacks of a series arrangement. Thermometers were provided for reading the temperature of the return-flow, which usually differed from that of the bath by something of the order of 0°·01 for each degree of difference of temperature between the water bath and the atmosphere. All the jackets were double, the inner flow of water being shielded by an outer flow at practically the same temperature; with the exception of about 2 feet of rubber tubing, all the cooling surface was on the return flow and it is reasonable to suppose that 90 per cent. of the drop of temperature took place there. Thus, although the readings of the polarimeter changed by about 0°·01 for each 0°·01 C., the regulation of temperature was probably quite sufficiently accurate for the purpose.

6. The *water-jackets* (fig. 3) were designed originally for use with organic liquids. But, unlike these liquids, quartz is an excellent conductor of heat and takes up a steady temperature within about 3 minutes, whereas liquids require at least this number of hours. But in spite of this excellent conduction, it is necessary to use great care to protect the ends of the quartz from atmospheric heating or cooling. This was discovered when cylinders which gave rotations of 1476°·14 and 1479°·99 before measuring their lengths, were found to give 1476°·21 and 1483°·03 after measurement; these differences were traced to the somewhat large changes of atmospheric temperature which had taken place in the interval. In these preliminary tests the cylinders were merely laid in a jacketed tube of 15 mm. diameter freely open at the ends and the variation was exceptionally large. In the final experiments all risk of temperature errors was eliminated (*a*) by using long columns of quartz so that the cooling of the ends was relatively much less important (*b*) by adding to each jacket a pair of heavy metal cylinders in good thermal contact with the jacket and having an aperture of only 10 instead of 15 mm. (*c*) by keeping the temperature of the room within about 2° of that of the bath. Arrangements were also provided whereby four cover-slips could be interposed between the ends of the quartz and the outside air; but these were not considered necessary and were discarded after the values for mercury green had been read.

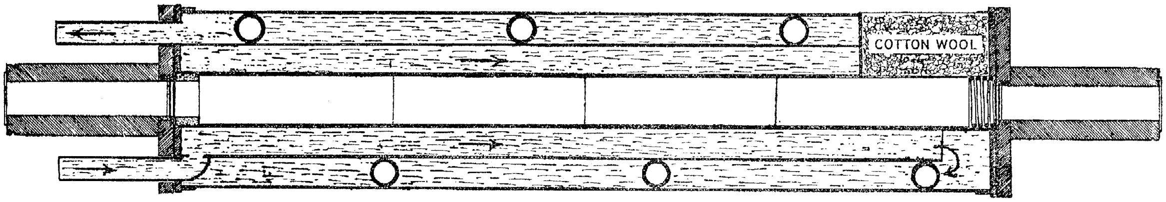

Fig. 3. Water-jacket for quartz cylinders.

The jacket is double, a spiral of compo-tubing being used to direct the water in the outer section. The quartz is held between a cylinder of cork on the left and a strong spiral spring on the right. Four cover-slips are shown, one at each end of the two brass extension pieces, protecting the quartz from cooling by the outer air. A slot at the top of the jacket was closed by cotton wool.

7. The *lengths* of the quartz cylinders were measured at the National Physical Laboratory to 0·0001 mm., with an estimated error of about 0·0003 mm. The conditions of working were such that greater reliance could be placed on measurements made with the separate cylinders and at atmospheric temperatures rather than on long columns jacketed to some fixed temperature. The accuracy of the length-measurements was of the same order as that of the measurements of optical rotation. The extreme variation between the individual cylinders of lævo-quartz corresponded with a difference of 0·0012 mm. in length or 0°·03 in rotatory power. The difference between the two groups of four cylinders could be represented by an error of 0·0016 mm. or 0°·04 and the difference before and after regrinding by the same figures; these differences are of the order of 0°·0002 per mm. and correspond with a possible error in the mean of about 0°·0001 per mm.

