

Bakerian Lecture: Optical Rotatory Dispersion. Part II: Tartaric Acid and the Tartrates

Thomas Martin Lowry and Percy Corlett Austin

Phil. Trans. R. Soc. Lond. A 1922 **222**, 249-308
doi: 10.1098/rsta.1922.0008

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VIII. BAKERIAN LECTURE.—*Optical Rotatory Dispersion.—Part II. Tartaric Acid and the Tartrates.*

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Lecture delivered June 2, 1921—MS. received July 18, 1921.

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I. OPTICAL ROTATORY POWER OF TARTARIC ACID AND THE TARTRATES.

THE optical rotatory power of tartaric acid was discovered in 1832 by BIOT ('*Mém. Acad. Sci., Paris, 1835, vol. 13, Table G, p. 168* ; paper read November 5, 1832), who devoted one of his longest memoirs ('*Mém. Acad. Sci., 1838, vol. 15, pp. 93–279* ; paper read January 11, 1836) to a detailed account of its properties when mixed with water, with alcohol and with wood-spirit.

BIOT found that tartaric acid, when "dissolved in different fluid media, exercises on the planes of polarisation of light a special power, which distinguishes it from all the other substances hitherto studied." These had agreed with quartz in obeying, at least approximately, BIOT'S LAW, according to which "the rotation of the different simple rays is reciprocal to the square of their wave-lengths" ('*Mém. Acad. Sci., 1817, vol. 2, pp. 49, 57 and 135* ; paper read September 22, 1818). This agreement had been verified in the case of turpentine, alone and mixed with ether, and of cane-sugar dissolved in water (i.) by comparing the tints with those produced by equivalent plates of quartz, and (ii.) by eliminating the effects of rotatory polarisation with the help of a quartz

plate of opposite sign acting as a compensator ('Mém. Acad. Sci.,' 1817, vol. 2, pp. 103–114). When tartaric acid was compared with quartz, however, no such parallelism was observed, the rotations for the chief colours being as follows :—

	Red.	Orange.	Yellow.	Green.	Blue.	Indigo.	Violet.
Quartz	18·99	21·40	23·99	27·86	32·31	36·13	40·88
Tartaric acid	38·7	40·29	42·51	46·11	44·40	42·9	39·38

('Mém. Acad. Sci.,' 1838, vol. 15, p. 236). Similar phenomena were observed when tartaric acid was dissolved in alcohol (*ibid.*, p. 245); but BIOT found that "when it combines with basic substances in the same media, it loses its special action and imprints on the products the properties common to all other bodies endowed with rotatory power" ('Mém. Acad. Sci.,' 1838, vol. 16, p. 229; paper read November 27, 1837).

BIOT's experiments on tartaric acid and the tartrates covered so wide a range that the whole of the work described in the present paper may be regarded as a logical extension of his investigations, aided on the physical side by modern optical theories and by modern apparatus, and on the chemical side by structural formulæ and by stereochemical notions which were only struggling for recognition even in the closing years of BIOT's life. The contributions which he made to the fundamental problem of determining the form of the curves of rotatory dispersion are discussed below in a separate paragraph, but reference may be made here to a few of the many topics covered by his investigations.

(a) *Influence of Water on the Rotatory Power of Tartaric Acid.*

BIOT discovered that "in aqueous solutions of tartaric acid at a given temperature, the rotatory power of the acid calculated for each simple ray is always of the form $A + Be$, where e represents the proportion by weight of water in the solution" ('Mém. Acad. Sci.,' 1838, vol. 15, p. 216; compare *ibid.*, p. 207), the specific rotation being therefore a linear function of the concentration. This linear law was first described in a sealed communication deposited in the Archives of the Academy on August 25, 1834, and opened on December 7, 1835. A note added on the latter date ('Comptes Rendus,' 1835, vol. 1, p. 459) stated that the law was an approximation which did not apply to dilute solutions. BIOT made use of the linear law to construct a diagram ('Mém. Acad. Sci.,' 1838, vol. 15, fig. 4, facing p. 652), in which the rotatory power for light of different colours is shown as a series of straight lines inclined at different angles to the axis of concentration. This diagram shows a marked similarity to the "characteristic diagram" constructed 75 years later by ARMSTRONG and WALKER ('Roy. Soc. Proc.,' 1913, series A, vol. 88, pp. 388–403), the chief difference being that the rotations for green light are

represented by a line inclined at an arbitrary angle, instead of at 45 degrees, to the horizontal axis; the anomalous dispersion in concentrated solutions is shown by the intersection of the lines showing the rotatory power of the acid for light of different colours, and the removal of some of the more obvious anomalies on diluting the solutions is shown by the gradual separation of the lines until they follow the normal sequence of the primary colours of the visible spectrum.

(b) *Rotatory Power of Amorphous Tartaric Acid.*

Our own investigations (pp. 266 to 271) have shown that Biot's linear law is only an approximation, and that an equation with five arbitrary constants would probably be required to express completely the relationship between rotatory power and concentration. With the help of his diagram and formula, Biot was, however, able to calculate by extrapolation the rotatory power of pure anhydrous tartaric acid at different temperatures and for light of different colours. In particular, he concluded that the rotatory power A of the anhydrous acid for the red light transmitted through glass coloured by cuprous oxide would change sign at 23° C., being positive above this temperature and negative below it ('Mém. Acad. Sci.,' 1838, vol. 16, p. 269). This prediction was verified dramatically some years later when LAURENT in 1849 discovered a method by which moistened tartaric acid could be fused and cooled to a transparent glass in thicknesses up to 76 mm. ('Ann. Chim. Phys.,' 1850, vol. 28, p. 353). Biot then found that the hot, pasty acid produced a strong dextrorotation, which became negative on cooling. A 70 mm. column of the acid at $+3.5^{\circ}$ C. gave $\alpha_{\text{red}} = -3.28^{\circ}$, when $[\alpha]_{\text{red}} = -2.787^{\circ}$, agreeing very closely with the value $[\alpha]_{\text{red}} = -2.752^{\circ}$ calculated by extrapolation from the rotatory power of concentrated aqueous solutions of the acid (*ibid.*, p. 366).

(c) *Rotatory Power of the Tartrates.*

Whilst his first long memoir on tartaric acid ("Méthodes mathématiques et expérimentales, pour discerner les Mélanges et les Combinaisons, définies ou non définies, qui agissent sur la Lumière Polarisée; suivies d'applications aux combinaisons de l'acide tartrique avec l'eau, l'alcool, et l'esprit de bois," 'Mém. Acad. Sci.,' 1838, vol. 15, pp. 93–279) dealt with solutions of the acid in water, alcohol, and wood spirit, his second memoir ("Mémoire sur plusieurs Points Fondamentaux de Mécanique Chimique"; 'Mém. Acad. Sci.,' 1838, vol. 16, pp. 229–396) described the changes which are produced in the rotatory power of tartaric acid by adding other acids (sulphuric, hydrochloric and citric, *loc. cit.*, 271–304), alkalis (potash, soda and ammonia, *loc. cit.*, 307–377) and earths (alumina and beryllia, *loc. cit.*, 377–385). The action of alkalis was of special interest in that the tartrates derived from them showed none of the anomalies of the acid, their rotatory dispersion conforming approximately to the law of inverse squares and agreeing generally with that of quartz. Our own measurements have shown that this conclusion

is broadly correct, since aqueous solutions of sodium tartrate show a closer approximation to the requirements of BIOT'S Law than in the case of any other substance that we have yet investigated ; the agreement is, however, even here not exact, and the complex character of the rotatory dispersion of the acid is shown, although in a much less striking way, in the salts derived from it.

(d) *Influence of Boric Acid.*

Of wider general interest is BIOT'S discovery of the remarkable exaltation of rotatory power which is produced by the addition of boric acid to tartaric acid. The properties of the boro-tartaric solutions were first described in outline in his sealed note to the Academy ('Comptes Rendus,' 1835, vol. 1, p. 458, compare 'Mém. Acad. Sci.,' 1838, vol. 16, p. 271), but a detailed description was given ten years later as part of a long memoir "On the employment of polarised light to study various questions of chemical mechanics" ('Ann. Chim. Phys.,' 1844, vol. 11, pp. 82-112; see also 'Ann. Chim. Phys.,' 1860, vol. 59, pp. 229-256). It is characteristic of the thoroughness with which BIOT worked, that he extended his observations to include not only aqueous solutions, but also glassy amorphous mixtures of the two anhydrous acids ('Ann. Chim. Phys.,' 1850, vol. 28, p. 368). The exaltation of rotatory power which BIOT observed on the addition of boric to tartaric acid appears in many other substances which resemble tartaric acid in containing two hydroxyl-groups attached to adjacent carbon-atoms. It is generally accompanied by an increase of electrical conductivity, and in recent years has been made the basis of a general method of determining the configuration of hydroxylic-compounds of the sugar group (see especially MAGNANINI, 'Zeitschr. physikal. Chem.,' 1890, vol. 6, p. 67; 'Berichte Deut. Chem. Ges.,' 1891, vol. 24 ref., p. 894; BOESEKEN, 'Berichte,' 1913, vol. 46, p. 2612; IRVINE, 'Trans. Chem. Soc.,' 1914, vol. 105, p. 898; 1915, vol. 107, pp. 1221 and 1230).

Later workers, whilst confirming the accuracy of his general conclusions, have added many details to the broad outlines of BIOT'S work. Thus ARNDTSEN ('Ann. Chim. Phys.,' 1858, vol. 54, p. 411), during a summer spent in Paris, showed that BIOT'S maximum in the green disappeared at the violet end of the spectrum at concentrations below 20 per cent. of tartaric acid; KRECKE ('Archives Néerlandaises,' 1872, vol. 7, p. 107) showed that even in a 50 per cent. solution the maximum vanished at the violet end of the spectrum when the temperature was raised to 50° C.; and WENDELL ('Wiedemann's Ann. Phys. Chem.,' 1898, vol. 66, pp. 1149-1161) confirmed the observations of ARNDTSEN and of KRECKE as to the displacement of the maximum towards the violet by dilution and by heating, and the increase of rotatory power which accompanies these changes. LEPESCHKIN ('Berichte Deut. Chem. Ges.,' 1899, vol. 32, pp. 1180-1184), working in the opposite direction, observed in a supersaturated solution at 20° C. a negative rotatory power, analogous with that which had been recorded by

BIOT for the anhydrous acid, and by ARNDTSEN ('Ann. Chim. Phys.,' 1858, vol. 54, p. 415) for very strong alcoholic solutions; this negative rotation for dark-blue light became positive for light of longer wave-lengths, reaching a maximum dextrorotation in the yellow region of the spectrum. WINTHER ('Zeitschr. physikal. Chem.,' 1902, vol. 41, pp. 181-189), who made a detailed study of the effects of temperature and concentration on the rotatory power of the acid in aqueous and in alcoholic solutions, extrapolated to 100 per cent. tartaric acid, and concluded that the maximum might be displaced still further, disappearing at the red end of the spectrum when the temperature of the anhydrous acid fell below 20° C. This conclusion was not confirmed by BRUHAT ('Trans. Faraday Soc.,' 1914, vol. 10, p. 89), whose extrapolation gave a maximum between the yellow and the red, whilst his observations of the glassy acid at 15° C. indicated that a maximum could still be seen in the red region of the spectrum.

