THE
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NATURAL AND MAGNETIC ROTATORY DISPERSION IN THE INFRA–RED SPECTRUM.

BY L. R. INGERSOLL.

INTRODUCTION.

IN spite of the large amount of investigation which has been carried out on the rotation of the plane of polarization by naturally active substances for wave-lengths of the visible spectrum and to a certain extent in the ultra-violet, apparently nothing has hitherto been done on the infra-red side save in the case of the one substance, quartz.

Hussel,[1] using the phosphoro-photographic method of Lommel made measurements of the rotatory dispersion of this crystal to wave-length 1μ, while Carvallo,[2] Dongier[3] and others,[4] using modifications of the original method of Desains,[5] extended this spectral region to beyond 2μ. In none of these investigations, however, were other substances studied, possibly because of the difficulties involved in measuring the much smaller rotations usually found in materials other than quartz.

By a slight modification of the method and apparatus already developed and used by the writer[6] for measuring magnetic rotation in the early infra-red it has been found possible to determine the rotation of naturally active substances as well, in this spectral region, and with an accuracy at least comparable with that of the best visual observations. This is sufficient to handle even substances of small rotatory power, and accordingly the rotatory dispersion of several organic liquids and solutions,

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[1] A. Hussel, Wied. Ann., 43, p. 498 (1891).

[2] E. Carvallo, Comptes Rendus, 114, p. 288 (1892).

[3] R. Dongier, Comptes Rendus, 125, p. 228 (1897) & 126, p. 1627 (1898).

[4] G. Moreau, Ann. Chim. Phys., 30, p. 433 (1893), and A. Hupe, Wied. Ann. Beib., 19, p. 501 (1895).

[5] P. Desains, Pogg. Ann., 128, p. 487 (1866).

[6] Phil. Mag. (6), 11, p. 41 (1906), and 18, p. 74 (1909). PHYS. REV., 23, p. 489 (1906).

as well as of quartz, has been determined for the spectral region in which it is possible to work with this method, viz., from about the *D* lines to a little beyond 2μ. In some cases supplementary visual observations have been made to carry the series farther towards the blue end of the spectrum.

Magnetic rotation measurements on these substances have also been made at the same time to add further evidence on Wiedemann's law of the proportionality of magnetic and natural rotations for different wave-lengths. This law, first enunciated by G. Wiedemann[1] in 1851 as the result of experiments on turpentine for a series of five Fraunhofer lines, has been the subject of some controversy. Disch[2] concluded from experiments on ethyl valerate and quartz that it holds approximately for the visible spectrum, but more recently Darmois[3] finds that for a number of compounds of the terpene series, at any rate, the law does not hold at all. He concludes that Wiedemann's relation, then, was the result of pure chance and has no longer any significance. Very recently, however, Lowry[4] in the course of an extremely careful investigation of the rotatory dispersion of quartz finds that the law applies with great accuracy for this material over the range of spectrum ($\lambda = .43\mu$ to $.67\mu$) which he has been able to investigate. He suggests that its validity may be confined to crystals and that active liquids may constitute exceptions.

It becomes, then, a matter of considerable interest to test this law further, over the greatest possible spectral range and with an experimental arrangement which shall afford identical conditions (of wave-length, temperature, part of crystal used, etc.) for each series of measurements.

Temperature coefficients of both natural and magnetic rotation have also been determined in one or two cases in the present work, with the view of attempting to decide whether or not these coefficients depend on the wave-length. Soret and Sarasin[5] found an apparent increase of the natural coefficient for quartz in the shorter wave-lengths. Molby[6] has also recently found indications of the same thing over the range from room to liquid air temperatures. On the other hand, v. Lang,[7] Sohncke[8] and Gumlich[9] have not been able to draw any such conclusions, their results on this crystal pointing to an independence of wave-length.

[1] G. Wiedemann, Pogg. Ann., 82, p. 215 (1851).

[2] J. Disch, Ann. d. Phys., 12, p. 1153 (1903).

[3] E. Darmois, Ann. Chim. Phys., 22, p. 495 (1911).

[4] T. M. Lowry, Phil. Trans., 212, p. 261 (1913).

