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## ULTRA-VIOLET ROTARY DISPERSION.

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THE power of rotating the plane of polarization of transmitted radiation is particularly interesting in the region of the very short wave-lengths. In the first place it affords an indication of what the limiting value of the rotation would be for infinitely short waves. From theoretical considerations we might expect this limiting value to be either zero or infinity, possibly a finite constant. Again, rotary dispersion in the ultra-violet affords valuable data for the theory of rotation in the neighborhood of an absorption band. Theoretically, we should have a greatly enhanced rotation near every absorption band and a large rotation of opposite sense in the middle of the band. Now all transmission spectra end sooner or later in the ultra-violet in an absorption band, so that the ultra-violet region is an excellent one for obtaining the data desired.

Previous work in the ultra-violet has been confined to quartz and sodium chlorate. Soret and Sarasin<sup>1</sup> have observed the rotation of quartz out as far as the cadmium line 26, wave-length 214.3  $\mu\mu$ , where they found the rotation per millimeter thickness 236 degrees, while in the yellow it is only about 21 degrees and in the infra-red about ten. Guey<sup>2</sup> observed the rotation of sodium chlorate out as far as wave-length 250  $\mu\mu$ . The rotation of this substance is

<sup>1</sup> Compt. rend., 95, 636, 1882.

<sup>2</sup> Compt. rend., 108, 348, 1889.

small, increasing from three degrees in the yellow to fifteen degrees at 250.

Rotation in the neighborhood of an absorption band has been observed by Schmauss<sup>1</sup> working with the magnetic rotation of cyanine and other dyestuffs in alcohol solution, and by Cotton<sup>2</sup> who observed the structural rotation of copper and chromium tartrates. Zeeman<sup>3</sup> has observed the magnetic rotation of sodium vapor up to and within the lines. Several other observers have worked on anomalous rotation, that is, rotation which decreases with decreasing wave-length.

The methods available for work in the ultra-violet and in regions of strong absorption are but limited in number. Previous work has been done by visual methods with a fluorescent eyepiece. Guye used a quartz-wedge polariscope with his eyepiece. But visual methods fail when the transmitted radiation is excessively feeble and one must resort to the cumulative methods of photography. Glan or Foucault nicols can be used out as far as 230  $\mu\mu$ , where the calcite begins to absorb. Schmauss inserted a block of quartz and a plate of gypsum with his rotating column of fluid. This method might be used photographically but gypsum is opaque in the ultra-violet and suitable transparent biaxial crystals are not available. A much simpler and entirely satisfactory method was suggested by the apparatus used by Minor<sup>4</sup> for determining the refractive and absorptive indices of the metals in the ultra-violet. This method consists in inserting with the rotating column a pair of quartz rotation wedges. Such wedges produce interference bands which are easily photographed. Inserting a rotating body with the wedges produces a displacement of these bands and the amount of the shift is an accurate measure of the amount of rotation introduced.

#### APPARATUS AND METHOD.

It is, of course, a great saving of time in exposing and measuring to be able to photograph the rotation of the whole spectrum on a single plate. This was found to be feasible experimentally. To

<sup>1</sup> Ann. der Physik, 2, 280, 1900.

<sup>2</sup> Jour. de Ph. (3), 5, 237, 1896.

<sup>3</sup> V. K. Ak. van Wet., 1902-3, pp. 6-11.

<sup>4</sup> Ann. der Physik (4), 10, 581, 1903.

accomplish this we must get the interference bands and spectrum lines in focus at the same place, that is the rotating wedges must be placed at the slit or an image of the slit of the spectroscopy used in producing the spectrum. The final arrangement adopted is shown in the figure.

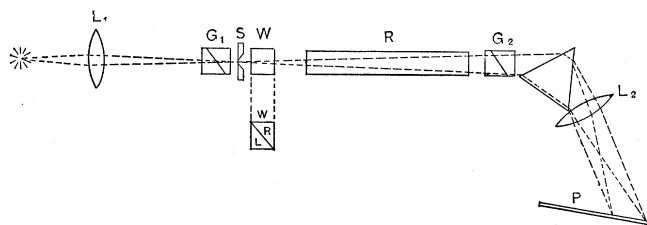


Fig. 1. Diagram of Apparatus.

An image of the spark source is thrown on the slit *S* and a spectrum formed on the photographic plate *P*. Before entering the slit, the light is polarized by the Glan nicol *G*<sub>1</sub> and immediately afterward passes through the rotation wedges *W*. A second Glan nicol *G*<sub>2</sub> is placed near the prism and the tube of rotating solution inserted between this nicol and the wedge pair. The distance *L*<sub>1</sub> — *S* and *S* — *P* are made very great so that the light is very nearly parallel as it passes through the wedges and rotating substance. The nicols were used parallel so that the central straight band was dark on the photographic plate.

A spark between electrodes made of an alloy of zinc and aluminium was used as a source of radiation through all the work. The spark spectrum of this alloy contains a convenient number of lines very evenly distributed. A crystal of some sodium salt was held in the spark from time to time. This not only brought up the photographic intensity in the yellow but so increased the possible length of the spark that much more capacity could be used and the intensity of the source increased many times. The Glan nicols were 20 mm. cubes and were found to be admirably adapted to this use. The nicols do not require very accurate adjustment for this kind of work. The slit was set permanently at about 0.3 mm. opening and firmly mounted on a massive metal plate on which the wedges could be mounted and very accurately adjusted. The slit was fitted with a transverse wire cross hair that could be raised and

lowered until its image very nearly bisected the central dark interference band on the photographic plate. It is then opposite that part of the wedges where they are of equal thickness. The wedges were cut to order, one of right and one of left rotating quartz 16 mm. thick and 20 mm. square. The tube *R* for holding the rotating liquid was closed at the ends with a pair of very carefully matched quartz plates, right and left rotating, giving no appreciable resultant rotation. These plates were 25 mm. in diameter and 2.872 mm. thick. A number of different tubes were used, some 5 cm. and some 60 cm. in length, according to the capacity and rotating power of the liquid being investigated. The tube most in use was one of glass 37 cm. in length with the ends very carefully ground to parallelism and the quartz end plates cemented on. The tube and wedge pair require very careful adjustment, otherwise the interference bands would not be regular and sharply defined. These adjustments were made by means of the reflected image of the slit, using an acetylene source. All the quartz parts of the apparatus as well as the Glan nicols, were specially ordered from Messrs. Steeg and Reuter and were of most admirable workmanship. The most difficult and important adjustment of all is finding the proper position and angle for the photographic plate in order that the image of the cross wire and the interference bands may be sharp and straight throughout the whole spectrum. The proper angle having been determined, the plate holder was provided with permanent ways and a micrometer screw. The prism was set at minimum deviation for the end of the visible spectrum, wave-length  $400 \mu\mu$ . Zero plates were taken with the tube filled with water or alcohol, with the tube empty and with the tube entirely removed. After the rotating substance had been inserted, a second photograph was taken. This showed the interference bands displaced up or down along the spectrum lines and the amount and direction of this displacement shows the amount and direction of the rotation at each wave-length. The displacements were measured with a Gaertner micrometer microscope refitted with a low power microscope and glass bed plate. The very highest grade of photographic plates, made of very plane glass and with films free from spots are of course essential for this work. Cramer's instantaneous isochro-

matic plates were found to be entirely satisfactory. Metol-hydroquinone developer gives a hard, clear negative excellent for measuring. Over-exposure and over-development made the bands still sharper and narrower. The time of exposure varied from two minutes to half an hour.