New ground has been broken in the detailed investigation by WINTHER and by PATTERSON of the tartaric esters which show similar anomalies to those which BIOT had discovered in tartaric acid.* Very noteworthy also is the achievement of BRUHAT (*loc. cit.*), who by means of special apparatus succeeded in measuring the rotatory power of fused and superfused tartaric acid for several wave-lengths at temperatures from 180° to 15° C., thereby bringing the acid into line with its esters as they had been investigated 12 years earlier by WINTHER. The investigation of tartar emetic and of the related compounds of arsenic and bismuth has also given interesting results, which are described in detail below (pp. 284 and 285).

2. ROTATORY DISPERSION IN QUARTZ AND IN TARTARIC ACID.

BIOT's measurements of the optical rotatory power of tartaric acid indicated the existence of two types of rotatory dispersion, which may be described provisionally as the "quartz type" and the "tartaric acid type." Since these correspond to some extent with the later classification of rotatory dispersion as normal and anomalous, or as simple and complex, it will be desirable to set out the essential features of these various methods of classification.

(a) BIOT's *Two Types*.

BIOT divided optically active substances into two groups according as they obeyed the law of inverse squares, $\alpha = k/\lambda^2$, or showed large deviations from this law. The maximum in the optical rotatory power of tartaric acid, which he observed in the green region of the spectrum, was merely an incidental feature in the exceptional behaviour of the acid, and did not receive any of the emphasis which has since been placed upon

* For a study of the form of the dispersion-curves for ethyl and methyl tartrates see LOWRY and DICKSON, 'Trans. Chem. Soc.,' 1915, vol. 107, pp. 1173-1187; LOWRY and ABRAM, *ibid.*, pp. 1187-1195.

it.* On the other hand, the extreme sensitiveness of the rotatory power of tartaric acid to changes of temperature, concentration and solvent was regarded by BIOT as one of the chief anomalies in the behaviour of this exceptional substance. BIOT had laid stress on the fact that the optical rotatory power† of a substance was usually independent of the conditions under which it was observed; thus the rotatory power of turpentine was not affected by diluting it with other essential oils ('Mém. Acad. Sci.,' 1817, vol. 2, p. 115), or with ether (*ibid.*, p. 116), and it even retained its optical activity when examined as a vapour in a column 30 metres in length (*ibid.*, pp. 126–133, compare GERNEZ, 'Ann. de l'École Norm.,' vol. 1, p. 1); cane sugar, too, showed a very similar rotatory power when examined in the amorphous solid state as "barley sugar" and when this same product was dissolved in water ('Mém. Acad. Sci.,' 1835, vol. 13, pp. 126–132). The marked influence on the rotatory power of tartaric acid of dilution with water or of addition of boric acid was therefore attributed to chemical changes just as definite as those involved in the conversion of the acid into its salts. This early view, which had fallen into disrepute for many years, has now become prominent again, more especially as an explanation of variations of rotatory power in those cases of anomalous rotatory dispersion of which tartaric acid is still the chief type.

(b) *Normal and Anomalous Rotatory Dispersion.*‡

Only a short time elapsed before BIOT's law of inverse squares was recognised as being inexact. BIOT had suspected almost from the first that small variations of dispersive power might exist in different compounds; in 1836 he obtained clear evidence of this fact by balancing against one another columns of turpentine and of oil of lemon which produced approximately equal and opposite rotations, when he found that "the compensation of the deviations, although very close for all the rays, was, however, neither complete nor general" ('Comptes Rendus,' 1836, vol. 2, p. 543); cane-sugar

* For early examples of this emphasis, see ARNDTSEN, 'Ann. Chim. Phys.,' 1858, vol. 54, p. 409; KRECKE, 'Arch. Néerlandaises,' 1872, vol. 7, p. 114; LANDOLT, 'Liebig's Annalen,' 1877, vol. 189, p. 274.

† BIOT described as the *molecular rotatory power of substances* ('Mém. Acad. Sci.,' 1838, vol. 15, p. 95; compare 'Mém. Acad. Sci.,' 1835, vol. 13, p. 116) the rotation that would be produced by a column 1 mm. thick and of unit density; this is one-hundredth part of what is now called the *specific rotatory power* of the substance.

‡ The term "normal dispersion" was used by ARNDTSEN in 1858 ('Ann. Chim. Phys.,' 1858, vol. 54, p. 412) to describe the case in which "the angle of rotation increases continuously with the refrangibility of the rays." The term "anomalous (rotatory) dispersion" appears to have been introduced in 1877 by LANDOLT ('Liebig's Ann. der Chemie,' 1877, vol. 189, p. 274), who described under this heading (1) a maximum which travels from the violet to the green region of the spectrum as the concentration of the aqueous solution of tartaric acid increases, and (2) a reversal of sign in the rotatory power of the anhydrous acid and of its alcoholic solution. KRECKE, five years earlier ('Arch. Néerland.,' 1872, vol. 7, pp. 98, 110 and 114), had referred less specifically to the "remarkable anomalies" which are observed in the optical properties of tartaric acid.

and invert-sugar gave, on the other hand, a very exact compensation ('Ann. Chim. Phys.,' 1844, vol. 10, p. 35). After BIOT's death the law of inverse squares was generally abandoned, even as a first approximation. The result was most unfortunate, since the experimenters who proved the inaccuracy of BIOT's formula did not possess the mathematical skill that was required to replace it by another formula that was more exact. There can be little doubt that, as more exact methods of measurement were developed, BIOT himself would have investigated the deviations from this law, and might well have discovered the small but important correction which DRUDE introduced many years later when he wrote $\alpha = k/(\lambda^2 - \lambda_0^2)$ instead of $\alpha = k/\lambda^2$.

This discovery was extremely likely in view of the fact that, as early as 1817, BIOT, in applying the law of inverse squares to the rotatory power of quartz, had used a graphical method in which virtually the reciprocal of the rotatory power was plotted against the square of the wave-length* ('Mém. Acad. Sci.,' 1817, vol. 2, plate 3 facing p. 136). This device of plotting $1/\alpha$ against λ^2 is, however, the simplest method of checking the validity of DRUDE's formula, and has been used extensively in recent years as a convenient test for this purpose (LOWRY and DICKSON, 'Trans. Chem. Soc.,' 1913, vol. 103, p. 1075; LOWRY and ABRAM, 'Trans. Faraday Soc.,' 1914, vol. 10, p. 104; compare also FRANKLAND and GARNER, 'Trans. Chem. Soc.,' 1919, vol. 15, p. 640, footnote, and RUPE and AKERMANN, 'Ann. der Chem.,' 1920, vol. 420, p. 12). The mere plotting out on BIOT's original plan of a series of accurate experimental data would therefore have disclosed to him both the existence and the magnitude of DRUDE's correction.

In the absence of BIOT's mathematical genius, however, nearly all the work on rotatory dispersion during the next half-century became semi-qualitative in character, the data being represented by curves of unknown form, instead of by mathematical equations. This fact affords an explanation of the exaggerated importance which was attached to the more conspicuous anomalies, as well as of the utter confusion into which all attempts to classify rotatory dispersion fell. Thus, in the absence of any precise knowledge of the real form of the dispersion curves, KRECKE seized upon "the anomaly that, in concentrated solutions of tartaric acid, the green rays are turned more than the red and violet rays" ('Arch. Néerlandaises,' 1872, vol. 7, p. 114). LANDOLT in 1877 recognised two anomalies, namely, (i.) that in aqueous solutions of tartaric acid "if one increases the concentration, the maximum rotation wanders [from the violet] towards the red end of the spectrum, and in solutions containing 50 per cent. tartaric acid, the green rays are most strongly deflected," (ii) "that tartaric acid in the anhydrous state must deflect the rays C D E to the right, b F e to the left, and that for a certain kind of light, whose wave-length lies between the lines E and C, there can be no rotation at all" ('Liebig's Ann. der Chem.,' 1877, vol. 189, p. 274).

* The lengths of the columns of quartz required to produce a rotation of $n\pi/2$ were plotted against the square of the wave-length as a series of straight lines diverging from the origin where $l = 1/\alpha = 0$ and $\lambda^2 = 0$; DRUDE's equation gives straight lines diverging from $1/\alpha = 0$, $\lambda^2 = \lambda_0^2$.

From this time onwards attention became concentrated almost exclusively upon the maximum and the reversal of sign, but more especially upon the maximum, the presence or absence of which became almost the sole criterion for discriminating *anomalous* from *normal* rotatory dispersion. Thus GROSSMANN speaks of “anomalous rotatory dispersion and change of sign of rotation” as if they were two totally distinct phenomena (‘Trans. Faraday Soc.,’ 1914, vol. 10, p. 61), whilst WINTHER actually limits the idea of anomalous rotatory dispersion to those cases in which there is a maximum *in the visible region of the spectrum*; he therefore speaks of a dispersion-curve as becoming “normal, in that the maximum passes into the ultra-violet,” whilst a curve which cuts the axis is described as “normal with a maximum in the infra-red” (‘Zeitschr. f. Physikal. Chem.,’ 1902, vol. 41, p. 188; and 1903, vol. 45, p. 337).