[5] Soret and Sarasin, Sur la Polarisation Rotatoire du Quartz, Geneva, 1882.

[6] F. A. Molby, PHYS. REV., 31, p. 291 (1910).

[7] V. v. Lang, Sitzungsber. d. k. Ges. d. Wiss. zu Wien, 71, p. 707 (1875).

[8] L. Sohncke, Wied. Ann., 3, p. 516 (1878).

[9] E. Gumlich, Wied. Ann., 64, p. 333 (1898).

It has seemed worth while, then, to supplement these observations with measurements over the six-fold greater spectral region which the writer has investigated, and to extend them to the magnetic rotation as well; also to test one or two other substances in addition to quartz.

METHOD AND APPARATUS.

The method need be outlined only briefly as it has—save for the slight but essential modification which admits of its application to the measurement of natural rotations—been already described in previous papers by the writer.[1] The general disposition of the apparatus is evident from
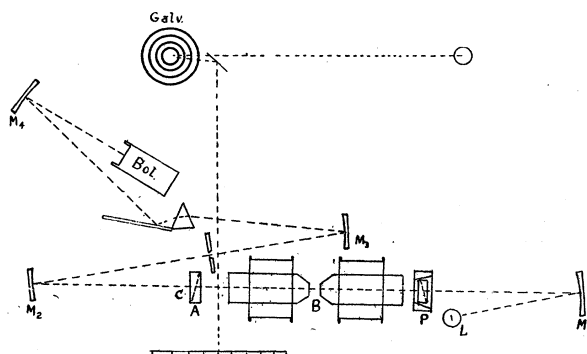

Fig. 1.

Fig. 1. Light from the flat strip tungsten lamp L,[2] after reflection from M_1 is polarized by P, transmitted down the axis of the electromagnet, and, after division into two beams by the (double image prism) analyzer A, falls on the slit of the spectrometer. The two images on the slit, of mutually perpendicular planes of polarization, form two spectra on the strips of the differential bolometer which is connected with a sensitive Thomson galvanometer. If the polarizer is oriented so that its plane makes an angle of 45° with each of the principal planes of the analyzer the intensity of radiation on each strip of bolometer will be the same and the galvanometer will show no deflection: but if a rotation is produced, as by a cell with sugar solution placed at B, a galvanometer deflection will result which may be used to measure such rotation. The magnetic rotation produced by exciting the electromagnet is obviously measurable in the same way.

[1] Loc. cit., particularly Phil. Mag., 18, p. 77 (1909).

[2] These lamps were specially made and furnished for this investigation through the kindness of Director E. P. Hyde of the Nela Research Laboratory. They give a line source many times more brilliant than the Nernst glower formerly used and of great constancy. Without them the present work would have been practically impossible.

A modification of the method as already mentioned will be seen to be necessary for the present work from the following considerations: Magnetic rotation, being produced by merely exciting the magnet, does not involve in the process of measurement any shift of the substance under test, *i. e.*, its removal from the field. Natural rotation, on the other hand, obviously cannot be produced or reversed in this simple way and it would seem to be necessary to remove the test cell entirely to get the zero from which the rotation is to be measured. This, however, must be avoided if possible as it is almost certain to involve slight shifts of the beam of light and a consequent lack of uniformity accompanied by a spurious galvanometer deflection.

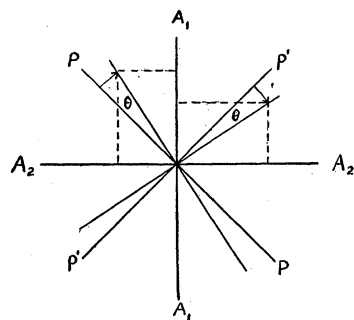To avoid this, the polarizer, which was mounted in a large divided circle, was arranged so that it could be rotated exactly 90° between stops. Fig. 2 shows almost at a glance the results of such rotation. The original plane of polarization P being rotated by the substance through the small angle θ, gives unequal components on the two principal planes of the analyzing double image prism. A rotation of the polarizer to P' will exactly interchange these two components and a doubled galvanometer deflection will result. The process is analogous to reversing the direction of the field in measuring magnetic rotations.

Fig. 2.