## OBSERVED DATA ON ROTARY DISPERSION:

Out of the large number of rotating substances available, some thirty were tried as promising transparency in the ultra-violet and of these, eight were found to be suitable for observation. The results are given in the order in which they were obtained. Of the other promising substances tried, quinine (sulphate) in water solution was found to become densely opaque just beyond the visible violet. The absorbed ultra-violet quickly precipitated the salt from a saturated solution. Morphine sulphate showed similar properties. Santonin, which possesses the extraordinary rotation of 200 degrees in the yellow and 535 degrees at the end of the visible violet,<sup>1</sup> becomes strongly absorbent just beyond. The various iron double tartrates, which absorb nearly the entire spectrum, show but moderate rotating power in their transmission bands.

*Cane Sugar*,  $C_{12}H_{22}O_{11}$ .—This, in concentrated solution, begins to absorb just beyond the visible, but by taking a very dilute solution and making a long exposure, the rotation was obtained out as far as wave-length 252  $\mu\mu$ . The concentration used was 3.45 grams of sugar to 100 grams of solution, density 1.013, tube length 77.32 cm., temperature 18 degrees. In the table of data below, the column marked  $\lambda$  refers to wave-lengths, that marked

$\lambda$	180° mm.	Ref. mm.	Ref. deg.	Null.	Ob. Rotn.	Sp. Rotn.
589	3.402	1.920	101.6	83.6	18.0	66.8
467	2.134	1.311	110.7	79.6	31.1	115.2
425	1.730	1.094	113.8	77.2	36.6	134.1
395	1.492	0.954	115.0	75.4	40.6	150.4
358	1.182	0.799	121.7	72.6	49.1	182.0
334	0.992	0.708	128.7	70.8	57.9	214.8
309	0.810	0.642	142.6	68.5	74.1	274.8
281	0.637	0.588	165.1	65.6	99.5	368.9
256	0.527	0.574	196.4	62.6	133.8	496.0
252	0.486	0.554	205.7	61.9	143.8	533.5

<sup>1</sup> Nasini, Ac. dei Lincei, 3, 13, 1882.

$180^\circ$  gives the width of an interference band in mm. That marked Ref. (mm). gives the distance from the image of the cross wire to the center of the interference band use for reference. Under Ref. (deg.) is given the same distance expressed in degrees. "Null" is the corresponding distance before rotation occurred. Then follow observed rotation and specific rotation.

From wave-length 358 on, the second band was used for reference instead of the first. The distances given in the third column were obtained by subtracting the width of a band from the observed distances. The specific rotation is calculated from the observed rotation by means of the formula

$$R - r/lpd,$$

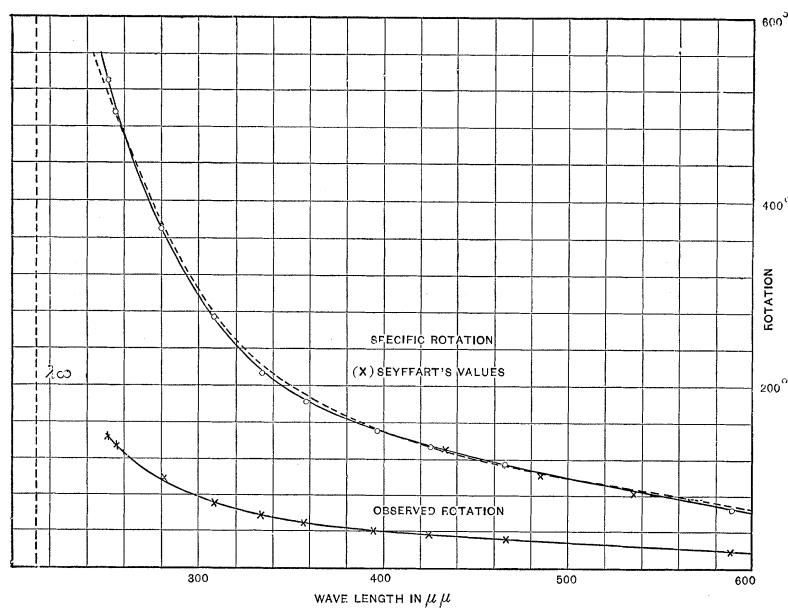


Fig. 2. Rotation of Cane Sugar.

where  $l$  is the length of the observed column of solution expressed in decimeters,  $d$  is the density of the solution and  $p$  is the ratio of the weight of the dissolved solid to the weight of the solution in a given volume. It is the concentration of the solution divided by its density. The factor  $l/pd$  merely corrects for the presence of the neutral solvent.

The dispersion curve is remarkably uniform and shows steadily increasing values toward the shorter wave-lengths, rising well out in the absorption band at 250 to a rotation of  $560^\circ$ . No exterior limit to the absorption band could be observed; it probably continues through the remainder of the spectrum. Some previous observations of Seyffart in the visible spectrum are given.

*Camphor*,  $C_{10}H_{16}$ .—Camphor has a strong absorption beginning just beyond the visible. Readings were obtained as far as 334. The material used appeared very pure, but as camphor is such an

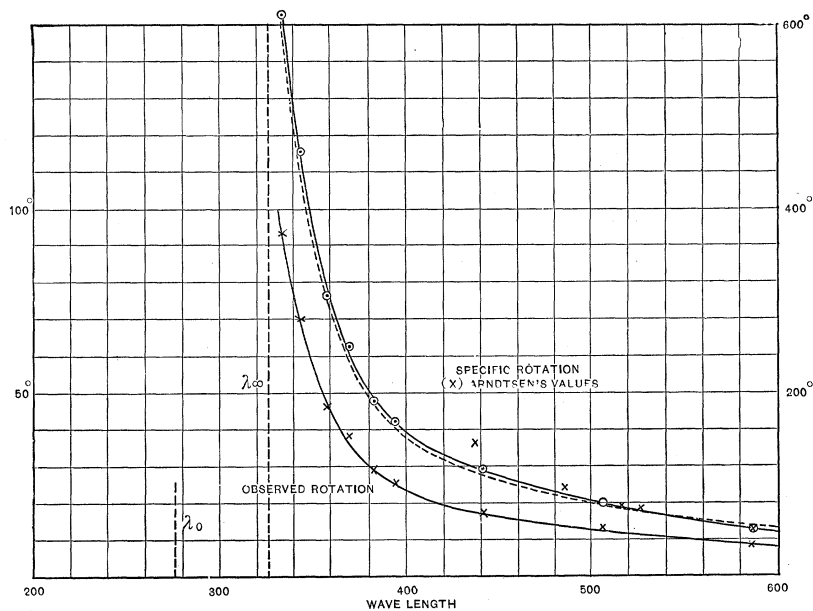


Fig. 3. Rotation of Camphor.

excellent solvent for organic impurities, it was twice distilled before dissolving in freshly distilled ethyl alcohol for use. The concentration used was 34.70 grams of camphor to 100 grams of solution density 0.864, temperature  $18^\circ$ .