A much more rational description has been given by TSCHUGAEFF, who states that “most of the colourless active bodies exhibit normal rotatory dispersion, the numerical value of the optical rotation continuously increasing with decreasing wave-lengths,” whilst the term anomalous “is generally applied to those cases in which the optical rotation passes through a maximum or through a zero value or decreases with decreasing wave-length” (‘Trans. Faraday Soc.,’ 1914, vol. 10, p. 70). This qualitative description is in close agreement with “An Exact Definition of Normal and Anomalous Rotatory Dispersion” (LOWRY, ‘Trans. Chem. Soc.,’ 1915, vol. 107, p. 1195), which has recently been put forward as a result of exact analyses of the mathematical form of a large number of typical dispersion-curves. These analyses have shown that in practice a clear distinction may be drawn between “anomalous” curves, which cut the axis of zero-rotation, and “normal” curves, which do not cut the axis; the normal curves rise steadily from zero towards an infinite rotation as the wave-length decreases, and are similar to rectangular hyperbolas in their general appearance; the anomalous curves exhibit, in different regions of the spectrum, all the features that have been described as anomalies, including an inflexion, a maximum, a reversal of sign, and other related characteristics which appear simultaneously whenever the curve is drawn across from one side of the axis to the other.

(c) *Simple and Complex Rotatory Dispersion.*

About 1898, DRUDE (see ‘Theory of Optics,’ 1907, p. 413), making use of the electronic theory of radiation, expressed the variation of rotatory power with wave-length by means of the general formula

$$\alpha = \frac{k}{\lambda^2} \sum \frac{\theta_h f_h' N_h}{1 - \left(\frac{\tau_h}{T}\right)^2} = \sum \frac{k_n}{\lambda^2 - \lambda_n^2} \text{ (approximately)}$$

where the "dispersion constants" λ_n^2 , corresponding with the natural free periods $1/\lambda_n$ of the electrons, were deduced from measurements of refractive dispersion as expressed by the equation

$$N^2 = E + \sum \frac{M_n}{\lambda^2 - \lambda_n^2}.$$

in which N is the refractive index and E is the dielectric constant of the medium.

In those cases in which only one electron need be considered, the magnetic rotation could be expressed by an equation

$$\alpha = N \left(\frac{\alpha'}{\lambda^2} + \frac{b'}{\lambda^2 - \lambda_1^2} \right),$$

which involved four constants, of which two could be derived from measurements of refraction.

The importance of these equations did not appear immediately. Very few experimental data were available, and DRUDE applied his formulæ only to the magnetic rotations of carbon disulphide and of creosote and to the natural rotatory power of quartz, which he expressed by the two-term equation

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} - \frac{k_2}{\lambda^2},$$

containing two arbitrary constants k_1 , k_2 , and one constant, λ_1^2 , derived from measurements of refraction; the dispersion constant of the second term was omitted as being negligible in comparison with λ^2 . Perhaps on account of the lack of suitable data, the new formulæ were not applied to any single member of the vast array of optically active organic compounds which have been prepared and studied, more especially from the time of PASTEUR onwards.

In view of the very limited application of these formulæ by DRUDE himself, the indefinite number of arbitrary constants which they contained, and the fact that a complete knowledge of the refractive dispersion of the medium was presupposed, it is not surprising that DRUDE'S formulæ remained almost barren so far as their immediate application to measurements of rotatory dispersion was concerned. Fifteen years of work on rotatory dispersion ('Phil. Trans.,' A, 1912, vol. 212, p. 261; 'Trans. Chem. Soc.,' 1913, vol. 103, p. 1062 *et seq.*) have, however, provided ample data for testing the validity of these equations, and have established beyond question the fact that they are adequate to meet all the requirements of the most diverse and of the most exact measurements of rotatory dispersion. In the case of some scores of organic compounds,

both the optical and the magnetic rotations* can be expressed by a single term of the general equation (LOWRY and DICKSON, 'Trans. Chem. Soc.,' 1913, vol. 103, pp. 1067–1075; LOWRY and ABRAM, 'Trans. Chem. Soc.,' 1919, vol. 115, p. 300; RUPE and AKERMANN, 'Ann. der Chem.,' 1920, vol. 420, p. 4); liquids such as ethyl and methyl tartrates and aqueous solutions of tartaric acid, which show anomalous rotatory dispersion, require two terms of opposite sign (LOWRY and DICKSON, 'Trans. Chem. Soc.,' 1915, vol. 107, pp. 1173–1187; LOWRY and ABRAM, 'Trans. Chem. Soc.,' 1915, vol. 107, pp. 1187–1195); quartz, although showing no obvious anomalies, requires three terms of DRUDE'S equation in order to express the most recent measurements that have been made of its rotatory dispersion (LOWRY, 'Phil. Trans.,' A, 1912, vol. 212, p. 261). This determination of the exact form of the curves has led to an extremely easy and convenient classification of rotatory dispersion, as *simple* when one term of DRUDE'S equation is sufficient and *complex* when two or more terms are required (LOWRY and DICKSON, 'Trans. Faraday Soc.,' 1914, vol. 10, p. 102). The complex curves are only anomalous when they cross the axis of rotations and exhibit a reversal of sign; but a simple mathematical analysis has established the conditions under which a complex curve, expressed by two terms of DRUDE'S equation, ceases to be *normal* and becomes *anomalous* in the sense of the exact definition already referred to ('Trans. Chem. Soc.,' 1915, vol. 107, p. 1198).

3. THE ORIGIN OF ANOMALOUS ROTATORY DISPERSION.

(a) *Anomalous Rotatory Dispersion as a Problem in Chemical Mechanics.*

The present paper follows one on rotatory dispersion in quartz. It may be regarded as supplementing that paper by extending the new series of exact measurements from the first to the second of BIOT'S types of rotatory dispersion. It also carries the work forward from optically active crystals to optically active liquids, and so opens up again the complex chemical problems which led BIOT to describe most of his work on tartaric acid as a study in chemical mechanics rather than as an investigation of the physical properties of the acid. It is this underlying chemical interest that more especially

* The magnetic rotatory dispersion in carbon disulphide can be expressed, at least as well by a simple two-constant equation $\alpha = k/(\lambda^2 - 0.055)$, as by the four-constant equation used by DRUDE. Thus the five lines quoted by DRUDE ('Theory of Optics,' 1907, p. 431) give for k the values:—

	C.	D.	E.	F.	G.
$k =$	0.2224	0.2221	0.2226	0.2236	0.2224

whilst the observed and calculated dispersion-ratios compare as follows:—

Observed	0.592	0.760	1.000	1.234	1.704
Cal. (four constants)	0.592	0.762	0.999	1.232	1.704
Cal. (two constants)	0.593	0.762	1.000	1.228	1.706

Later measurements ('Trans. Chem. Soc.,' 1913, vol. 103, p. 1074) agree still more closely with a simple constant equation.

distinguishes the work on tartaric acid from that on quartz, and gives to it its own peculiar importance. From the physical point of view the contrast is not great, and almost the whole of the advantage rests with the quartz, the large rotatory power of which renders possible an accuracy of measurement that is probably at least 100 times greater than in the case of any other medium. But whereas the rotatory power of quartz is influenced only slightly by the experimental conditions, tartaric acid is subject to drastic changes of rotatory power as a result of very small changes of circumstance.

In recent years this extreme sensitiveness has been regarded by many writers as an inherent quality of the physical property of optical rotatory power; but all the new evidence goes to show that Biot was right in attributing it to chemical changes in the optically active liquid. One point must, however, be made clear immediately: whatever the nature of these chemical changes may be, they must proceed to equilibrium with very great rapidity, since even the most careful experiments ('Trans. Chem. Soc.,' 1915, vol. 107, pp. 1177 and 1189) have failed to detect any lag in the adjustment of rotatory power in the tartaric esters when conditions have been altered. In this respect these changes may be compared with the dissociation of nitrogen peroxide, with the dissociation and association of water, or even with the phenomena of ionisation in aqueous solutions, all of which appear to depend on very rapid or instantaneous reactions. Under these circumstances, only static methods of investigation are available, *i.e.*, the liquid must be proved to be complex by recognising in it the attributes of a mixture, rather than by isolating its components and watching them change gradually into one another with lapse of time.

(b) *Anomalous Rotatory Dispersion observed in Natural and Artificial Mixtures.*

What evidence is there, then, that tartaric acid gives rise to a complex product when it is dissolved or melted in order to convert it into an isotropic, optically active medium? Biot found evidence of widespread chemical change in the progressive alterations of rotatory power that were produced alike by the addition of water or alcohol, of soda or potash, of ammonia, and of sulphuric and boric acids; but this argument is obviously limited to the changes which accompany dissolution and cannot be applied to the mere fusion of the anhydrous acid. A more general argument is afforded by the experiments in which Biot attempted to neutralise the optical rotatory power of lævorotatory turpentine by compensating it with a column of dextrorotatory oil of lemon ('Comptes Rendus,' 1836, vol. 2, p. 543); not only was the compensation "neither complete nor general," but "when the principal section of the analysing prism coincided with the original plane of polarisation, there was produced an extraordinary image of blue-violet colour, dark, and sensibly free from red; and, on turning the prism a little to the right or to the left of this position, the tint of the image varied in a contrary sense to the refrangibility, things which are entirely different from those which a single one of the two essences could produce alone." Similar effects were observed in

artificial mixtures of lævorotatory turpentine with dextrorotatory camphor, as well as in some natural turpentine-oils.

On the basis of BIOT'S experiments, as well as of his own observations of the unequal dispersive power of different liquids, ARNDTSEN ('Ann. Chim. Phys.,' 1858, vol. 54, p. 421) put forward for the first time a precise explanation of "the singular dispersion of the planes of polarisation of tartaric acid," as follows:—

"If one should imagine two active substances which do not act chemically upon one another, of which one turns the plane of polarisation to the right, the other to the left, and, in addition that the rotation of the first increased (with the refrangibility of the light) more rapidly than that of the other, it is clear that, on mixing these substances in certain proportions, one would have combinations which would show optical phenomena precisely similar to those of tartaric acid, as M. BIOT has already proved by his researches on different mixtures of turpentine and natural camphor. One might then regard tartaric acid as a mixture of two bodies differing only as regards their optical properties, of which one had a negative rotatory power, the other a positive rotatory power, and of which the rotations varied in different proportions with the refrangibility of the light."

This hypothesis, made more than 60 years ago, appears to us to afford a correct explanation of the peculiar rotatory dispersion of tartaric acid and its derivatives. In its support we submit (i.) the mathematical evidence that the form of the dispersion-curves is in harmony with this view, and (ii.) the chemical evidence that mixtures of isomerides in equilibrium actually exist, *e.g.*, in the case of nitrocamphor, and that their behaviour is in accordance with that which must be postulated for the "two kinds of optically-active molecules" assumed by ARNDTSEN.