8. The *readings* were taken in accordance with the principle utilised by Von Lang ('Wien. Ber.,' 1876, vol. 74, 209–214) and by Soret and Sarasin ('Geneva Archives,' 1882, p. 54), according to which the measurements are most trustworthy when made by contrasting dextro- and lævo-quartz, rather than by reading either crystal separately against a zero taken in the ordinary way. This principle was regarded as specially important in the present investigation, because the glare of satellites, &c., was entirely without effect when reading a zero at which all the lines were extinguished together, whereas it became almost the dominant factor when reading long columns of quartz. For this reason it was felt that better results would follow from reading a lævo-column of 226·3670 mm. against the dextro-column of 181·4382 mm., than by attempting to read the whole of the available 500·8 mm. of lævo-quartz, either against a column of quartz of less than one-half this length, or against a zero. Valuable check-readings could be obtained by reading the two columns of quartz against one another with both a positive and a negative half-shadow angle. The readings of the dextro- and lævo-quartz, read separately against a zero, are, however, of value in considering the relative accuracy of the different experiments, since their concordance could not be seen until all the measurements had been taken and the results reduced to unit length.

7. *Tabulated Observations. Form of the Dispersion Curve.*

Table I. shows for a series of 24 lines:—

A. The wave-lengths in Ångstrom units;

B. The actual rotations produced by the dextro- and lævo-columns of quartz, read against a zero, with both positive and negative half-shadow angles;

C. The ratio of the readings for each wave-length relatively to those for mercury green in the case of—

(*a*) dextro-quartz, average of + and − half-shadow angles;
(*b*) lævo-quartz, " " " " " ;
(*c*) dextro against lævo, half-shadow angle +;
(*d*) " " " " " −;

D. The mean values of these dispersion-ratios and the average deviation (ranging from 1 to 13 parts per million) of the four ratios from the mean;

E. The rotation in degrees per millimetre taking for mercury green the value 25·5371 discussed and adopted in § 5;

F. The rotations in degrees per millimetre calculated for each of the 24 wave-lengths from the formula

$$\alpha = \frac{11{\cdot}6064}{\lambda^2-\lambda_1^2} + \frac{13{\cdot}42}{\lambda^2-\lambda_2^2} - \frac{4{\cdot}3685}{\lambda^2},$$

where

$$\lambda_1^2 = 0{\cdot}010627,\ \lambda_2^2 = 78{\cdot}22,\ \lambda = \text{wave-length in microns.}$$

G. The differences between the calculated and observed rotations in degrees per millimetre.

TABLE I.—Rotatory Dispersion of Quartz in the Visible Region of the Spectrum.

	A.	B.	C.	D.	E.	F.	G.
	Wave-length.	Observed rotations.	Dispersion ratios.	Mean ratios (with average error × 10⁶.)	Rotation in degrees per millimetre.		
					Observed.	Cal-culated.	Differ-ence.
Lithium red	6708·2	D + 2999·95° L + 3743·38° D − 3000·12 L − 3743·16	D ·647508 + ·647527 L ·647539 − ·647523	·647525 ± 9	16·5359	16·5356	+0·0003
Cadmium red . . .	6438·47	D + 3269·82 L + 4079·67 D − 3269·91 L − 4079·68	D ·705746 + ·705734 L ·705733 − ·705743	·705739 ± 5½	18·0225	18·0243	−0·0018
Zinc red	6363·7	D + 3352·49 L + 4183·03 D − 3352·59 L − 4182·93	D ·723589 + ·723598 L ·723604 − ·723597	·723597 ± 4	18·4786	18·4728	+0·0058
Sodium yellow, D₁ .	5896·16	D + 3937·02 L + 4912·28 D − 3936·98 L − 4912·25	D ·849735 + ·849753 L ·849760 − ·849745	·849735 ± 8	21·7001	21·7001	±0·0000
Sodium yellow, D₂ .	5890·19	D + 3945·80 L + 4923·05 D − 3945·72 L − 4923·25	D ·851628 + ·851630 L ·851644 − ·851642	·851636 ± 7	21·7483	21·7467	+0·0016
Mercury yellow . .	5790·49	D + 4090·41 L + 5103·62 D − 4090·38 L − 5103·57	D ·882843 + ·882855 L ·882859 − ·882848	·882852 ± 6	22·5455	22·5472	−0·0017
Copper yellow . . .	5782·30	D + 4103·18 L + 5119·45 D − 4103·22 L − 5119·43	D ·885607 + ·885602 L ·885600 − ·885604	·885603 ± 2	22·6157	22·6150	+0·0007
Mercury yellow . .	5769·45	D + 4122·13 L + 5143·13 D − 4122·04 L − 5143·13	D ·889683 + ·889696 L ·889698 − ·889687	·889691 ± 6	22·7201	22·7218	−0·0017
Copper yellow . . .	5700·39	D + 4229·16 L + 5276·65 D − 4229·15 L − 5276·70	D ·912792 + ·912795 L ·912801 − ·912798	·912797 ± 3	23·3101	23·3097	+0·0004
Silver green	5471·72	D + 4614·09 L + 5756·92 D − 4614·12 L − 5756·88	D ·995877 + ·995875 L ·995874 − ·995874	·995875 ± 1	25·4318	25·4293	+0·0025