The curve is an excellent example of the dispersion in the neighborhood of a broad band. The dispersion remains regular and normal up to near where the absorption begins and there increases very sharply. The essentially different value obtained by Arndtsen

at wave-length 438 might easily have been caused by a slight shifting of the absorption band due to a trace of impurity or isomeric camphor. Camphoric acid was tried but it transmitted only the visible spectrum and its rotation showed no unusual features.

$\lambda$	180° mm.	Ref. mm.	Ref. deg.	Null.	Ob. Rotn.	Sp. Rotn.
589	2.505	1.277	91.62	83.61	8.01	52.4
506	1.880	0.985	94.4	81.1	13.3	87.2
441	1.425	0.760	96.0	78.1	17.9	117.2
395	1.095	0.615	101.1	75.4	25.7	168.1
383	1.030	0.594	103.9	74.6	29.3	191.9
370	0.940	0.515	111.9	73.5	38.4	251.4
358	0.897	0.593	118.9	72.6	46.3	303.0
344	0.786	0.620	142.0	71.6	70.4	462.0
334	0.706	0.644	164.3	70.8	93.5	612.5

*Limonene and Pinene.*—Two of the principal components of turpentine, dextro-limonene and lævo-pinene, were tested and found to absorb slightly at wave-length 420 and quite completely even in columns but 4 cm. thick at 390. The observed rotations are here recorded, however, on account of the striking dissimilarity in the

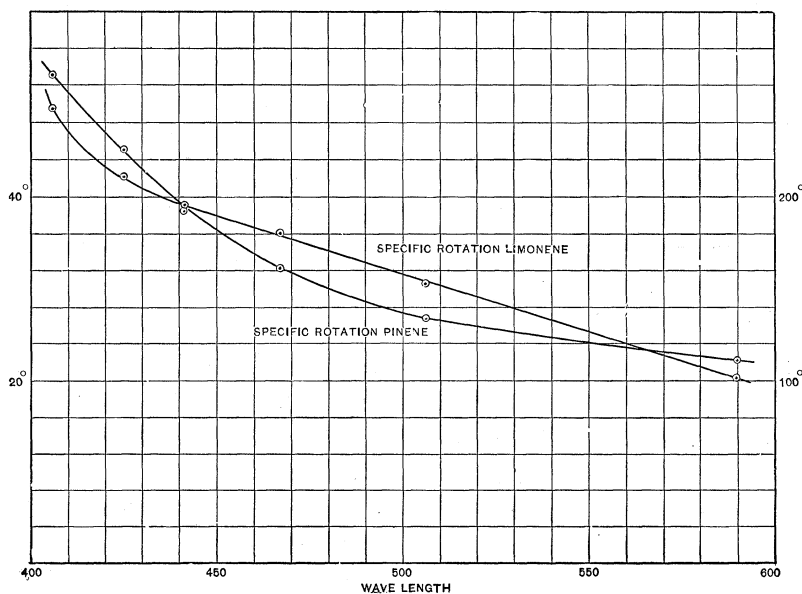


Fig. 4. Rotation of Limonene and Pinene.



dispersion curves of the two substances and the departure of both curves from the normal form that we should expect.

*Specific Rotation.*

$\lambda$	Limonene.	Pinene.
589	100.7	22.35
506	153.6	26.92
467	180.1	32.20
441	194.5	37.64
425	211.4	45.01
406	248.0	53.35

Neither curve is of the normal type as are those of sugar and camphor. The curvature of the pinene curve is remarkably uniform while that of the limonene is very small throughout most of its length.

*Lactose*, Milk Sugar,  $C_{12}H_{22}O_{11} + H_2O$ .—The lactose used was the chemical preparation supplied by Merck and proved quite trans-

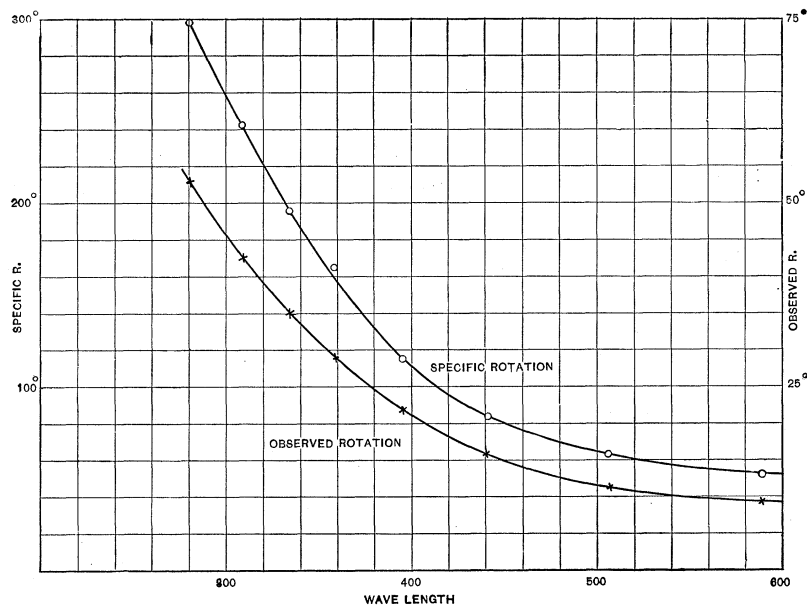


Fig. 5. Rotary Dispersion of Lactose.

parent in the ultra-violet. Readings were obtained as far as  $281 \mu\mu$ , absorption being noticeable beyond  $350$ . A water solution was

used having the density 1.025 and containing 15.81 per cent. of lactose. The temperature was 19°.

$\lambda$	180° mm.	Ref. mm.	Ref. deg.	Null.	Ob. Rotn.	Sp. Rotn.
589	2.987	1.398	84.15	95.4	9.25	52.4
506	2.250	1.047	83.83	95.0	11.17	63.3
441	1.695	0.744	77.0	94.9	15.9	90.1
395	1.219	0.444	73.1	94.9	21.8	114.2
358	1.020	0.377	66.6	95.8	29.2	165.3
334	0.855	0.294	61.9	96.9	35.0	196.4
309	0.707	0.224	57.6	100.4	42.8	242.4
281	0.581	0.171	55.2	108.1	52.9	299.5

The rotary dispersion is small and uniform, such as would correspond with a broad absorption band with diffuse edges. The curves are normal and typical.