To interpret these galvanometer deflections in terms of degrees and minutes of rotation by the active substance, the polarizer was turned by a measured amount—usually about 3 degrees—and a comparison of the resulting galvanometer deflection with that above noted gave at once an accurate measurement of the (magnetic or natural) rotation for any chosen wave-length. It should be noted that while this was the general method the procedure had to be varied somewhat for rotations as large as those encountered in quartz.

Sources of error incidental to the bolometric method have been discussed at some length in the previous articles and only some special precautions need be mentioned here.

A large (9 cm. high) 45° prism of dense glass gave somewhat higher dispersion than that used in most of the writer's previous experiments, although energy requirements preclude very great advances along this line. A test was made in the case of quartz of the errors due to slit and

bolometer widths by exaggerating the effect; the conclusion reached was that the maximum error from this cause did not exceed ½ per cent. The wave-length scale of the prism had originally been determined by double dispersion and comparison with rock salt. Repeated careful checks of the position of a number of infra-red solar absorption lines indicated that the probable error in the wave-length scale should be less than .01μ.

To eliminate a variety of errors, each measurement was preceded by a blank run with the cell or crystal in position C where it should, of course, produce no deflection, any effect shown here was applied as a small correction. Some precautions had to be used in this connection, particularly in the case of quartz, because of the slight polarizing action of the glass prism of the spectrometer. On the magnetic side careful tests for spurious rotations indicated that these did not in any case exceed 0.0006°.

Perhaps the best indication of the general accuracy of the results comes from the comparison which was made in several cases of the rotation measured bolometrically for the wave-length of the D lines with the same rotation measured with sodium light by the customary visual method using a tri-field polarizer. The agreement in every case was within 1 per cent.

RESULTS.

Six representative substances were tested, including a crystal, two organic liquids, two aqueous and one alcohol solution. One of the
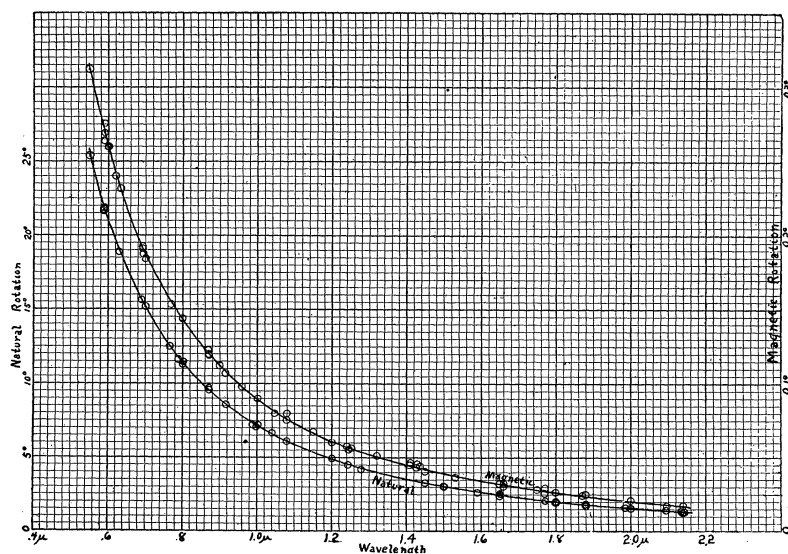

Fig. 3.

Rotary Dispersion Curves for Quartz.

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solutions (tartaric acid) shows anomalous rotatory dispersion in the visible spectrum.

Quartz.

The sample tested was a clear piece of right-handed quartz 5.030 mm. thick. The rotation for the D line and 20° C. was found to be 21.739° per mm., in excellent agreement with the value of 21.728° found by Lowry. The actual measurements are plotted in Fig. 3 and are seen to lie with few exceptions very well on the curve. The tabulated values were read from the smooth curve (plotted on a large scale).

TABLE I.

Quartz—Rotation per Mm. at 20° C.