Silver green . . .	5465·66	D+4624·92 D−4624·88	L+5770·34 L−5770·30	D L	·998206 ·998194	+ ·998203 − ·998197	·998200	± 4½	25·4911	25·4895	+0·0016
Mercury green . .	5460·97	D+4633·20 D−4633·21	L+5780·78 L−5780·74	D L	1·000000 1·000000	+1·000000 −1·000000	1·000000		25·5371	25·5362	+0·0009
Thallium green . .	5350·65	D+4939·10 D−4939·5	L+6037·55 L−6037·68	D L	1·044433 1·044433	+1·044430 −1·044437	1·044433	± 2	26·6718	26·6720	−0·0002
Copper green . . .	5218·45	D+5104·58 D−5104·68	L+6369·03 L−6368·74	D L	1·101748 1·101741	+1·101752 −1·101734	1·101744	± 6	28·1353	28·1371	−0·0018
Silver green . . .	5209·25	D+5124·40 D−5124·45	L+6393·70 L−6393·65	D L	1·106021 1·106027	+1·106024 −1·106024	1·106024	± 1½	28·2447	28·2434	+0·0013
Copper green . . .	5153·33	D+5244·02 D−5244·01	L+6562·85 L−6562·79	D L	1·131833 1·131827	+1·131833 −1·131827	1·131830	± 3	28·9036	28·9039	−0·0003
Copper green . . .	5105·75	D+5349·54 D−5349·48	L+6674·48 L−6674·42	D L	1·154601 1·154597	+1·154605 −1·154593	1·154599	± 4	29·4851	29·4848	+0·0003
Cadmium green . .	5085·82	D+5394·03 D−5394·06	L+6730·15 L−6730·05	D L	1·164215 1·164224	+1·164223 −1·164217	1·164220	± 4	29·7308	29·7332	−0·0024
Zinc blue	4810·71	D+6080·74 D−6080·78	L+7586·82 L−7586·65	D L	1·312429 1·312412	+1·312428 −1·312413	1·312420	± 8	33·5154	33·5165	−0·0011
Cadmium blue . . .	4799·91	D+6109·85 D−6109·87	L+7623·31 L−7623·03	D L	1·318710 1·318715	+1·318724 −1·318700	1·318712	± 7	33·6761	33·6798	−0·0037
Zinc blue	4722·26	D+6329·81 D−6329·62	L+7987·33 L−7897·29	D L	1·366162 1·366134	+1·366159 −1·366134	1·366148	±13	34·8875	34·8898	−0·0023
Zinc blue	4680·38	D+6453·72 D−6453·63	L+8052·30 L−8052·03	D L	1·392916 1·392926	+1·392940 −1·392903	1·392921	±12	35·5712	35·5701	+0·0011
Cadmium blue . . .	4678·37	D+6459·88 D−6459·74	L+8059·43 L−8059·63	D L	1·394241 1·394199	+1·394215 −1·394220	1·394219	±12	35·6043	35·6034	+0·0009
Mercury violet . .	4358·58	D+7538·28 D−7538·19	L+9405·19 L−9405·24	D L	1·627001 1·626987	+1·626994 −1·626990	1·626992	± 4½	41·5487	41·5481	+0·0006

The tabulation of the average errors gives a very fair idea of the degree of accuracy attained in the actual reading of the lines. As these errors average about 5 parts per million and do not exceed 13 parts per million, even in the case of the blue lines, it may be presumed that the first five decimals in the ratios can be relied on throughout the table, the probable error in nearly all the lines amounting only to a few units in the sixth decimal. These figures are multiplied by 25·5371 to give the rotations in degrees per millimetre; but when tabulated to four places of decimals the errors in the last significant figure are reduced to a quarter of their previous values; the average error of reading is thus 0°·0001 per mm. or less in 12 of the 24 lines; in the case of eight more lines it is 0°·0002 per mm. or less and in three lines only it reaches its highest value at 0°·0003 per mm.; the fourth decimal is, therefore, subject on the average to an error of reading of only a little over one unit.