*Maltose* and *Glucose*,  $C_6H_{12}O_6$ .—The purest chemically prepared glucose obtainable was slightly yellow in solution, absorption began

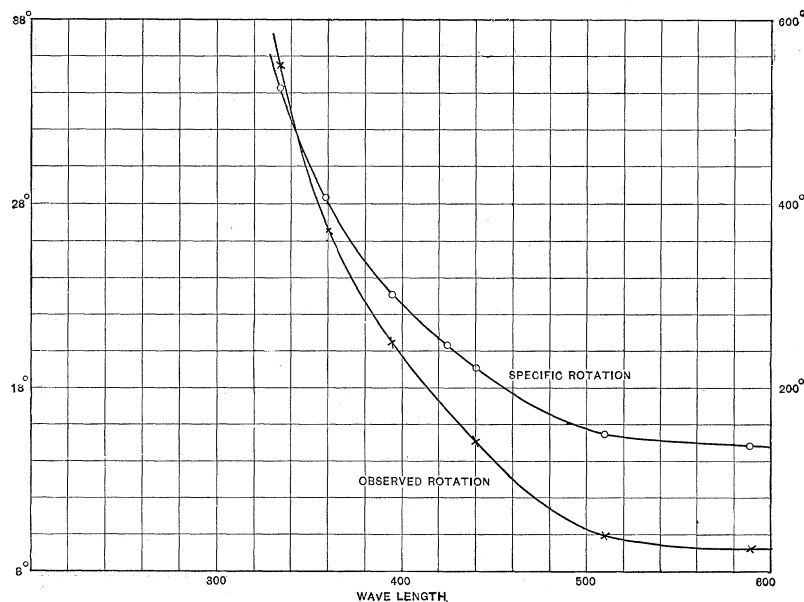


Fig. 6. Rotary Dispersion of Maltose.

in the green and became very strong in the violet. Shaking up the solution with bone-black and filtering through sand and charcoal

did not improve its transparency. Maltose proved more transparent and with a very dilute solution readings were obtained out to  $334 \mu\mu$ . The density of the solution was 1.005 and it contained 1.794 per cent. of maltose. Tube length 37.59 cm., temperature  $19^\circ$ .

$\lambda$	180° mm.	Ref. mm.	Ref. deg.	Null.	Ob. Rotn.	Sp. Rotn.
589	2.918	1.394	86.10	95.41	9.31	137.5
506	2.200	1.038	84.9	95.0	10.1	149.3
441	1.684	0.750	79.9	94.9	15.0	221.9
425	1.526	0.662	78.2	94.9	16.7	246.8
395	1.290	0.537	74.4	94.9	20.5	303.0
358	1.023	0.389	68.4	95.8	27.4	405.1
334	0.85	0.29	61.4	96.9	35.5	524.8

The dispersion curves are of the ordinary type except that there is a slight irregularity in the green and just beyond the visible such as would be caused by a shoulder in the absorption curve in the blue.

*Tartaric Acid*,  $H_2C_4H_4O_6$ .—This, as well as nearly all of its salts, is quite transparent in the ultra-violet when very pure. Measurements were made out as far as wave-length 281 without difficulty. A water solution was used having a density 1.236 and containing 28.625 per cent. of the acid crystals.

$\lambda$	180° mm.	Ref. mm.	Ref. deg.	Null.	Ob. Rotn.	Sp. Rotn.
589	2.982	1.362	82.35	95.4	13.05	9.82
506	2.283	1.068	84.3	95.0	10.7	8.06
467	1.894	0.895	85.0	94.9	9.9	7.49
425	1.555	0.747	86.4	94.9	8.5	6.39
395	1.357	0.661	87.7	94.9	+ 7.2	+ 5.42
358	1.055	0.644	109.8	95.8	-14.0	-10.58
334	0.864	0.694	144.6	96.9	47.7	35.82
309	0.721	0.829	269.0	100.4	168.6	126.8
281	0.629	1.522	436.7	108.1	328.6	247.4

The rotary dispersion of tartaric acid is remarkable for the reversal of the sense of the rotation and for the abrupt change from a small constant positive rotation in the visible spectrum to a very large negative rotation in the ultra-violet. The reversal of the sense of the rotation at a certain wave-length has long been known and studied. In less concentrated solutions the reversal occurs in the visible spectrum. Hence at a given wave-length, within certain

limits, the sense of the rotation reverses at a certain concentration. To account for these exceptional properties of tartaric acid it is usual to assume that the molecules are not all alike in structure. But for the physical discussion of the rotary dispersion we must regard a solution of this substance as of fixed definite composition which is of course independent of the wave-length.

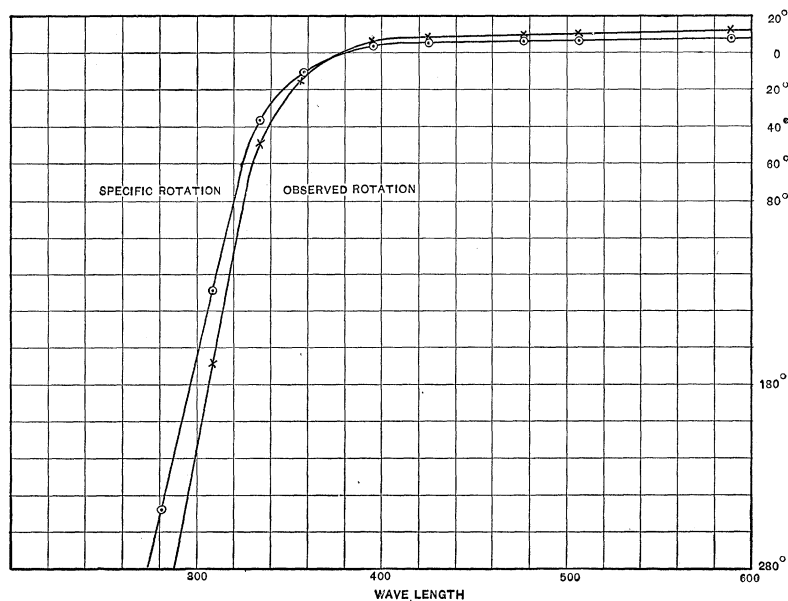


Fig 7. Rotary Dispersion of Tartaric Acid.

*Ammonium Tartrate*  $(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$ .— A 16.24 per cent. water solution was used. Density, 1.070; temperature, 19°; tube length, 37.59 cm.

$\lambda$	180° mm.	Ref. mm.	Ref. deg.	Null.	Ob. Rotn.	Sp. Rotn.
589	3.123	1.269	73.2	95.4	22.2	34.2
506	2.351	0.858	65.7	95.0	29.3	44.9
467	1.977	0.649	59.1	94.9	35.8	54.9
425	1.609	0.459	51.4	94.9	43.5	66.7
395	1.356	0.328	43.6	94.9	51.3	78.6
358	1.067	0.201	34.0	95.8	61.8	94.7
334	0.921	0.142	28.8	96.9	68.1	104.3
309	0.749	0.102	24.5	101.2	76.7	117.4
281	0.578	0.061	18.4	105.5	86.6	132.7

The dispersion curves for ammonium tartrate are quite regular and are rather an extreme type of very small rate of change of dispersion like the turpentine components. Camphor and tartaric acid are the opposite extreme.