(c) *Anomalous Rotatory Dispersion produced by the Partial Compensation of two Simple Dispersions.*

The measurements described below afford strong support to ARNDTSEN'S theory, since it has been established by visual and photographic readings that the dispersion curves for tartaric acid, like those of its esters ('Trans. Chem. Soc.,' 1915, vol. 107, pp. 1173–1195), can be represented over a wide range of wave-length and to a close degree of approximation by two terms of DRUDE'S equation, thus

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} - \frac{k_2}{\lambda^2 - \lambda_2^2}.$$

This equation is a direct mathematical expression of the view that the anomalous rotatory dispersion of tartaric acid is produced by the counterbalancing action of two components of opposite rotatory power and unequal dispersion. It is, however, not in itself a conclusive argument for the presence of two kinds of optically active molecules

in these liquids since the two compensating terms in the equation may be due to (i.) two electrons with opposite influence on the rotatory power, as in the case of quartz, where, however, they do not give rise to anomalous dispersion, (ii.) two radicals of opposite activity united in one molecule, as in the cases of *l*-menthyl *d*-camphor β -sulphonate (TSCHUGAEFF, 'Ber. Deutsch. Chem. Gesell.,' 1911, vol. 44, p. 2023; 1912, vol. 45, p. 2759; compare 'Trans. Faraday Soc.,' 1914, vol. 10, p. 73) and *l*-menthyl *d*-diphenylmethylacetoacetate (RUPE and KÄGI, 'Ann. der Chem.,' 1920, vol. 420, p. 38); (iii.) two molecules of opposite rotatory power, either easily convertible, as in the case of the isomeric nitro-camphors (LOWRY, 'Trans. Faraday Soc.,' 1914, vol. 10, p. 100), or fixed, as in the artificial mixtures of BIOT ('Comptes Rendus,' 1836, vol. 2, p. 543), and of VON WYSS ('WIEDEMANN'S Ann. Phys. Chem.,' 1888 [2], vol. 33, p. 567). To decide between these three possibilities, further consideration is needed both of the chemical and of the physical properties of the solution as set out in the following paragraphs.

(d) *Dynamic Isomerism as an Explanation of Anomalous Rotatory Dispersion.*

The view that the two terms in the equations showing the effect of wave-length on the rotatory power of tartaric acid and its derivatives are due to two electrons, as in the case of quartz, is rendered improbable by the fact that substances of similar type do not show this effect. Thus, if tartaric acid be regarded as a dicarboxylic acid of the sugar-group, belonging to the C_4 series and containing two asymmetric carbon atoms, it might be expected that the methyl-glucosides, which belong to the C_6 series and contain five asymmetric carbon atoms, would give even more complex dispersion-curves; actually, however, their dispersion can be expressed accurately by a simple one-term formula. The hypothesis of two radicals of opposite optical activity is even less easy to apply to tartaric acid, unless some form of molecular rearrangement is first postulated, since the two active radicals of which it is composed are not only of the same sign, but are of identical structure, and would therefore give identical rotatory dispersions.

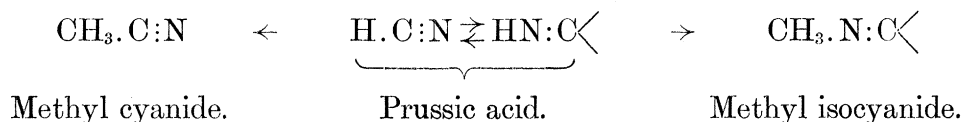
It is, indeed, impossible to discover, in the simple structural formula



commonly assigned to tartaric acid, any justification for its anomalous rotatory power, and some change of molecular structure appears to be inevitable if its peculiar physical properties are to be accounted for, since the complex dispersion of the acid is just as exceptional amongst simple organic compounds as would be the appearance of a bright blue or green colour in a simple compound of the alcohol or sugar group. If then, some form of molecular rearrangement must be assumed, no simpler hypothesis can be adopted than that of ARNDTSEN, which suggests that the rearrangement is incomplete, so that one of the two compensating factors required to account for the complex or anomalous dispersion of the medium is merely the original

form of the acid, whilst the other is a product of change, of opposite sign and unequal dispersion, but of a character sufficiently commonplace to give rise to a simple, instead of a complex, dispersion-curve when studied as a separate entity. This product might be an ion, a hydrate, a polymer, or an isomer of the original form of the acid; but, since the amorphous acid and its liquid esters exhibit a full range of anomalies in the absence of any solvent, the first two possibilities are ruled out, and the alternatives are reduced to two, involving (i.) polymerisation or depolymerisation as suggested by WENDELL ('WIEDEMANN'S Ann. Phys. Chem.,' 1898, vol. 66, p. 1156), or (ii.) isomeric change. These alternatives may even be combined, since when isomeric change takes place, it is not unusual for one or other of the isomers to undergo association if the physical and chemical conditions are favourable.

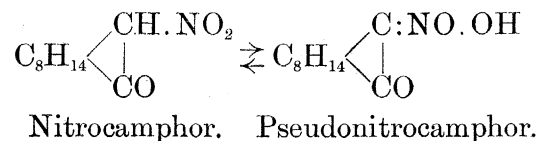
ARNDTSEN'S hypothesis may then be interpreted in the light of modern knowledge, by suggesting that tartaric acid and its esters afford yet another example of "dynamic isomerism" or reversible isomeric change. This phenomenon was discovered in 1877 by BUTLEROW ('Liebig's Ann. der Chem.,' 1877, vol. 189, p. 77), who made use of it in order to account for the production of two types of derivatives from prussic acid, a result that could be explained most readily by assuming that the liquid acid was a mixture of the two parent-compounds, thus



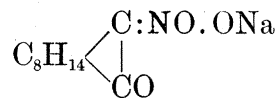
These two isomerides have not yet been isolated, although BUTLEROW was able to demonstrate the existence of a similar equilibrium between two isomeric olefines when isodibutylene was dissolved in strong sulphuric acid. If tartaric acid gave rise, when fused or dissolved, to a similar mixture of isomerides with suitable optical properties, ARNDTSEN'S hypothesis would afford a complete explanation of the anomalous dispersion of the acid.

(e) *Plastic and Fixed Derivatives of Nitrocamphor and of Tartaric Acid.*

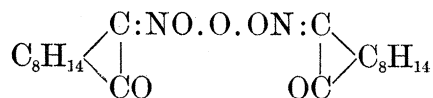
Nitrocamphor, which exists in solution in two optically active forms, of opposite sign and unequal dispersion, affords a still more striking example of dynamic isomerism. The ordinary form of the compound is lævorotatory, but its rotatory power in freshly prepared solutions changes from left towards right, giving rise to the phenomenon of mutarotation, or change of rotatory power with time (LOWRY, 'Trans. Chem. Soc.,' 1899, pp. 75, 211) as the result of a reversible isomeric change, which can be expressed by the balanced equation:



In the case of nitrocamphor, only one form of the parent substance is known, although derivatives of both types have been prepared, including dextrorotatory salts, such as

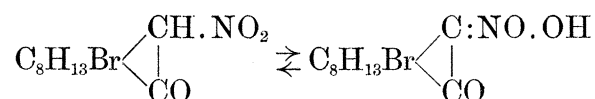


and a dextrorotatory anhydride



derived from the acidic pseudo-form of the nitro-compound.

In the case of π -bromonitrocamphor, however, both isomers have been isolated and have been found to change in opposite directions to an equilibrium mixture of intermediate rotatory power (*ibid.*, p. 225).



Nitrocamphor agrees with tartaric acid in that its optical rotatory power is exceptionally sensitive to changes of conditions, no doubt in part as a result of the displacement of the point of equilibrium, *e.g.*, in different solvents. As in the case of tartaric acid, the rotations may even exhibit a change of sign under some extreme conditions; thus in certain oxygenated solvents nitrocamphor, which is usually lævorotatory, gives small dextrorotations, just as dextro-tartaric acid, when dissolved in an excess of alkali, may give small lævorotations (see pp. 280-282 below).

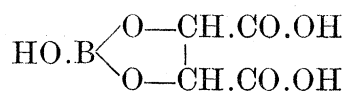
It is, however, characteristic of nitrocamphor that it is able also to give derivatives of fixed type (compare the conversion of prussic acid into methyl cyanide and methyl isocyanide) in which the plasticity of the parent substance has disappeared. Thus by chlorination nitrocamphor is converted into two derivatives of the normal nitro type, whilst in the formation of the anhydride and of the salts a complete conversion into the acid pseudo-nitro type takes place. The chloro-nitrocamphor corresponding to nitrocamphor itself gives $[\alpha]_D - 5^\circ$ in chloroform, whilst the anhydride gives $[\alpha]_D + 167^\circ$ in chloroform.

In the case of tartaric acid, it has been less easy to discover fixed derivatives to correspond with these compounds, since (as has already been noted) the esters show just the same anomalies as the acid itself, and any molecular rearrangement which involves the hydrogen atoms of the carboxyl groups is therefore ruled out as an explanation of the flexible rotatory power of the acid. Bror in 1835 ('Comptes Rendus,' 1835, vol. 1, pp. 458-459) appeared to have found a solution of this problem when he stated, in his sealed note to the Academy, that "The combinations of tartaric acid with solid bases, also with boric acid, give products endowed with rotation towards the right ;

but the relative intensity of these rotations for the different simple rays, obeys the general law of this phenomenon, to which tartaric acid alone is a marked exception, at least among all the bodies which I have been able to study hitherto."

Preliminary observations appeared to confirm BIOT'S observations, since the dispersions of the tartrates in aqueous solutions not only approximated very closely to the requirements of the simple dispersion formula, but, in the case of sodium tartrate, showed a surprisingly close agreement with the law of inverse squares. The conclusion that the rotatory dispersion of the tartrates is "simple" was, however, open to grave suspicion on account of the extreme smallness of the dispersion-constants, corresponding with absorption-bands not far removed from zero wave-length. Moreover, on calculating a simple dispersion formula for sodium tartrate from the data for Hg 5461 and Hg 4359, selected from a particularly long series of readings (including 16 wave-lengths in the visual and 6 wave-lengths in the photographic region of the spectrum, instead of the short series of four or five wave-lengths which we have generally used in investigating cases of simple rotatory dispersion), we obtained an unmistakable series of positive differences from red to green, negative between green and violet, and positive again beyond the violet mercury line. These differences were observed in two solutions of different concentrations, and could not therefore be accidental. It was therefore clear that the curves for the metallic tartrates were not really simple, but complex, with a large positive and a small negative term, so that the anomalies would be pushed right out into the ultra-violet region of the spectrum where the solutions are too opaque for observation by ordinary methods.