The errors discussed in the preceding paragraph refer merely to the discrepancies introduced into the dispersion-ratios by changing from dextro- to lævo-quartz or from a positive to a negative half-shadow angle. They do not take any account of errors due to imperfect purification of the light or to incorrect figures for the wave-length (or optical mass centre) of the lines, which may in some cases be appreciable, *e.g.*, in the case of the two green copper lines, which are known to include satellites. Even the ordinary wave-length determinations may contribute appreciable errors, since an error of 0·01 Ångstrom unit would introduce an error of three units in the sixth decimal of the dispersion-ratios.

Some idea of the maximum amount of these irregular errors can be obtained from the values of the rotations calculated from a formula. Any attempt to discuss fully the equation to the dispersion-curve would be premature until work now in progress, on the rotatory dispersion in quartz, in the ultra-violet and in the infra-red regions of the spectrum, has been carried to completion; but a preliminary survey, for which I am greatly indebted to Mr. T. W. Dickson, of the City and Guilds College, South Kensington, has shown—

(1) That the simple equation

$$a = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k'}{\lambda^2},$$

which Drude ('Theory of Optics,' p. 414) regarded as sufficient for calculating the rotatory dispersion of quartz to two places of decimals, is quite inadequate to represent the values now given to four places of decimals;

(2) But the equation

$$a = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_2}{\lambda^2 - \lambda_2^2} + \frac{k}{\lambda^2},$$

where $\lambda_1^2 = 0·010627$, $\lambda_2^2 = 78·22$ gives values which, in the case of 22 out of 24 wave-lengths, differ on the average from the observed figures by only a single unit in the third decimal place, *i.e.*, by 1 part in 25,000. This agreement is somewhat remarkable in an equation containing only three arbitrary constants.

The equation given above also shows a remarkably close agreement with a preliminary series of observations in the infra-red. It is, therefore, evident that the infra-red absorption is an essential factor in determining the optical rotation in quartz, both in the infra-red and in the visible region of the spectrum, and that DRUDE was in error in supposing "that the kinds of ions whose natural rotations lie in the infra-red are inactive" (*loc. cit.*, p. 413).

The equation does not agree so well with preliminary measurements in the ultra-violet region and cannot be made to do so without sacrificing the concordance obtained in the values for the visible region of the spectrum. It is considered probable that further experience may demand either (1) some modification in the value $\lambda_1^2 = 0{\cdot}010627$ at present accepted for the wave-length of the ultra-violet absorption, or (2) substitution for the term $\frac{k}{\lambda^2}$ of a term of the ordinary form $\frac{k_3}{\lambda^2 - \lambda_3^3}$. The exact nature of the modification needed to bring the values for the ultra-violet region into agreement with the observed figures will be discussed only when the experimental work in this region has been completed.

For the present the calculated values serve mainly to place a limit upon the maximum error from all sources that can be ascribed to the measurements now recorded. The readings for the red zinc line appear to be quite abnormal, as they differ from the calculated value by 0°·006 per mm. and cannot be brought into agreement by any modification of the constants without spoiling the concordance of the rest of the figures. Deviations amounting to nearly 0°·004 per mm. are observed in the case of the blue cadmium line; but these form part of a group of negative differences and must be attributed, at least to some extent, to imperfections in the formula, which (as has already been suggested) requires the addition of a fourth arbitrary constant to bring it into complete accord with the experimental figures. The necessity for a fourth term is shown by the fact that whilst the concordance between the observed and calculated values is very good at the ends and in the middle of the series, the differences being

Li 6708, +0·0003; Hg 5461, +0·0009; Hg 4359, +0·0006;

there is a predominance of positive differences in the first twelve and of negative differences in the last twelve values.