Wave-length, μ	Natural Rotation.					Magnetic Rotation, Observed.	Mag. R $\overline{\text{Nat. } R}$
	Observed.		Calculated.		Temp. Coeff.		
	Present Work.	Others.	Lowry For-mula.	Gumlich For-mula.			
.5495	25.403°		25.201°			0.3120°	0.0123
.5893	21.739	21.728° (Lowry)	21.728	21.719°	.000164	.2694	.0124
.600	20.914		20.915		(39°−129° C.)	.2595	.0124
.700	15.139		15.124			.1860	.0123
.800	11.432		11.443		.000185	.1425	.0125
.900	8.873		8.953		(21°−141° C.)	.1119	.0126
1.00	7.121		7.189		.000152	.0890	.0125
1.08	6.123	6.18 (Carvallo)	6.122	6.20	(20°−141° C.)	.0752	.0123
1.10	5.904		5.893			.0724	.0123
1.20	4.918		4.911			.0603	.0123
1.30	4.101		4.151			.0516	.0126
1.40	3.515		3.549			.0448	.0127
1.45	3.272	3.43 (Carvallo)	3.295	3.41		.0418	.0128
1.50	3.030		3.055		.000156	.0389	.0128
1.60	2.662		2.669		(20°−125° C.)	.0341	.0128
1.70	2.348		2.341			.0303	.0129
1.715	2.304	1.83 (Moreau)	——			——	——
1.77	2.153	2.28 (Carvallo)	2.144	2.28		.0277	.0129
1.80	2.070		2.035		.000166	.0266	.0128
1.82	2.020	2.22 (Dongier)	2.017	2.15	(20°−113° C.)	.0259	.0128
1.90	1.827		1.835			.0234	.0128
2.00	1.614		1.636			.0205	.0127
2.10	1.431		1.466			.0179	.0125
2.14	1.372	1.60 (Carvallo)	1.404	1.55		.0169	.0123

Dispersion Formulæ.—Of the numerous formulæ which have been suggested to represent the natural rotatory dispersion of quartz we shall consider only two. The one used by Gumlich[1] is of the type

$$R = \frac{A}{\lambda^2} + \frac{B}{\lambda^4} + \cdots$$

to five terms. These five constants naturally permit a close fitting of calculated to experimental results and this Gumlich has done, using his own results in the visible spectrum, Soret and Sarasin's for the ultra-violet and Carvallo's and Dongier's infra-red observations quoted in Table I., in determining the constants.

Lowry[2] finds that the formula

$$R = \frac{11.6064}{\lambda^2 - \lambda_1^2} + \frac{13.42}{\lambda^2 - \lambda_2^2} - \frac{4.3685}{\lambda^2} ,$$

where

$$\lambda_1^2 = 0.010627; \quad \lambda_2^2 = 78.22,$$

λ being expressed in microns, represents his measurements in the visible spectrum with great accuracy. Using this formula *without changing the constants* in any way, the figures in Table I. were calculated. It will be noted that the agreement with the writer's observed values is exceedingly good throughout the range of the spectrum, the average divergence indeed being only a fraction of a per cent.

Wiedemann's Law.—Magnetic rotations for a field of approximately 9,400 gausses were made with the quartz in the same position as for the naturally active work. The ratios in Table I. show some variation, it is true, but part of this, at any rate, may be accounted for by the fact that the magnetic rotations were small and the probable error consequently larger than for the other rotations. There is certainly no consistent variation with wave-length and on the whole the results point strongly to the validity of Wiedemann's law for quartz over the whole spectral range investigated.

Temperature Coefficients.—The experimental arrangements for determining temperature coefficients of rotation were somewhat simpler than perhaps would have been the case if this had been the primary object of the investigation. The quartz was mounted in a simple brass cell, heated by a winding of resistance wire, the temperature being determined with a mercury thermometer. The results in Table I. vary somewhat but show no definite relation between coefficient and wave-length. Their mean value is in agreement with Gumlich's determination of 0.000165

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[1] Loc. cit., p. 350.

[2] Loc. cit., p. 287.

(0°–100° C.) for the visible spectrum. Because of the very small changes involved the coefficient of magnetic rotation proved very hard to determine with any accuracy. The figures obtained, however, indicate a value somewhat higher than for the natural rotation.

Organic Liquids.