In the case of boric acid we were more fortunate, since when an excess of boric acid was added to tartaric acid the aqueous solution of boro-tartaric acid gave a simple dispersion curve, with a normal value, 0.0246, for the dispersion-constant λ_0^2 . Boro-tartaric acid then appears to be a "fixed" derivative of tartaric acid, in which the acid has been locked up in one of its two alternative forms. A similar result was obtained with tartar emetic, which gives very large dextrorotations, but a perfectly simple dispersion, with a dispersion-constant $\lambda_0^2 = 0.0494$. Boro-tartaric acid, which has many analogies amongst the polyhydric alcohols of the sugar group (see p. 252) is probably



and it is possible that the simple character of its rotatory dispersion may be due to the bridge between the two asymmetric carbon atoms which is shown in this formula.

The search for a "fixed" derivative of the elusive lævorotatory modification of the acid proved even more difficult than in the case of the dextrorotatory component. The negative rotations discussed on pp. 280 to 284 of this paper are usually complex in their dispersion, but we were fortunate in discovering that the lævorotatory solutions obtained by dissolving tartar emetic in an excess of alkali are not only comparable in

rotatory power with the parent substance, but like it exhibit a perfectly simple rotatory dispersion, with a dispersion-constant $\lambda_0^2 = 0.0627$.

After the mathematical evidence set out under (c) above, the discovery of these fixed compounds is the most important evidence that has yet been put forward in support of ARNDTSEN'S hypothesis. If it is difficult to discover in the formula commonly assigned to tartaric acid any physical basis for the anomalous optical properties of the acid and of so many of its derivatives, it would be at least equally difficult to discover either in boro-tartaric acid or in tartar emetic any factor which would account for the disappearance of the anomalies, apart from the view which has already been advanced that in these compounds the plastic acid has been fixed in one of its labile forms.

4. EXPERIMENTAL METHODS.

The experimental work described in the present paper was undertaken with the object of applying to the problems investigated by BIOT the exact methods of measuring rotatory dispersion which have been developed during the past 15 years, and which have already been applied (as described in the preceding paper of this series) to the exact determination of the optical rotatory power of quartz. Thus Section 5 describes a critical investigation of the relationship between the rotatory power and concentration of aqueous solutions of tartaric acid, and a detailed study of the deviations from BIOT'S linear law, as revealed by exact measurements for a series of eight wave-lengths in the visible region of the spectrum. Section 6 describes an investigation of the relationship between optical rotatory power and wave-length for a series of aqueous solutions of tartaric acid; this was undertaken in order to test in the case of tartaric acid the equations which had already been proved to be adequate to express the anomalous rotatory dispersion of the tartaric esters. The remaining sections of the paper deal with the influence of various chemical agents on the rotatory power of tartaric acid, in extension of the early pioneering work of BIOT.

The optical apparatus used in the experiments on tartaric acid was the same as that which has already been described in the preceding paper of the present series. An important improvement has, however, been effected in the matter of light-sources. In the experiments on quartz the cadmium lines were read with the help of light derived from an open arc burning between electrodes of a cadmium-silver alloy (LOWRY, 'Phil. Mag.,' 1909, vol. 18, pp. 320-327). Five years later a description was given of "An enclosed cadmium arc for use with the polarimeter" (LOWRY and ABRAM, 'Trans. Faraday Soc.,' 1914, vol. 10, pp. 103-106); this arc was of an experimental type, requiring the continuous use of a Gaede pump to maintain the vacuum, and merely served to show how very valuable an efficient lamp of this type would be in all optical experiments which demand intense sources of monochromatic light. During the period covered by the experiments now described we have had the privilege of using the enclosed cadmium arc designed by Dr. SAND and described by him at the Manchester meeting of the British Association ('B.A. Report,' 1915, vol. 85, p. 386). This lamp has proved to be per-

fectly adapted to the work we have been doing, and in some respects is even more convenient than the mercury arcs which are now available for experimental work. The importance of this development may be shown by the statement that whereas twenty years ago the sodium light was the only practical light-source for use in polarimetry, this line is now usually left to the last because it is more troublesome and in every way less satisfactory to read than the lines derived from the enclosed mercury and cadmium arcs.

Photographic observations form an essential feature of the experiments which are now described. The method used was described in outline in 1908 ('Roy. Soc. Proc.,' 1908, A, vol. 81, 472-474), but has reached its highest development in connection with observations of the rotatory power of quartz for ultra-violet light, of which a detailed account will be given in the third paper of the present series.

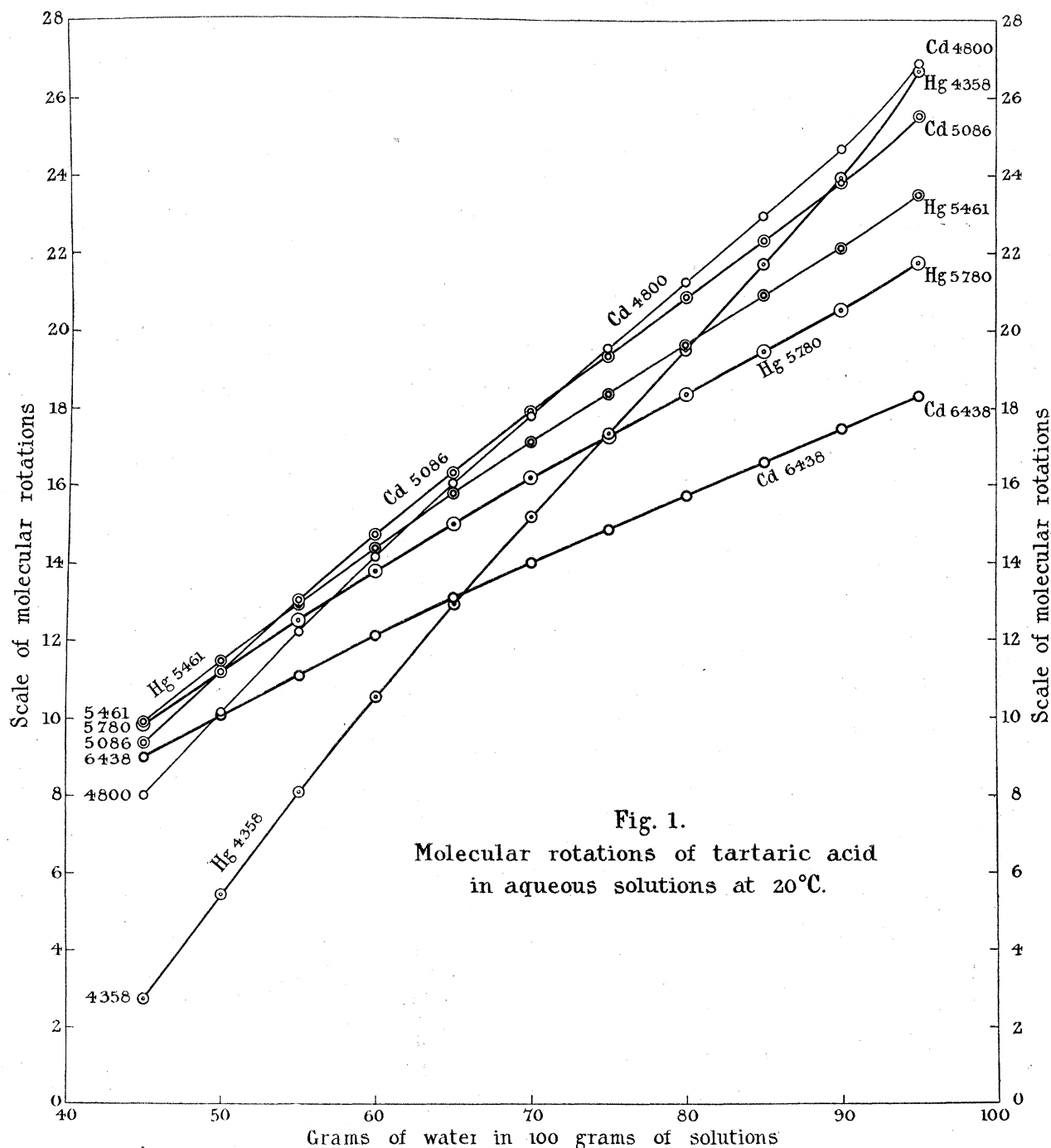
5. SPECIFIC ROTATORY POWER OF TARTARIC ACID FOR LIGHT OF DIFFERENT WAVE-LENGTHS.

A long series of observations was made, in order to establish standard values for the specific rotatory power of tartaric acid in aqueous solutions at 20° C. Similar observations have been made by a number of observers using monochromatic sodium light (PRIBRAM and GLÜCKSMANN, 'Monatshefte,' 1898, vol. 19, p. 136), or patches picked out from a continuous spectrum, with the help of a spectroscope or by means of light-filters (WENDELL, 'Wied. Ann.,' 1898, vol. 66, p. 1153; WINTHER, 'Zeitschr. Physikal. Chem.,' 1902, vol. 41, p. 166); but no values have been given hitherto for the pure light-sources, derived from the spectra of mercury and of cadmium, which have now become the common standards in polarimetric work. The values placed on record in Table I. make good this deficiency; they also provide data for testing, for a considerable series of pure monochromatic light-sources, the linear relationship between concentration and rotatory power which was put forward by BIOT in 1834, as well as the parabolic relationship used by WINTHER in 1902.

In order to secure exact values for the specific rotatory power of the acid, all the solutions for these experiments were prepared from exactly-weighed quantities of acid and water. Two samples of acid were used, one of them (for which we are indebted to Messrs. Bennet, Lawes & Co.) being a specially pure sample, containing less than 0.05 per cent. of ash, and practically no trace of lead. In order to avoid changes of concentration caused by evaporation, the precaution was taken of using solutions which had not been filtered; small traces of insoluble matter were found to come almost exclusively from the Wedgwood mortar used to powder the crystals, and, when the further precaution was taken of merely crushing the crystals in an agate mortar, the amount of solid undissolved was negligible. The rotations of the solutions were determined in a polarimeter-tube 6 decimetres long, which had been calibrated to check the length of the column, and was maintained at a constant temperature by a rapid flow of water at 20° C. Two, three, or even four series of readings were taken, as shown in Table I., with solutions prepared independently of one another, until it appeared probable that

the casual errors had been reduced to a few hundredths of a degree. Table I. shows the observed rotations, α , and the specific rotatory powers $[\alpha]$ derived from them, for 11 solutions containing from 5 to 55 grams of acid in each 100 grams of solution; the corresponding molecular rotatory powers are also shown in the table.