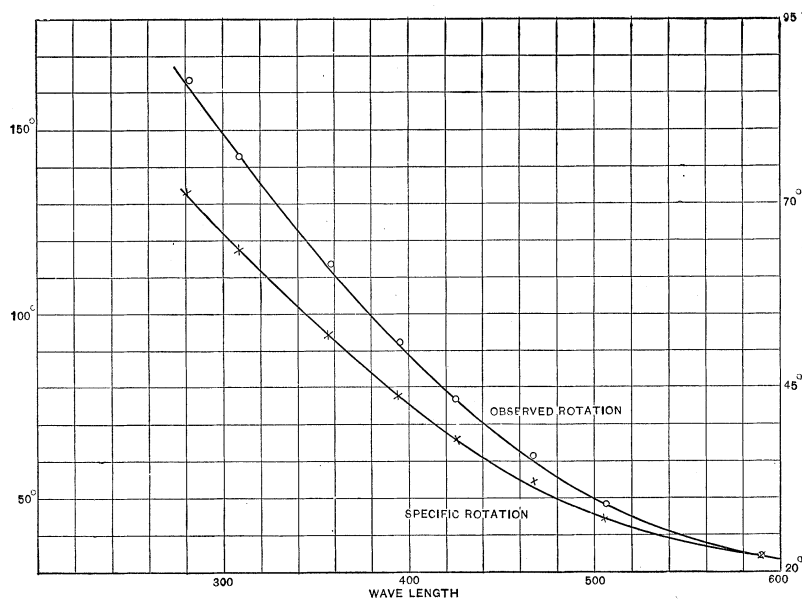


Fig. 8. Dispersion of Ammonium Tartrate.

*Potassium Sodium Tartrate*, Rochelle Salt,  $\text{KNaC}_4\text{H}_4\text{O}_6 + 4\text{H}_2\text{O}$ .  
— Water solution, density, 1.078, containing 18.75 grams of salt to 100 grams of solution. Absorption band intense beyond 300  $\mu\mu$  and extends down into the visible blue.

$\lambda$	180° mm.	Ref. mm.	Ref. deg.	Null.	Ob. Rotn.	Sp. Rotn.
589	3.007	1.320	79.0	95.4	16.4	29.7
506	2.243	0.956	76.8	95.0	18.2	33.0
467	1.898	0.744	70.5	94.9	20.4	36.9
425	1.553	0.593	68.7	94.9	25.6	46.4
395	1.345	0.494	66.1	94.9	28.8	32.2
358	1.065	0.366	61.8	95.8	34.0	62.3
334	0.851	0.274	58.8	96.9	38.1	69.0
309	0.68	0.22	58.4	100.4	42.0	76.1

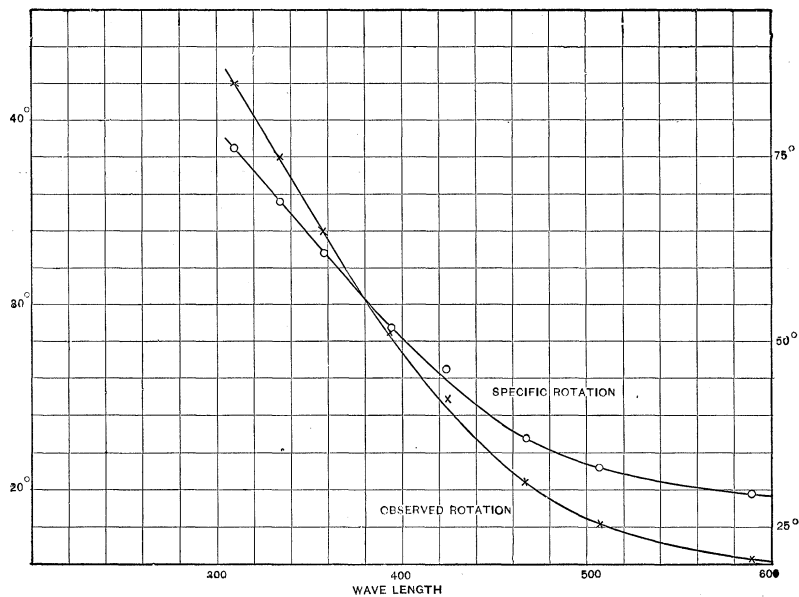


Fig. 9. Potassium Sodium Tartrate.

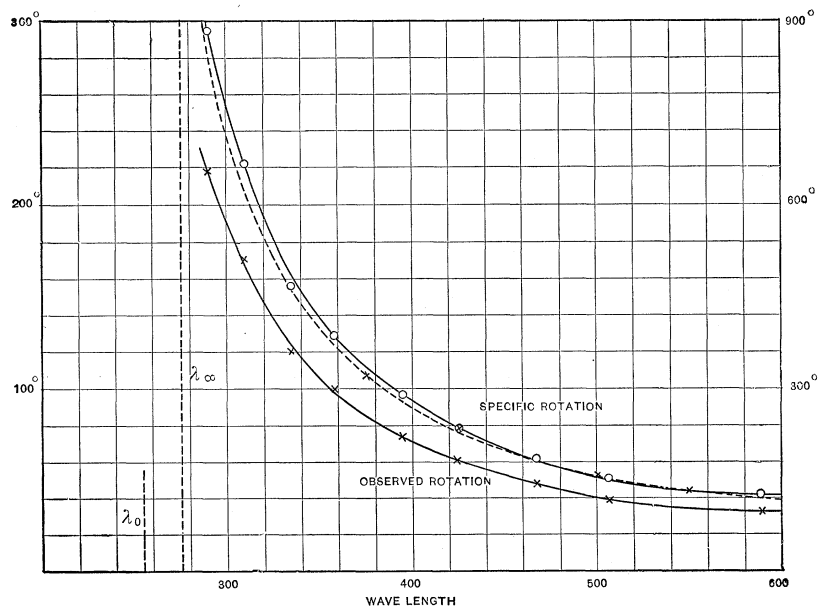


Fig. 10. Rotation of Potassium Antimony Tartrate.

The dispersion curves are of the regular form, the dispersion being unusually constant in the ultra-violet, indicating perhaps that the maximum of the absorption is still far distant or else that the absorption does not become very intense.

*Potassium Antimony Tartrate*, Tartar Emetic,  $2\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 + \text{H}_2\text{O}$ . — Water solution, density 1.032, containing 6.635 per cent. of salt. Absorption perceptible only in the ultra-violet.

$\lambda$	180° mm.	Ref. mm.	Ref. deg.	Null.	Ob. Rotn	Sp. Rotn.
589	2.977	1.044	63.3	95.4	32.1	124.8
506	2.247	0.681	54.6	95.0	40.4	157.0
467	1.867	0.480	46.4	94.9	48.5	188.4
425	1.527	0.283	33.4	94.9	61.5	238.8
396	1.306	0.146	29.14	94.9	74.7	290.0
358	1.039	1.013	175.7	95.8	100.1	388.8
334	0.868	0.751	155.7	96.9	121.2	471.0
309	0.722	0.441	110.4	101.2	170.8	663.5
290	0.644	0.24	167.3	105.5	228.2	886.5

The specific rotatory power is large even in the visible, but in the edge of the absorption band reaches the remarkable value of nine hundred degrees. The rate of increase of dispersion is remarkably uniform, like that of pinene and in marked contrast to that of camphor and tartaric acid.