Thus, if all the values be included, the average differences are

Wave-length 6708 to 5461	+0·0007
Wave-length 5351 to 4359	−0·0007;

if the reading which shows the largest difference in each group be excluded, the average differences are

Wave-length 6708 to 5461	+0·00025
Wave-length 5351 to 4359	−0·00036.

These differences show clearly that the calculated curve is too flat from 5351 to 4359 and not quite flat enough from 6708 to 5461.

In estimating the actual errors of experiment, this limitation of the calculated curve must be taken into account, since this consideration serves to reduce the average error of the 24 readings from 0·0015 to less than 0·0008 and the average error of 22 out of 24 readings from 0·0011 to less than 0·0005; the average error of experiment is, therefore, probably not greater than 0°·0005 per mm. But even if no such allowance be made, it may be seen from the table that 10 out of 24 observed values differ by less than 0·001, 9 more by less than 0·002, 3 more by less than 0·003 and one each only by 0·004 and 0·006 from the calculated values.

8. *Comparison with Earlier Observations. Optical Mass-centre of Sodium Light.*

Comparison with previous observations is almost impossible, except in the case of sodium light, for which the figures are

	SORET and SARASIN.		LOWRY.	
	R Quartz "IV" (60 mm).	L Quartz "II" (30 mm).	R Quartz.	L Quartz.
D_1* . . .	21·696	21·684	21·6988	21·7004
D_2* . . .	21·724	21·727	21·7471	21·7485
Mean . .	21·710	21·706	21·7230	21·7245

In order to secure a wider basis for comparison and incidentally to determine the optical mass-centre of the light of the sodium doublet, readings were taken with a small piece of the lævo-quartz, 25·902 mm. in length. The rotations were

Mercury green	661°·47
Sodium yellow	562°·82

$$\left\{\begin{array}{lcl} \text{Ratio} & = & 0{\cdot}85086 \\ \text{Ratio for } D_1 & = & 0{\cdot}84975 \\ \text{Ratio for } D_2 & = & 0{\cdot}85164 \end{array}\right\}$$

Whence, taking $D_1 = 5896{\cdot}155$, $D_2 = 5890{\cdot}186$, the optical mass-centre of the doublet is found to be 5892·64 and the ratio of the intensities of the two lines $D_1 : D_2 = 1 : 1{\cdot}42$. These figures agree fairly closely with the numbers 5892·5 and 1 : 1·6 calculated by LANDOLT from the data of LIPPICH and DIETRICH ('Optical Rotating Power,' p. 403).

Confirmation was also obtained of the observations of ZÖLLNER and of EBERT ('LANDOLT,' pp. 407–413) which showed that the optical mass-centre was shifted

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* Following LANDOLT ('Optical Rotating Power,' p. 403) the less refrangible line is distinguished as D_1.

towards the red on increasing the brightness of the lines. Thus sodium light, produced by placing a piece of sodium bicarbonate on the grid of a Mecker burner, gave the reading 562°·84, where light from a bead heated by an oxygen-jet in the flame of the burner (fig. 2A) gave 562°·80, the light being purified in each case by a D.V. prism on the eye-piece of the polarimeter; the mean of these two readings was used in the calculation of the optical mass-centre.

The observations of ZÖLLNER ('LANDOLT,' p. 408) to the effect that the D_2 line widens symmetrically whilst D_1 widens more rapidly towards the red, are likewise in accord with the experience gained in the present experiments, where steady values for D_2 were obtained in the very first series of readings, whilst D_1, although only slightly weaker, gave very variable readings and was by far the most troublesome line of the whole series to read.

Whilst there is no great satisfaction, in view of the uncertainties as to its mass-centre, in giving figures for the sodium doublet, there is no other way of securing a comparison with the observations of other workers. The figures for light of wave-length 5892·64 are

LOWRY . . .	R Quartz	21·7270	Tabulated value 21·7283.
	L ,,	21·7286	

Comparison in the form given above with the observations of SORET and SARASIN is difficult, as their values for D_1 and D_2 differ by 0°·028 per mm. in one case and 0°·043 per mm. in the other and are obviously uncertain even in the second decimal; but SORET and GUYE, working with SORET and SARASIN'S Quartz "IV" found the value 21·7195, as compared with the values 21·7205 and 21·7132 which they quote from SORET and SARASIN; the mean value may be taken as 21·718. LANDOLT has calculated the values 21°·724 from the readings of VON LANG; 21°·723 from the readings of SORET and GUYE; 21°·724 from readings given by GUMLICH for plates from 5 to 10 mm. in thickness, the individual values ranging from 21°·717 to 21°·731: and 21°·722 from the readings of SCHÖNROCK for a plate only 5 mm. thick. The general average, 21°·723 is a little lower than the value given by the faulty specimens of quartz rejected in the course of the present investigation, for which the value 21·7255 may be taken and indicates that these were rather above than below the general average of quality of the specimens used in earlier investigations.