The data used in testing BIOT'S linear law and WINTHER'S parabolic formula are shown in Table II. BIOT'S linear law, although based originally upon somewhat rough measurements, is very good as a first approximation. Thus, in fig. 1, in which the



molecular rotatory power of the acid is plotted against the percentage by weight of water in the solution, the curves are seen to be inflected, but the deviations from the linear law, though quite real, are by no means conspicuous. More remarkable still is the fact, which BIOT discovered in 1850, that extrapolation by means of the linear law leads to substantially correct values for the specific rotatory power of the anhydrous glassy or amorphous acid. In our own calculations we have used, for each of a series of nine wave-lengths, a linear formula based on the values for the specific rotatory powers of the acid in solutions containing 55 and 85 per cent. of water; the rotatory powers of the anhydrous acid, as shown under $e = 0$ in Table II., are derived by interpolation from the observations of BRUHAT ('Trans. Faraday Soc.,' 1914, vol. 10, p. 89), and the differences between the observed and calculated values are:—

$$1\cdot2, 1\cdot5, 1\cdot6, 1\cdot7, 1\cdot7, 1\cdot7, 1\cdot8, 0\cdot6^\circ, \text{Mean } 1\cdot5^\circ.$$

This agreement is remarkably close, having regard to the facts that (i.) the linear law is only an approximation, (ii.) the extrapolation covers nearly half of the total range of concentration, and amounts in the case of the violet mercury line to an extension of over 12 degrees in the range of rotatory powers.

In view of the fact that the linear law is valid to this extent over the wide gap between the anhydrous acid and its saturated solutions in water, we were prepared to find that, although closer examination would show marked deviations in the values for dilute solutions, no substantial errors would occur in the case of the more concentrated solutions. This anticipation was, however, by no means correct. Basing the linear formula again on the rotatory powers of the acid in solutions containing 55 and 85 per cent. of water, we find that the deviations which are produced by increasing the concentration to *water* 45 per cent., *acid* 55 per cent., are even greater than those which result from diluting to *water* 95 per cent., *acid* 5 per cent.; and this is true, not only for one wave-length, but for the whole range of wave-lengths shown in Table II. The linear law is thus shown to be even less exact in concentrated than in dilute solutions.

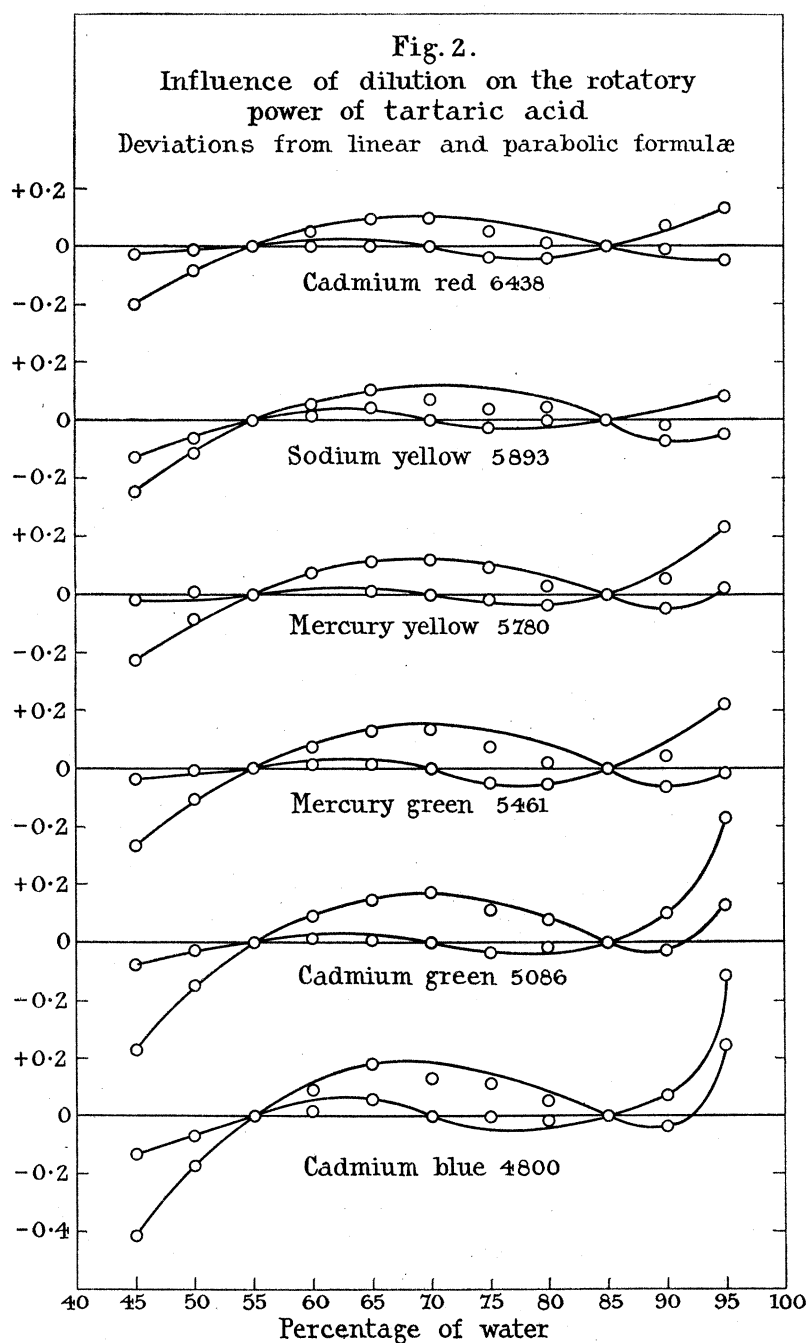
A natural sequel to the recognition of the fact that the linear law is inexact, is the introduction of a third term into the equation, which thus changes from

$$[\alpha_1] = A_1 + B_1e \quad \text{to} \quad [\alpha_2] = A_2 + B_2e + C_2e^2.$$

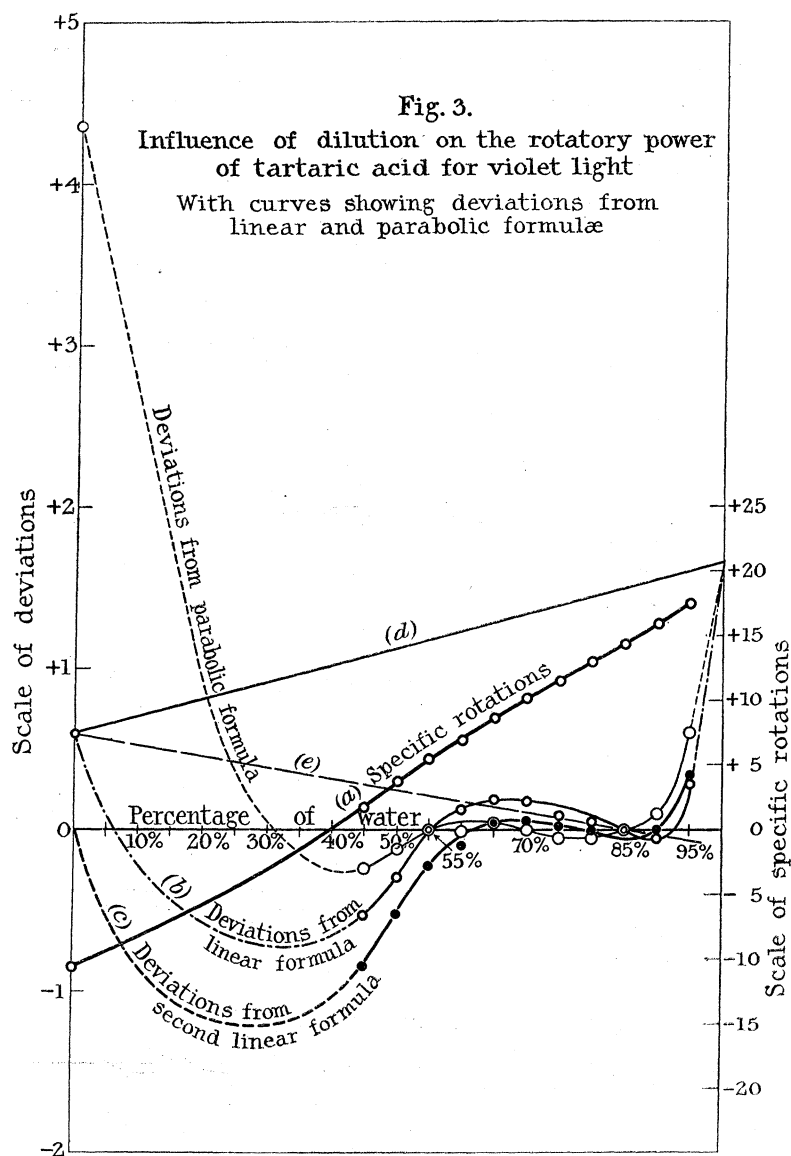
This method of expressing the specific rotatory powers of the acid was adopted by WINTHER in 1902. Its application to the data now recorded is shown in Table II. The parabolic formulæ were all based on the readings for solutions containing 55, 70 and 85 per cent. of water; in a few cases these readings may have been less exact than others that might have been selected; but no great advantage would have been obtained from any laborious attempt to smooth the values or to adjust the curves, since the general results were perfectly obvious when the errors were examined over the whole of the series of nine wave-lengths. Within the range from 55 to 85 per cent. of water, the

agreement was much better than with the linear formula, as was inevitable since there was exact agreement at three points instead of two; in the more concentrated solutions, also, the parabolic formula gave rather better results than the linear law; but in the more dilute solutions the errors were increased very considerably by the introduction of a third term, with the result that outside the limit of 55 to 85 per cent. of water, the parabolic was distinctly worse than the linear formula.