These ten dispersion curves show very clearly that they could not be made congruent by merely altering the scale on which they are plotted, nor could they be made even approximately straight lines by plotting logarithms of wave-lengths instead of wave-lengths. The cane sugar, lactose and ammonium tartrate curves have somewhat the form of the exponential, but camphor, limonene, maltose and potassium antimony tartrate curves could not be represented by an exponential or logarithmic function even approximately. All the curves are of the form of parts of hyperbolas of higher degree

$$Rf(\lambda) = \text{const. or } Rf(\lambda) = \varphi(\lambda).$$

But if we are to use an algebraic dispersion formula, we see from the irregularities of the curves that it must contain at least four constants. For instance, consider the simplest possible form, the Laurent expansion of the actual function whatever that is, namely:

$$R = A + B/\lambda + C/\lambda^2 + \dots$$

A curve like Fig. 10 could be very approximately represented by the first three terms of this series since its curvature is quite uniform. Dispersion like that of cane sugar (Fig. 2) could be represented fairly well by four terms of the series since its change of curvature is uniform. But to represent the dispersion of camphor (Fig. 3) or of tartaric acid (Fig. 7) would require at least five terms, since the curvature is at least quadratic in  $\lambda$ . Evidently no mere expansion formula will satisfactorily represent such dispersion as we have here to deal with. For use in determining the constants of dispersion formulas the following values of the rotation were taken from the plotted curves:

$\lambda$	Sugar.	Camph.	Limon.	Pinene.	Lact.	Malt.	Tart. Acid.	Am. Tart.	KNa Tart.	KSb Tart.
600	62.1	46.1	95.6	21.8	51.9	135.9	9.4	32.9	29.4	125
575	71.1	54.1	111.0	22.9	53.6	138.3	8.9	35.4	29.8	128
550	80.3	62.0	126.8	24.2	56.0	141.9	8.4	38.2	30.7	135
525	89.7	71.4	142.2	25.6	59.5	145.8	7.9	41.7	31.8	143
500	99.8	81.7	158.0	27.6	64.6	157.0	7.5	45.8	33.6	158
475	110.3	94.3	173.9	30.8	71.2	176.5	7.0	51.1	35.9	177
450	122.2	109.8	189.6	36.4	80.1	207.7	6.6	57.8	39.6	204
425	134.6	129.7	211.0	44.9	92.2	246.8	6.1	65.9	44.7	238
400	149.9	158.6	290	56.1	110.1	291.5	6.0	75.4	50.6	281
375	167.4	221.7			137.3	350.7	1.4	86.0	57.3	334
350	192.9	378.3			171.4	440.6	16.8	97.5	67.9	418
325	252.2				210.9	586	56.8	109.5	78.6	548
300	297.7				258.3		166.0	121.4	88.9	758
275	394.4				310		296.8	142		1020
250	543.0									

#### THE MECHANISM OF ROTATION.

In attempting to develop a consistent possible mechanism of rotation and rotary dispersion, we are led at the outset to distinguish three entirely different rotatory processes, independent of one another and superposable upon each other without interference. These three processes are concerned with the magnetic rotation exhibited by all substances, the structural rotation of some crystals and torsionally strained solids and the molecular rotation shown by certain organic fluids and solids. Naturally active fluids and crys-



tals in a magnetic field rotate just as much on their own account as though the field were not there. And in the very rare instances in which active fluids crystallize so as to rotate structurally as well, the rotation due to each mechanism may be shown to exist independently of the other. It is significant that empty ether is not even magnetically rotating, the presence of matter is necessary to give the magnetic field an effective hold on the light waves.

Dissolve in a transparent solvent a substance having a narrow absorption band and the magnetic rotation of the solution will be greatly enhanced in the neighborhood of the absorption band. But if the solvent be itself rotationally active and the absorbing solute non-active, the rotation of the solution will not differ from that of the pure solvent. The absorbing particles must form a part of the rotating molecule itself before they can affect the rotation. In crystalline rotation it is sufficient that the added particles form an integral part of the crystalline structure.

Molecular rotation is exhibited by such crystals as can occur in twin pairs, one of these forms rotating right-handedly and the other an equal amount left-handedly. The forms of these twin pairs are images of each other, but only such images as are not superposable on each other. In this case the rotation appears to be due entirely to the manner in which the molecules are packed together, for structural rotation is always lost on fusion or solution. It may be imitated by a pile of mica plates arranged with the principal section of each plate turned  $60^\circ$ ,  $90^\circ$  or  $120^\circ$  from the last. But the mechanism of the rotation caused by the mica plate pile can hardly be the same as that of active crystals.

The molecules of active fluids exhibit the same asymmetry of structure as to active crystals. The four atoms or radicles at the extremities of the four carbon bonds are such that they are capable of forming two essentially different molecular structures. These twin pairs are non-superposable images of each other. An active fluid or solution has of course the same rotating power in every direction just as a pile of active crystals would, and probably for about the same reason. Change of state does not affect molecular or magnetic rotation; even in vapor form the specific rotation is the same.

In each of the three kinds of rotation it has been shown that a light wave is resolved into two circularly polarized components in traversing the rotating medium. Fresnel in 1823 showed the existence of circular double refraction in quartz, von Fleischl<sup>1</sup> tested active fluids and recently Brace<sup>2</sup> has shown the same to exist in magnetically active glass. Now it may be shown mathematically that the resultant of two circularly polarized waves of equal amplitude, but different (not complex) velocities is a plane polarized wave whose plane of polarization rotates as the wave advances. Hence any substance that has the power of breaking up a linear vibration into its circular components will rotate the plane of vibration, since the one essential for having this power is that right and left circularly polarized waves are transmitted with unequal velocities. If the velocities are real, say  $V_1$  and  $V_2$ , then the rotation per unit length, expressed in radians is

$$\frac{\pi}{T} \left( \frac{1}{V_2} - \frac{1}{V_1} \right) \text{ or } \pi \left( \frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right)$$

where  $T$  is wave-period and  $\lambda$  wave-length. In terms of circular refractive index the rotation is therefore

$$R = \frac{\pi}{\lambda} (n_2 - n_1).$$

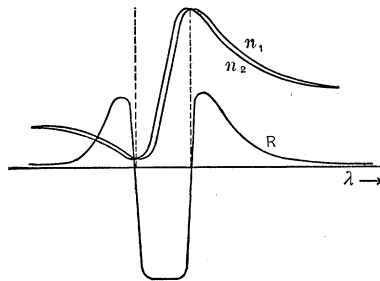


Fig. 11.

The figure shows the essential relation existing between difference in velocity (or difference in index) and rotation, independently of any theory of the mechanism of rotation. The ordinates of the

<sup>1</sup> Wied. Ann., 24, 127, 1885.

<sup>2</sup> Phil. Mag. (6), 1, 464, 1901.

rotation curve have been plotted proportional to the difference in the ordinates of the index curves. Now  $n_2$  and  $n_1$  are the same functions of  $\lambda$  and may be made congruent by changing  $\lambda$  by a constant. Call this constant  $a$ . Then if  $n_1 = f(\lambda)$ ,  $n_2 = f(\lambda + a)$ . On the diagram,  $a$  is seen to be the distance between the maxima (or minima) of  $n_1$  and  $n_2$ . Hence  $n_2 - n_1 = f(\lambda + a) - f(\lambda)$ . Expand this in a Taylor series and substitute in the above formula for the rotation and we have at once the rotatory dispersion formula

$$R = \frac{\pi}{\lambda} \left( a \cdot f'(\lambda) + \frac{a^2}{2} \cdot f''(\lambda) + \dots \right).$$

leaving the molecular (or magnetic) constant  $a$  to be determined by experiment. Using but the first term of this expression, we have the familiar rotary dispersion formula

$$R = \frac{k}{\lambda} \cdot \frac{dn}{d\lambda}.$$

It is remarkable that by the above formula the rotation is proportional to the tangent of the angle of slope of the index curve and the figure shows this property very clearly. If the wave velocities are complex quantities, as they are when the absorption is finite, the rotation is not so simply expressed. This case will be discussed later with the mathematical theory of rotation.