Liquids were tested in a cell 36 mm. diameter and 9.54 mm. thick, formed by drilling a hole through a plate of glass of this thickness. The sides were of thin plate glass which had been optically tested for strains. While they had no effect on the natural rotation as measured, correction had to be made, of course, for their magnetic rotation. It may be of interest to note that ordinary finely sifted Portland cement proved the most suitable substance for fastening the parts of the glass cell together. When adjoining surfaces were ground to give a good adhesion to the cement these cells proved entirely satisfactory for all the liquids and solutions tested.

Limonene and pinene were the organic liquids selected for test. The (dextro[1]) limonene was furnished through the kindness of Professor Kremers and Dr. Wakeman, of the pharmacy department, to both of whom the writer has been greatly indebted during the course of this investigation. Its density at 20° C. was .845 and boiling point 175° C. The $(d - \alpha)$ pinene was kindly furnished by Dr. Schorger, of the Forest Products Laboratory. It was distilled from Port Orford cedar, boiling point 155° C., density at 15° C. .863, and it had one of the highest recorded rotations for this substance. It was redistilled the day before testing.

The results are shown in Table II., the natural and magnetic rotations having been read from the smooth curves. The ratios of the two show no consistent variation with wave-length, indicating that Wiedemann's law holds as well for these liquids as for quartz. It is of interest to note in this connection, however, that the temperature coefficients for the two rotations may be quite different as shown by the results on limonene. This difference is exaggerated if the coefficients of specific rotation are calculated, taking account of the change in density with temperature; the specific natural rotation coefficient of this substance averages .0012 with the magnetic less than one fourth as much. Both show much greater and more irregular variations with wave-length.

The specific natural rotations listed in Table II. are expressed in the usual way in terms of a decimeter thickness and unit density.

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[1] It is to be noted that what the chemist calls a dextro rotation is really a left-handed twist when viewed from the customary standpoint of the physicist, *i. e.*, along the path of the light. Thus right-handed quartz and dextro limonene really rotate in opposite directions.

TABLE II.

Optical Rotation of Two Terpenes at 22° C.

Wave-length, μ.	Limonene.						Pinene.			
	Observed Natural Rotation.	Temp. Coeff. (25°-120°C.) Nat. R.	Specific Rotation.	Observed Magnetic Rotation.	Temp. Coeff. (25°-120°C.) Mag. R.	Mag. R / Nat. R.	Observed Natural Rotation.	Specific Rotation.	Observed Magnetic Rotation.	Mag. R / Nat. R.
.50	13.915°		173.0°	3.571°		.257	5.716°	69.90°	3.252°	.569
.5893	9.665		120.1	2.475		.256	3.968	48.48	2.291	.577
.60	9.220		114.6	2.363		.257	3.818	46.59	2.196	.575
.70	6.482	−.00201	80.56	1.639	−.00114	.253	2.708	33.09	1.463	.540
.80	4.950	−.00206	61.55	1.229		.248	2.066	25.24	1.119	.541
.90	3.825		47.54	0.938		.245	1.606	19.61	0.870	.542
1.00	3.024	−.00205	37.61	0.747	−.00114	.247	1.286	15.71	0.702	.546
1.10	2.500		31.09	0.622		.249	1.058	12.93	0.573	.542
1.20	2.059	−.00201	25.60	0.522		.253	0.876	10.73	0.495	.564
1.30	1.734		21.57	0.445		.257	0.742	9.06	0.433	.584
1.40	1.509		18.76	0.383		.254	0.640	7.82	0.365	.570
1.50	1.325	−.00192	16.48	0.342	−.00117	.258	0.542	6.62	0.303	.560
1.60	1.191	−.00192	14.81	0.308	−.00123	.259	0.500	6.11	0.273	.547
1.90	0.870		10.82	0.232		.266	0.408	4.99	0.232	.567
2.00	0.780		9.70	0.208		.267	0.380	4.64	0.222	.583

Absorption Bands.—Both limonene and pinene show marked absorption bands at 1.2μ and 1.4μ while the extinction at 1.8μ is too great to allow of reliable measurements in this region. Theories of optical activity agree that absorption which is electronic in character may produce anomalies in the rotatory dispersion curve. Drude associates such anomalies only with those electrons which vibrate along spiral paths, but the recent theory proposed by Gray[1] and experimentally verified for solutions of neodymium nitrate, assumes that any absorption band belonging to an electron in an active molecule may be accompanied by an anomaly.