The real character of the deviations was only revealed when the errors of the various formulæ were plotted against the concentrations as in figs. 2 and 3. As in the case of



solution volumes (BOUSFIELD and LOWRY, 'Phil. Trans.,' A, 1905, vol. 204, p. 283) the errors in the measurement of specific-rotatory power increase with dilution, so that the course of the curves becomes uncertain as the proportion of water increases towards 100 per cent. It is, however, quite evident that the curve of errors, fig. 3*b*, for the linear formula intersects the zero-line at three points between $e = 0.45$ and $e = 1$.



Any attempt to flatten this curve, by the addition of a third term containing e^2 , is obviously doomed to failure, since the curvature from the straight line is in opposite directions at the two ends, and cannot be covered by a section of a parabola. The type of formula used by WINTHER is therefore only of value for interpolation over a narrow range, and is even worse than a simple linear formula for extrapolation. This is true not only for dilute solutions, where the errors immediately become larger, because the curvature

is in the wrong direction, but also for more concentrated solutions, as may be seen by comparing BRUHAT'S experimental values for the anhydrous acid, $e = 0$, on the one hand, with the values of A_1 in the linear equation, which showed deviations amounting, on the average, to 1.5° , and on the other hand, with the values of A_2 in the parabolic equation, which gives errors as follows :—

$$3.3, 2.9, 4.1, 4.5, 5.1, 4.5, 4.5, 4.3, \text{Mean } 4.1^\circ.$$

The complete course of the curve of rotatory power against concentration is shown, for the violet mercury line, by the heavy curve a in fig. 3. The ordinates of curve b represent the errors of a linear formula which is correct at 55 and 85 per cent. of water ; the curve c shows the errors of a parabolic formula which is correct at 55, 70 and 85 per cent. of water. The error ($+0.6$ degrees) in extrapolating by means of the linear formula to the anhydrous condition is shown on the left-hand side of the diagram, where a broken line is used to cover the interval between 0 and 45 per cent. of water in which no experimental values are available. A similar prolongation of the curve of errors on the right-hand side of the diagram indicates the most probable value for infinite dilution. If the aqueous solutions contained only an anhydrous acid and a fully-hydrated acid, both of constant specific rotatory power, the relationship between rotatory power and concentration should be expressed from end to end, if not by the straight line d , at least by a simple uninflected curve. The actual deviations from this ideal straight line are shown in fig. 3 by measuring the ordinates downwards from d instead of from the horizontal axis of zero rotation. It will be seen that this curve of deviations (which are all negative in sign) shows one minimum and two maxima, so that the exact relationship between rotation and concentration could only be expressed by an equation containing at least five arbitrary constants.

In view of the complexity disclosed by this preliminary analysis, we have not thought it worth while to pursue the subject further, except to point out that in the case of each wave-length it is possible to use a linear formula (as indicated by the straight line e , and the curve of errors c , in fig. 3), which is substantially correct both for the anhydrous acid and for aqueous solutions from, say, $e = 0.6$ to 0.9 , but widely divergent outside these limits. A series of values calculated from such a linear formula, for the mercury violet line, is given under $[\alpha_0]$ in Table II. ; this formula is correct for the anhydrous acid $e = 0$, and gives a \pm error at three other points lying near $e = 0.63$, $e = 0.80$ and $e = 0.91$.

6. ROTATORY DISPERSION IN AQUEOUS SOLUTIONS OF TARTARIC ACID.

In order to determine the exact form of the curves of rotatory dispersion in aqueous solutions of tartaric acid, eight solutions were originally prepared and examined, containing from 5 up to 70 grams of tartaric acid in 100 c.c. of solution. In two cases the readings were confined to the seven visible cadmium and mercury lines ; in four other

cases the series was extended to wave-length about 4150, by the inclusion of photographic readings, and in the case of two of the strongest solutions, readings were taken for 21 and 26 lines, extending to wave-lengths 4005 and 3941 respectively.

These solutions were filtered, in order to facilitate the reading of the more difficult blue and violet lines. The concentrations, as well as the specific and molecular rotations derived from them, were therefore less certain than those set out in the preceding section, and, when the latter had been completed, the earlier observations were regarded as obsolete, with the exception of the two long series which covered a very wide range of the spectrum, and were specially well adapted for testing the form of the dispersion-curves. The rotations for these two solutions are set out in Table III. (*a*) and (*b*). In order to bring them into line with the standard series of readings of Table I. the true concentrations of these two solutions were found by interpolation from the standard series, the concentrations deduced in this way being $e = 0.4590$ and 0.5875 , or 69.90 and 49.96 grams of tartaric acid in 100 c.c. of solution, as compared with the nominal values of 70 and 50 per cent. After making these very small corrections, the specific and molecular rotations of the two long series were included with the shorter standard series of Table I. amongst the data used in discussing the relation between rotatory power and wave-length.

The calculated rotations shown in Tables III. and IV. are derived from an equation of the DRUDE type containing one positive and one negative term, thus

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} - \frac{k_2}{\lambda^2 - \lambda_2^2}.$$

But whereas in the case of quartz the data are now so extensive and so accurate that *five* arbitrary constants can be determined exactly, the range and accuracy of the data in the case of tartaric acid and other optically-active organic compounds are only sufficient for the exact determination of *three* arbitrary constants; in other words, the effect of a small alteration in any one of four constants can be eliminated almost entirely by suitable alterations in the other three. This limitation has already been discussed in the case of ethyl tartrate, the rotatory-dispersion of which can be calculated almost equally well from formulæ in which the dispersion-constants are:—

- (i) $\lambda_1^2 = 0.035$, $\lambda_2^2 = 0.065$,
- (ii) $\lambda_1^2 = 0.030$, $\lambda_2^2 = 0.070$.
- (iii) $\lambda_1^2 = 0.025$, $\lambda_2^2 = 0.080$,

where the sum of the dispersion-constants λ_1^2 and λ_2^2 is almost constant (LOWRY and DICKSON, 'Trans. Chem. Soc.,' 1915, vol. 107, p. 1186). The best results are therefore obtained by assuming a steady value for one of the two dispersion-constants in a series of related compounds; thus, in 22 independent series of observations of tartaric acid and its esters, the value $\lambda_1^2 = 0.030$ may be maintained for the smaller of the two

dispersion-constants. This may be regarded as substantially correct for the whole of the series, since, in case after case, independent calculations have given numbers lying within a narrow range on either side of this average value.

Having thus established a fixed value for the smaller dispersion-constant, the magnitude of the larger dispersion-constant λ_2^2 may be deduced with a very fair degree of accuracy. Thus in the case of methyl and ethyl tartrates the values were as follows —

	<i>Methyl ester.</i>	<i>Ethyl ester.</i>
Pure ester	0·054	0·056
In ethylene chloride or bromide	0·058	0·061
In formaldehyde	0·070	0·070

The concordance in the values for the two esters when examined under similar conditions is a very fair indication of the accuracy of the dispersion-constants deduced in this way.

In the case of the two concentrated solutions of tartaric acid, the values of the second dispersion-constant deduced independently were 0·074 and 0·073. With these values, a close agreement was found between the observed and calculated rotations as set out in Table III., both in the visual and in the photographic regions. This agreement, following upon a similar concordance in 12 long series of observations of methyl and ethyl tartrate, is sufficient to establish the general validity of the two-term equation as an expression of the complex rotatory dispersion both of tartaric acid and of its esters.* It is then a simple problem to study the variations of the four constants of this equation as the concentration of the solution is increased or diminished. Preliminary observations indicated that the dispersion-constant λ_2^2 for tartaric acid in aqueous solutions might, with advantage, be reduced from 0·074 for solutions containing 70 grams of acid in 100 c.c. to 0·065 for solutions containing 5 grams in 100 c.c. ; but this diminution could not be confirmed in the more exact, though rather less extensive, observations set out in Table I. We have, therefore, preferred to make use of constant values, $\lambda_1^2 = 0·030$, $\lambda_2^2 = 0·074$, for the two dispersion-constants of this series of solutions rather than to introduce small variations which would merely have led to irregularities in the values of the “rotation-constants” k_1 and k_2 . The observed and calculated values of the molecular rotatory powers at eleven different concentrations are set out in Table IV. Table V. shows, for the 13 solutions for which data are given in Tables III. and IV., the magnitude of the four constants of the two-term equation, together with the wave-lengths at which the principal anomalies are found, namely, the inflection of the curve at λ_σ , the maximum at λ_μ and the reversal of sign at λ_ρ . These latter have been calculated from the equations, as a convenient method of interpolation ; wave-lengths

* In the case of the acid there are indications of a predominance of negative errors between the green and violet mercury lines ; this is, perhaps, an effect of ionisation, since nothing of the sort has been noticed in the case of the esters.

which depend on extrapolation beyond the range of the experimental data are printed in italics.

From Table V., and from the graphical representation of fig. 4, the following conclusions may be drawn :—

- (1) The reversal of sign (which has been observed hitherto only in the anhydrous acid, in alcoholic and in super-saturated aqueous solutions or in the ultra-violet region of the spectrum) is here recorded with the help of the camera, in the extreme violet region of the spectrum in unsaturated aqueous solutions containing only 50 grams of tartaric acid in 100 c.c. of the solution ($e = 0.5875$ or $P = 41.25$ per cent.).
- (2) The maximum rotation, which has usually been said to vanish on dilution, is here retained on the less refrangible side of the violet mercury line even at a concentration of only 5 grams per 100 c.c. This fact is of interest in connection with the statement of ARNDTSEN that at concentrations below 20 per cent. by weight “the dispersion becomes normal in so far as the angle of rotation increases continuously with the refrangibility of the light; yet the rotation increases so little from the ray F to the ray e , that one cannot doubt that it would have a maximum in the violet part of the spectrum” (‘Ann. Chim. Phys.,’ 1858, vol. 54, p. 412). Our observations prove the reality of this hypothetical maximum, whilst, at the same time, they show the futility of any definition of “normal dispersion” which depends merely on the removal of the maximum from the easily-visible into the violet or ultra-violet region of the spectrum; a similar usage of this term by WINTHER has already been criticised (LOWRY, ‘Trans. Chem. Soc.,’ 1915, vol. 107, p. 1195) on the ground that it implies a physiological definition of a purely physical property. Anomalous dispersion depending on the imperfect compensation of two simple rotatory dispersions of opposite sign may, as a matter of actual fact, be rendered normal by displacing the maximum to infinite wave-length in the infra-red; but any displacement in the opposite direction only exaggerates the invisible maximum in the ultra-violet region.*

7. TARTRATES OF THE ALKALI-METALS.

In his sealed note, communicated to the Academy on August 25, 1834, BIOT referred for the first time to the rotatory power of the tartrates in the following terms :—“The combinations of tartaric acid with solid bases give products endowed with rotation towards the right; but the relative intensity of these rotations for the different simple rays obeys the general law of this phenomenon, to which tartaric acid alone is a marked exception, at least, among all the bodies which I have been able to study hitherto” (‘Comptes Rendus,’ 1835, vol. 1, p. 458). A detailed study of the tints produced by

* For a series of curves illustrating this point, see ‘Trans. Chem. Soc.,’ 1915, vol. 107, p. 1200.