Some interest attaches to the dispersion-ratios of the defective cylinders of quartz which were rejected at the commencement of 1911. The best values for the extreme red and violet lines were

Li . . .	0·647589	instead of	0·647525	(+ 0·000064)
Hg . . .	1·626753	,, ,,	1·626992	(– 0·000239).

The differences for other lines were almost all positive towards the red and negative towards the violet. The behaviour of these specimens was in very close agreement with what would be expected in a substance obeying the same dispersion-law but possessing a rather lower dispersive power. The figures are of importance as showing that the defects reduced the dispersive power of the specimens, as well as the absolute values of the rotations. No such steady difference could be detected between the values for the specimens of dextro- and lævo-quartz finally selected. These gave the numbers

	Dextro.	Lævo.	
Li . . .	0·647508	0·647539	(− 0·000031)
Hg . . .	1·627001	1·626987	(+ 0·000014),

corresponding with errors of reading of about 0°·16 and 0°·07 respectively; the differences do not exceed the possible range of experimental error and (taking the lævo-cylinders as the standard) are also in the opposite direction to those recorded above for specimens that were known to be faulty.

9. *Tests of* Wiedemann's *Law.*

The law of the proportionality of natural and magnetic rotatory powers over a range of wave-lengths was discovered by G. Wiedemann in 1851 ('Pogg. Ann.', vol. 82, 215) from experiments on turpentine, using a series of five Fraunhofer lines. It was tested after an interval of over half a century by Disch ('Ann. d. Physik,' 1903 [IV.], vol. 12, 1153), whose results are given in a memoir which is of further interest as being the earliest in which the use of the Arons mercury lamp in polarimetric work is described. Disch found a steady difference between the two dispersions as is shown by the following ratios:—

Wave-length		6563	5893	5780	5461	4916	4359	4050
Ethyl valerate	natural . . .	1·000	1·258	—	1·500	1·924	2·573	—
	magnetic . .	1·000	1·167	—	1·380	1·746	2·267	—
Quartz . . .	natural . . .	1·000	1·254	1·307	1·475	1·846	2·400	2·826
	magnetic . .	1·000	1·251	1·301	1·464	1·821	2·316	2·672

It is remarkable that Disch should have concluded from these figures that "both the tables and the curves show that Wiedemann's Law holds to a very close approximation: the quotient n/m is as good as constant, the ratios for the optical and magnetic rotations are nearly equal to one another and accordingly the two curves fall almost together." The deviations, which amount to 12 per cent. in one case and 5 per cent. in the other, were attributed by Disch to a lack of optical homogeneity in the ester and to a lesser extent in the quartz.

As this matter was one of considerable importance, especially as regards the theory of magnetic rotation, experiments were made to test the law in the case of quartz as well as of a series of organic liquids whose optical and magnetic rotatory dispersions have been measured during the last six years. A description of the apparatus and methods used in these investigations will be given in a later paper dealing specifically with the rotatory dispersion of organic compounds. But the main results may be summarised in the words of a brief preliminary note, communicated to the Winnipeg meeting of the British Association in 1909, to the effect that "in the case of quartz there is an absolute agreement between the two dispersions, but every optically active liquid that has been examined shows a divergence between the two series of values, the optical dispersion being usually but not always higher than the magnetic dispersion."

Since the publication of this note, DARMOIS has described ('Ann. Chim. Phys.,' 1911 (VIII.), vol. 22, 247–281, 495–589) a series of measurements of the optical and magnetic rotatory dispersion of a number of compounds of the terpene series, some of the measurements being carried into the ultra-violet region. He concluded that "the law of proportionality was quite inexact, and that WIEDEMANN'S result was the result of a pure chance"; he further states that, since normal magnetic dispersion may accompany an anomalous optical dispersion, "WIEDEMANN'S Law has no longer any manner of significance."