The fact that limonene and pinene show no such anomalies may, however, be explained in several ways. The dispersion may not have been great enough to detect them, although this is considered unlikely as the bolometer subtended less than $.02\mu$ in this part of the spectrum. A more reasonable assumption is that these absorption bands are not primarily electronic in their origin and hence would not be expected to be accompanied by anomalies in dispersion.

[1] Frank Gray, PHYS. REV., 7, p. 472 (1916).

Solutions.

Three solutions were experimented with: a 20 per cent. (by weight) aqueous solution of cane sugar (density at 22° C., 1.081); a 28.62 per cent. aq. solution of tartaric acid (density at 22° C., 1.140); and a 34.70 per cent. solution of camphor in absolute alcohol (density at 20° C., 0.845). The last two were chosen because they (*i. e.*, same percentage solutions) had been previously examined by Nutting[1] in his study of ultra-violet rotatory dispersion. All show dextro-rotations in the spectral region examined in the present work.

The results are shown in Table III. The specific rotations (*i. e.*,

TABLE III.

Optical Rotation of Three Solutions.

Wave-length. μ.	Tartaric Acid (20° C.).			Cane Sugar (22° C.).			Camphor (20° C.).		
	Observed Natural Rotation.	Specific Rotation.	Mag. R $\overline{\text{Nat. } R}$	Observed Natural Rotation.	Specific Rotation.	Mag. R $\overline{\text{Nat. } R}$	Observed Natural Rotation.	Specific Rotation.	Mag. R $\overline{\text{Nat. } R}$
.45	0.365°	11.71°	——	——	——	——	——	——	——
.50	0.387	12.42	——	——	——	——	——	——	——
.55	0.369	11.84	——	——	——	——	——	——	——
.60	0.318	10.21	5.75	1.288°	62.48°	1.42	1.098°	39.26°	1.51
.70	0.227	7.28	5.68	0.922	44.68	1.40	0.725	25.92	1.64
.80	0.181	5.80	5.51	0.700	33.93	1.42	0.528	18.87	1.71
.90	0.147	4.71	5.34	0.543	26.32	1.44	0.388	13.87	1.75
1.00	0.118	3.78	5.34	0.428	20.76	1.47	0.308	11.01	1.80
1.10	0.098	3.15	5.31	0.351	17.02	1.48	0.245	8.75	1.89
1.20	0.082	2.63	5.25	0.293	14.21	1.55	0.194	6.93	2.13
1.30	0.067	2.15	——	0.246	11.93	1.52	0.164	5.86	2.16
1.40	——	——	——	——	——	——	0.145	5.18	2.17

the rotations per decimeter divided by the product of the density and percent (by weight) strength of solution) for tartaric acid and cane sugar are in good agreement with the values listed by Landolt in his *Optische Drehungsvermögen*, but the camphor is somewhat low. The curve of the natural rotatory dispersion of tartaric acid is shown in Fig. 4. The other curves are of the same general character as those for limonene or quartz and show no anomalies. Tartaric acid has long been known to exhibit anomalous rotatory dispersion and Nutting found that in solutions of this concentration the rotation changes sign at $\lambda = .38\mu$ and becomes negative for shorter wave-lengths and with much larger values. The interesting point about this curve in Fig. 4 is that the

[1] P. G. Nutting, PHYS. REV., 17, p. 1 (1903).

anomalous character disappears entirely after $\lambda = .6\mu$ and the dispersion is quite similar to that of the other substances for longer wave-lengths.