The mechanism of structural rotation is perhaps the simplest of all three kinds. That a crystal possess rotatory power it is sufficient that its dielectric elasticity be different in three different directions and that it possess the dissymmetry above mentioned. Analytically this condition of dissymmetry says that it must never be possible so to choose our coördinate system that our equations of propagation shall remain unchanged on reversal of the direction of all three coördinate axes. Such dissymmetry can be introduced by the addition of a differential quotient of uneven order to the second order term in the ordinary wave equation. Boussinesq, v. Lang, Briot, Sarrau and Drude use the differential coefficients of the first order, MacCullagh and Larmor use those of the third order. Magnetic rotation is expressed in a similar way by introducing uneven differential coefficients with regard to the time instead of a coördinate.

The mechanism of the rotation of fluids must be quite different from that of crystals. It is not sufficient to assume that the molecular elasticity, like crystalline elasticity, is different in different directions, since the light waves are so large in comparison to the molecular dimensions and the molecules of a fluid are not supposed to be so arranged that their effect would be cumulative. Nor would such intermolecular forces as the forces that would exist between the separate magnets of a freely suspended group give the molecules any selective effect on circularly polarized light waves. In any molecule except one of the very simplest type, the effect of a light wave on the charged particles of which it is composed would be to set them in motion in curved paths, but the resultant reaction of a large number of such molecules on a light wave would be zero so far as its direction of vibration was concerned. The one molecular property essential in affecting the azimuth of the wave which sets it vibrating appears to be that the charged particles of which it is composed tend to move in helical paths under the influence of a linear force. A crude analogue would be a corkscrew immersed in a fluid; a sudden impulse in the direction of its length would tend to rotate it as well as move it forward. In a medium composed of molecules having such properties, a right circularly polarized wave would travel with a different velocity from a left-handed circular wave, hence a plane polarized wave would be broken up into circular components and all the phenomena of rotation would occur. And the enantiomorphic dissymmetry above described is just what would give a molecule this rotatory property. This molecular characteristic will be the basis of the mathematical theory developed. The assumption of fixed, stable atomic orbits within the molecule is not sufficient to explain the observed phenomena of rotation as Larmor<sup>1</sup> has shown. Chiral properties depend essentially on *molecular* character.

#### THEORY OF ROTARY DISPERSION.

Instead of an equation stating that a linear force produces a solenoidal displacement of a charged particle, it is simpler to set up an equation which says that a solenoidal force is necessary to pro-

<sup>1</sup> Phil. Mag., 44, 503.

duce a linear displacement of the particle. Having constructed this equation of motion for a single particle, we solve it for the motion. The product of this displacement and the involved charge, summed up for all the different kinds of charged particles and summed again for all the charges of each kind in a unit volume, gives the total electric displacement. Substituting this electric displacement in the general Maxwell equations and taking the periodic solution for the motion, we have in the velocity of propagation of these waves the dispersion theory desired.

Now in general a charge  $e$  is acted on with a force  $eX$  by an electric force  $X$ . The displacement of the charge will be resisted by an inertia force, an elastic force and a frictional force. Hence

$$(1) \quad eX = m \frac{\partial^2 \xi}{\partial t^2} + \frac{4\pi e^2}{\theta} \xi + \varphi e^2 \frac{\partial \xi}{\partial t},$$

where  $m$  is the mass to which the charge  $e$  is supposed to be attached and  $\xi$  its displacement.  $\theta$  measures the ease with which the charge is displaced elastically, the factor  $e^2$  indicating that it is independent of the sign of the charge.  $\varphi e^2$  is the frictional coefficient, also independent of the sign of the charge. Now when the molecules are of the rotating kind, a solenoidal force proportional to  $\frac{\partial Y}{\partial z} - \frac{\partial Z}{\partial y}$  must be added to the linear force  $eX$  to produce the linear displacement  $\xi$ . We have then<sup>1</sup> as an extension of (1) to the motion of the charged particles composing a rotating molecule :

$$(2) \quad e \left[ X + \rho \left( \frac{\partial Y}{\partial z} - \frac{\partial Z}{\partial y} \right) \right] = m \frac{\partial^2 \xi}{\partial t^2} + \frac{4\pi e^2}{\theta} \xi + \varphi e^2 \frac{\partial \xi}{\partial t}.$$

If now there be  $N$  of these charged particles alike in unit volume, the current density for this kind is  $u_1 = eN d\xi/dt$ . Now we are dealing with substances (non metals) in which elastic forces exist and  $\theta$  is finite. Hence motion of the charged particle will be periodic, say  $\xi = Ae^{i\tau}$ . Substituting in (2) and solving for  $e\xi$ , the electric displacement concerned in the motion of the particle, we get for the current density :

<sup>1</sup>Drude, assuming quite a different mechanism of rotation, arrives at a similar equation. (See his Lehrbuch der Optik, p. 370.) The simple and ingenious development here presented (equations 1 to 13) is, I believe, due almost entirely to him.

$$(3) \quad u_1 = \frac{\theta N}{4\pi \left(1 + i\frac{a}{\tau} - \frac{b}{\tau^2}\right)} \frac{\partial}{\partial t} \left[ X + \rho \left( \frac{\partial Y}{\partial z} - \frac{\partial Z}{\partial y} \right) \right]$$

where

$$a \equiv \varphi\theta/4\pi \text{ and } b \equiv m\theta/4\pi e^2 \equiv \tau_1^2.$$

Hence the total current density arising from the displacements of all the charged particles of all kinds and of the free ether as well is :

$$(4) \quad u = \frac{1}{4\pi} \frac{\partial}{\partial t} \left[ \epsilon X + \rho \left( \frac{\partial Y}{\partial z} - \frac{\partial Z}{\partial y} \right) \right],$$

where  $\epsilon$  is the general (average) dielectric constant of the charge imbedded ether. Hence comparing with (3),  $\epsilon$  is seen to be

$$(5) \quad \epsilon = 1 + \Sigma \frac{\theta_1 N_1}{1 + i\frac{a}{\tau} - \frac{b}{\tau^2}}$$

and

$$\rho = \Sigma \frac{\theta_1 \rho_1 N_1}{1 + i\frac{a}{\tau} - \frac{b}{\tau^2}}$$

To get the equation for the propagation of a wave in a rotating medium, we have only to substitute the generalized current (4) in the fundamental Maxwell equations. We thus obtain three equations of the type :

$$(6) \quad \frac{1}{V^2} \frac{\partial^2}{\partial t^2} \left[ \epsilon X + \left( \rho \frac{\partial Y}{\partial z} - \frac{\partial Z}{\partial y} \right) \right] = \Delta X.$$

For a beam of light travelling along the  $Z$  axis we put

$$(7) \quad X = Ae^{\frac{i}{\tau}(t-pz)}, \quad Y = Be^{\frac{i}{\tau}(t-pz)}, \quad Z = 0,$$

where  $p$  is the reciprocal of the velocity of propagation and  $A$  and  $B$  are complex constants. Substituting in (6), we have to determine the velocity and amplitude and of the wave propagated the two equations :

$$(8) \quad \begin{aligned} \epsilon A - \frac{i}{\tau} \rho p B &= Ap^2 V^2, \\ \epsilon B - \frac{i}{\tau} \rho p A &= Bp^2 V^2. \end{aligned}$$