This conclusion, differing so entirely from that of DISCH, although based upon observations of much the same character, is not in agreement with the conclusions that have been drawn from the present series of experiments. These were summed up in the note already referred to, in a reference to the general "identity of the optical and magnetic dispersion in crystals." The view that WIEDEMANN'S Law holds accurately for crystals but not for active liquids is at present based upon observations in the case of crystals of quartz only, but it is hoped at a later date to test it by analogous observations on sodium chlorate and other crystals.

In measuring the magnetic rotatory dispersion of quartz 4 pieces of lævo-quartz of length 100·29 mm. were set up with 4 pieces of dextro-quartz of length 98·83 mm., giving a total length of 199·12 mm. with only 1·46 mm. of lævo-quartz uncompensated. The following readings were obtained for the magnetic rotatory power at 20° C.:—

Water, 200·34 mm., gave 12°·61 for wave-length 5461.
Quartz, 199·12 mm., gave 16°·29 ,, ,,

			Dispersion – Ratios.		
		Magnetic rotation.	Magnetic.	Optical.	Difference.
Li	6708	10°·53	0·646	0·648	+0·002
Na . . .	5893	13·86	0·851	0·851	±
Hg . . .	5461	16·29	1·000	1·000	±
Cd . . .	5086	19·01	1·167	1·164	−0·003
Cd . . .	4800	20·47	1·318	1·319	+0·001
Hg . . .	4359	26·50	1·627	1·627	±

The following values for 24 mm. thickness of silica discs, appear to indicate that the magnetic rotatory dispersion is a little higher in the vitreous than in the crystalline state :—

		Rotations.	Ratios.
Li	6708	1°·19	0·63
Hg	5461	1°·89	1·00
Hg	4359	3°·17	1·67

An equal length of quartz gave a rotation 1°·98 instead of 1°·89 for wave-length 5461. Later attempts to secure a rod of clear silica 100 mm. in length for accurate measurements of the magnetic rotatory dispersion, were not successful; although the material contained fewer bubbles than the discs prepared a few years before, the triple field of the polarimeter could not be seen through the rod, which gave instead a splendid demonstration of AIRY'S spirals.

As contrasted with the exact accordance, throughout the range from 6708 to 4359, of the two series of dispersion-ratios for quartz, it may be noted that the nearest approach to equality in a series of 23 alcohols was found in the alcohol phenylmethyl-carbinol which gave for the ratio 4359/5461

Magnetic 1·739, Optical 1·736.

But the accidental nature of this concordance is clearly shown by the fact that the next homologue phenylethyl-carbinol gave the values

Magnetic 1·731, Optical 1·674.

10. *Summary.*

(1) A large crystal of optically perfect lævo-quartz has been found which produced a rotation of 25°·5371 per mm. in light of wave-length 5460·97. Cylinders, also apparently perfect, cut from a crystal of dextro-quartz, produced a rotation of 25°·5361 per mm. Cylinders cut from plates of dextro- and of lævo-quartz which gave the figure 25°·5338 per mm. were shown to be faulty by a new test, in which the specimen, mounted between Nicol prisms set to extinction, is examined with monochromatic green mercury light, with the help of a telescope focussed on the interior of the crystal. A very sensitive test of the optical purity of quartz consists in measuring its optical rotatory power for mercury green light with both a positive and a negative half-shadow angle.

(2) The rotatory dispersive power of quartz has been determined by measuring the rotation produced in light of 24 wave-lengths from Li 6708 to Hg 4359, using a column of lævo-quartz 226·3670 mm. in length and a column of dextro-quartz 181·4382 mm. in length. The average error of the readings amounts to about 6 parts per million; the average error from all sources in the absolute values is probably not more than 0°·001 per mm.

(3) By taking into account the infra-red absorption it has been possible to calculate the rotations in degrees per millimetre with an average error not exceeding 0·0015 degrees per millimetre.

(4) WIEDEMANN'S Law of the proportionality of natural and magnetic rotations over a range of wave-lengths has been verified in the case of quartz but does not hold good in the case of optically active liquids.

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