The ratio of magnetic and natural rotations is seen to be less constant for these solutions than for the former substances. Camphor shows the greatest variation from Wiedemann's law, although tartaric acid would unquestionably prove a striking exception for wave-lengths shorter
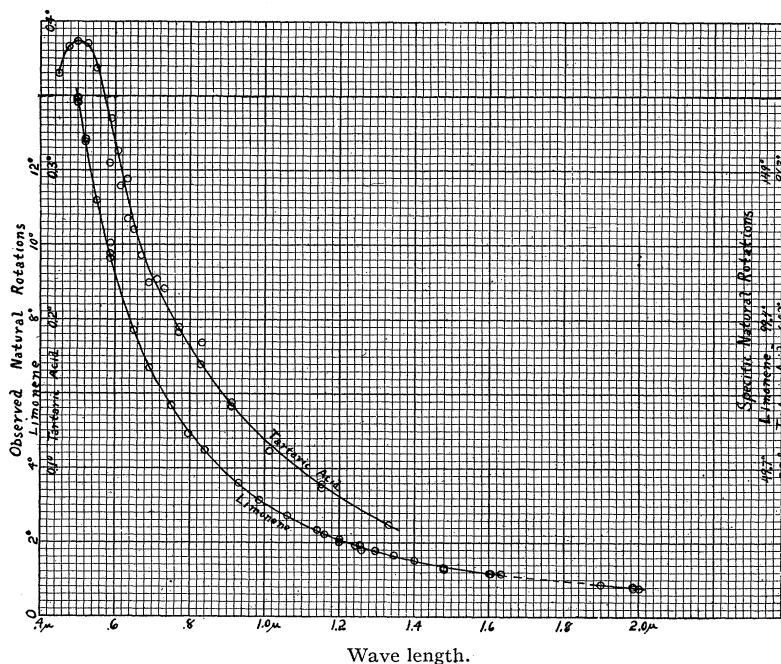

Wave length.

Fig. 4.

Rotatory Dispersion Curves for Limonene and Tartaric Acid.

than $.6\mu$ had the magnetic rotation been investigated in this region. These shorter wave-length points were obtained by visual measurements with a 20 cm. tube which did not lend itself readily to magnetic investigations. The magnetic rotatory dispersion of both tartaric acid and cane sugar solutions in the spectral region investigated is, however, practically identical with that of pure water and may be safely assumed to be such in this region also. In discussing Wiedemann's law for solutions some writers (vide Darmois, loc. cit.) attempt to separate the magnetic rotations of the solvent and solution, but the writer is sceptical of the value of such calculations and has not made use of them here.

Dispersion Ratios.—The relative dispersions of the various substances tested may be seen at a glance from the following table in which the

rotation for wave-length .6μ is called unity in each case. It will be noted that in practically all cases the rotations decrease in value more rapidly than the inverse square of the wave-length.

TABLE IV.

Wave-length, μ	Inverse Square	Quartz.		Limonene.		Pinene.		Cane Sugar.		Tartaric Acid.		Camphor.	
		Nat. R.	Mag. R.	Nat. R.	Mag. R.	Nat. R.	Mag. R.	Nat. R.	Mag. R.	Nat. R.	Mag. R.	Nat. R.	Mag. R.
.60	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
.80	0.563	0.547	0.549	0.537	0.520	0.541	0.510	0.544	0.543	0.569	0.543	0.481	0.547
1.00	0.360	0.340	0.343	0.328	0.316	0.337	0.320	0.333	0.344	0.371	0.344	0.281	0.335
1.30	0.213	0 196	0.199	0.188	0.188	0.194	0.197	0.191	0.204	0.211	——	0.149	0.213
1.60	0.141	0.127	0.131	0.129	0.130	0.131	0.124	——	——	——	——	——	——
2.00	0.090	0.077	0.079	0.084	0.088	0.099	0.101	——	——	——	——	——	——

In conclusion the writer takes pleasure in acknowledging his indebtedness to the Rumford Fund. A large share of the apparatus with which these measurements were carried out was originally purchased with grants from this source.

SUMMARY.

1. The natural and magnetic rotatory dispersions of quartz, limonene, pinene, and solutions of cane sugar, tartaric acid and camphor have been determined over a range of wave-lengths from the visible to beyond 2μ. The curves are all regular save in the case of tartaric acid in the shorter wave-lengths.

2. The natural rotation for quartz over the whole spectral range agrees very well with the formula used by Lowry, with constants determined by him from visible spectrum observations.

3. The temperature coefficients of rotation as determined for quartz and limonene show no definite dependence on wave-length. The natural and magnetic rotation coefficients have quite different values, however, in the case of limonene.

4. Wiedemann's law of the proportionality of natural and magnetic rotations holds with a fair degree of approximation for quartz and the two terpenes over the whole spectral range investigated. It does not hold as well for the solutions, the variation being greatest in the case of camphor.

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