Replacing  $A$  by  $A + iA'$  and  $B$  by  $B + iB'$ , we find equations (8) to be satisfied by the two sets of values :

$$(9) \quad \begin{aligned} \varepsilon - \rho^2 V^2 &= -\rho/\tau, & A &= B' \\ \varepsilon - \rho^2 V^2 &= +\rho/\tau, & B &= A'. \end{aligned}$$

Hence the velocity of propagation is double-valued, its reciprocal being :

$$(10) \quad \rho = \pm \frac{\rho}{2\tau V^2} + \frac{1}{V} \sqrt{\frac{\rho^2}{4\tau^2 V^2} + \varepsilon}.$$

Call these two values  $\rho_1$  and  $\rho_2$ . Substituting in (7) and taking real parts we have the two circular waves

$$(11) \quad \begin{aligned} X_1 &= A \cos 2\pi/T(t - \rho_1 z), & Y_1 &= A \sin 2\pi/T(t - \rho_1 z), \\ X_2 &= A \cos 2\pi/T(t - \rho_2 z), & Y_2 &= -A \sin 2\pi/T(t - \rho_2 z). \end{aligned}$$

When the rotation factor  $\rho$  is positive, the second (clockwise) wave is the faster of the two. The resultant of the two waves is

$$(12) \quad \begin{aligned} X &= X_1 + X_2 = 2A \cos \frac{1}{\tau} \left( t - \frac{\rho_2 + \rho_1}{2} z \right) \cos \frac{1}{\tau} \frac{\rho_2 - \rho_1}{2} z, \\ Y &= Y_1 + Y_2 = 2A \cos \frac{1}{\tau} \left( t - \frac{\rho_2 + \rho_1}{2} z \right) \sin \frac{1}{\tau} \frac{\rho_2 - \rho_1}{2} z, \end{aligned}$$

which is a plane polarized wave whose azimuth changes steadily with  $Z$ . At any  $z$ , the azimuth of the plane of polarization is given by

$$Y/X = \tan \frac{1}{\tau} \frac{\rho_2 - \rho_1}{2} z.$$

Hence in traversing a path of length  $l$ , the plane of polarization is rotated through the angle (expressed in radians)

$$(13) \quad R = \frac{l}{\tau} \frac{\rho_2 - \rho_1}{2} = \frac{l}{\tau} \cdot \frac{\rho}{2\tau V^2} = \frac{l}{\tau V} \frac{n_2 - n_1}{2}$$

where  $n$  is the refractive index for circularly polarized waves. These expressions are of the same general form as those previously arrived at from geometrical considerations, but we are now in a position to interpret the rotation constant and the circular refractive indices. The rotation constant itself,  $\rho$  is proportional to the num-

ber of charges per unit volume and hence in a manner to the optical density. It is roughly proportional to the elastic resistance to displacement and to the ratio of charge to mass (cf. equations 5 and 3). Writing (13c) in the form

$$R = \frac{l}{4\pi Vn} (n_2^2 - n_1^2),$$

and getting  $n$  from (5) by writing  $n^2(1 - ix)^2 = \epsilon$ ,  $x$  being the absorptive index for circularly polarized waves, we obtain for the rotation

$$(14) \quad R = \frac{l\tau}{4nV} \Sigma \frac{\theta_2(\tau^2 - \tau_2^2) - \theta_1(\tau^2 - \tau_1^2)}{(\tau^2 - \tau_1^2)^2 + a\tau^2},$$

a function having the general form of that represented in Fig. 11.

Now the refractive index of the fluids investigated has not been determined and (14) is further inconvenient on account of there being so many constants to determine. A formula just as simple and not containing  $n$  may be obtained by substituting (5b) directly in (13b). Retaining only the real part

$$R = \frac{l}{2\lambda^2} \Sigma \frac{\theta_1 \left( 1 - \frac{\tau_1^2}{\tau^2} \right)}{\left( 1 - \frac{\tau_1^2}{\tau^2} \right)^2 + \frac{a_1}{\tau^2}}.$$

Now the experimental work relates to a region in which  $\tau$  is much greater than  $\tau_1$ , hence neglecting the fourth power of that quantity in comparison with the second, we have finally the working formula

$$(15) \quad R = \frac{k_1(\lambda^2 - \lambda_1^2)}{\lambda^2(\lambda^2 - 2\lambda_1^2 + a_1)} + \frac{k_2(\lambda^2 - \lambda_2^2)}{\lambda^2(\lambda^2 - 2\lambda_2^2 + a_2)} + \dots$$

This formula fulfils all of the four conditions we have to impose upon it. Far from any region of absorption it expresses the inverse square law. Approaching a region of absorption, the denominator will approach the value zero more rapidly than the numerator and hence the rotation will increase much more rapidly than the inverse square of the wave-length. Within the region of absorption, for  $\lambda^2$  between  $\lambda_0^2$  and  $2\lambda_0^2 - a$ , the rotation is reversed in sign. It remains but to test the formula for the fourth requirement, namely that it closely represent the observed data using but one or two terms.



Using two terms, the observed and calculated curves would lie so near together as hardly to be distinguishable, since there would be six constants involved and the two curves would cross in at least six different places. However, using but a single term, the calculated curve lies very close to the observed. This single term test is the severest that could be applied, and the close agreement shows beyond question that the derived dispersion function is of the proper form. Since the absorption is not confined to a narrow band, we ought properly to take the sum of a number of terms having constants very nearly alike, but it may be shown mathematically that such a sum is very approximately equivalent to a single term with different constants. The constants determined for the single term formula are given below. Since differences of small quantities are involved, it is necessary to carry the calculations to seven figures.

	$\lambda_0$	$\lambda_\infty$	$a$	$k$
Cane sugar.	189.6317	213.2	0.0287058	22.7886
Camphor.	276.0559	326.05	0.0461062	16.2606
Tartaric acid.	373.300	257.7	0.211035	3.5006
Potas. ant. tartrate.	254.6130	274.9	0.0540385	38.9839

The constant  $k$  gives the rotation in degrees instead of radians.  $\lambda_0$  is the wave-length at which the dispersion curve would cross the wave-length axis if produced.  $\lambda_\infty$ , where  $\lambda_\infty^2 = 2\lambda_0^2 - a$ , is the ordinate toward which the dispersion curve tends to approach asymptotically. Very roughly, the smaller  $\lambda_0$ , the straighter the curve. The larger the constant  $a$ , the greater the departure from the  $1/\lambda^2$  law.

The curves calculated with the above constants are shown dotted in the figures. The characteristic (one term) form of the dispersion curve is seen to be midway between the extreme types observed, less nearly the arc of a circle than potassium antimony tartrate and not so much the shape of a sled runner as the sugar and camphor curves.

In conclusion I desire to express my warmest thanks to Professor Nichols, of the Physics Department, and to Professor Orndorff and Mr. Teeple, of the Department of Chemistry, for their unfailing courtesy in placing at my disposal the resources of their respective departments.

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