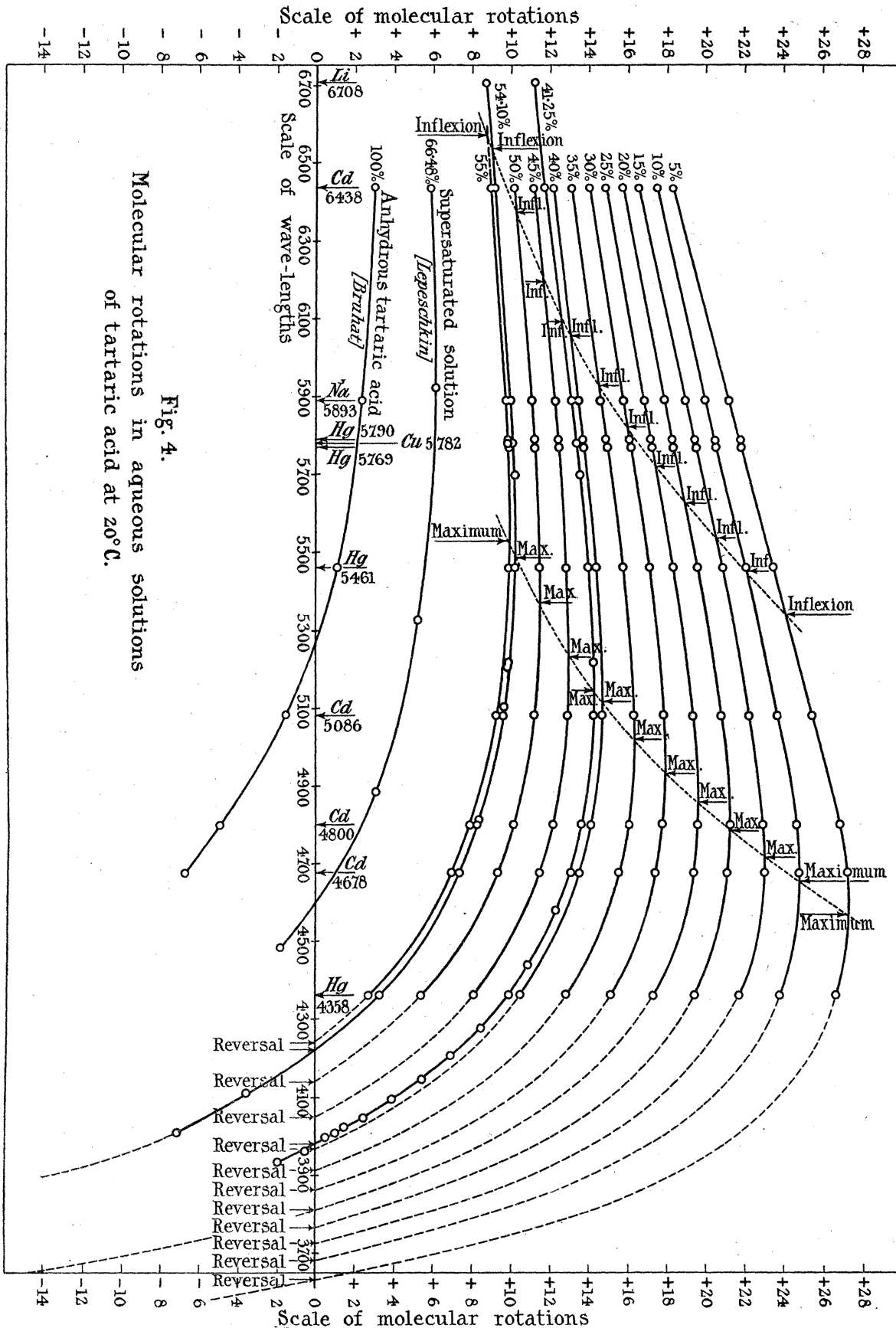


Fig. 4.
Molecular rotations in aqueous solutions
of tartaric acid at 20°C.

aqueous solutions of potassium, sodium and ammonium tartrates ('Mém. Acad. Sci.,' 1838, vol. 16, pp. 304–317) showed that these agreed very closely with those produced by quartz plates of suitable thickness, and with those calculated from BIOT'S law. A similar conclusion was reached by KRECKE, who measured the rotatory powers of the potassium, sodium and ammonium salts over the range from 0° to 100° C., and concluded that "the tartrates examined obey the laws of BIOT" ('Arch. Néerland.,' 1872, vol. 7, p. 114). KRECKE'S figures actually show small regular deviations in the case of potassium and sodium tartrates, and very marked deviations in the figures for ammonium tartrate and for Rochelle salt. Thus his figures for $[\alpha]_{\lambda}^2$ are as follows:—

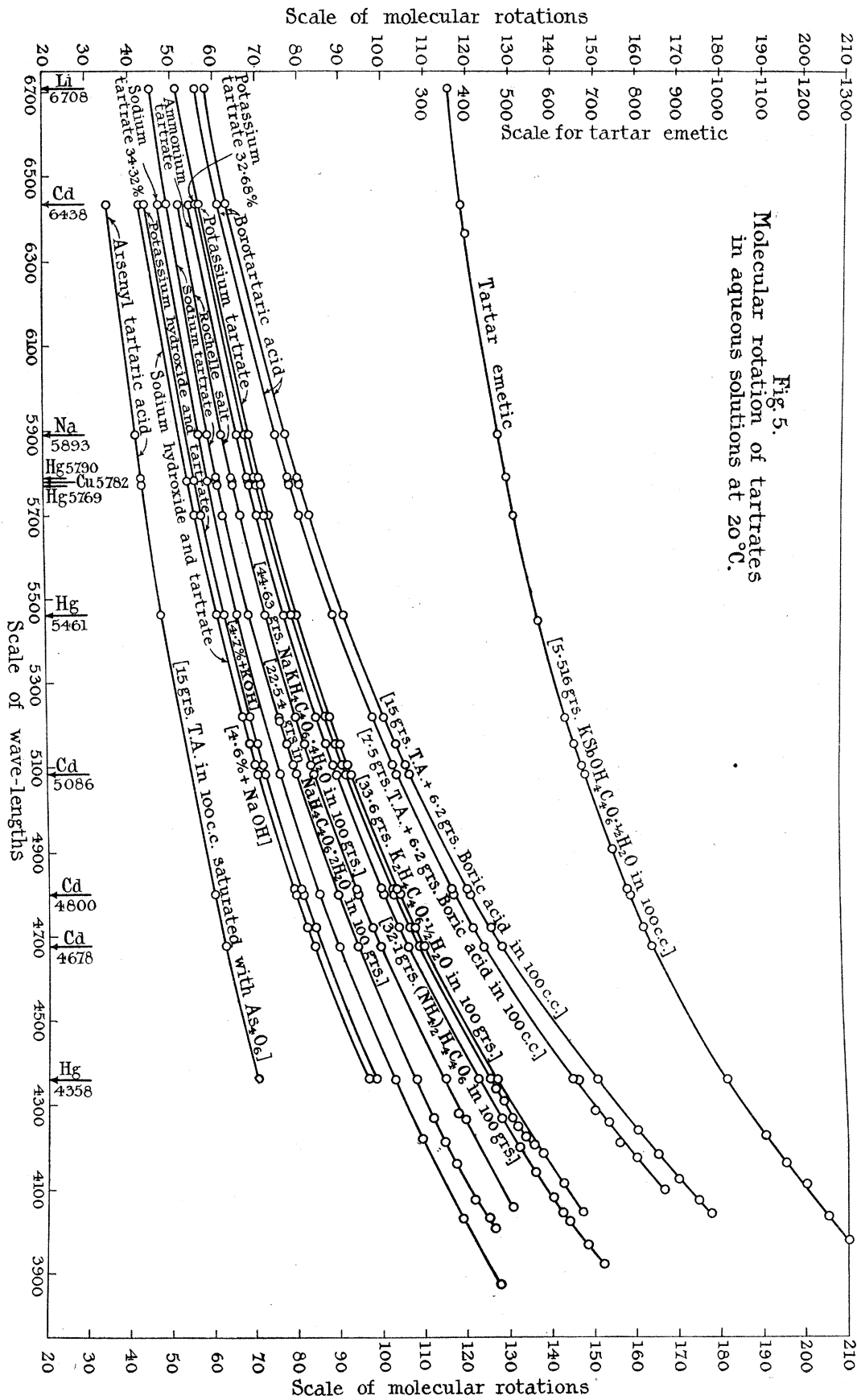
		C.	D.	E.	b.	F.
	°					
Tartaric acid 50%	0	2,427	2,227	1,602	1,533	1,331
„ „ 50%	100	5,792	5,289	4,942	4,928	4,646
Potassium tartrate 20%... ..	0–100*	9,407	9,245	9,166	9,285	9,479
Sodium tartrate 20%	0–100*	9,067	8,977	8,863	8,798	9,166
Ammonium tartrate 10%	25	13,376	12,860	11,948	12,081	12,608
Rochelle salt 20%	0–100*	8,179	7,944	7,542	7,508	7,673

The figures for tartaric acid, which are given for comparison, show the sensitiveness of the free acid to changes of temperature, as well as its complete liberation from the requirements of BIOT'S law. Thus the specific rotatory power of potassium tartrate for sodium light decreases by 3 per cent. only, from 27·223° to 26·415°, on raising the temperature from 0° to 100° C.; that of the sodium salt increases by 2 per cent., from 25·702° to 26·256° between 0° and 75° C., and then diminishes again to 25·211° at 100° C.; whilst in the case of Rochelle salt there is a regular increase of 9 per cent. from 21·820 at 0° to 23·993° at 100°. The rotatory power of the free acid, however, is practically three times as great at 100° as at 0° C.

Our own observations of the rotatory power of the tartrates of the alkalis are set out in Tables VI., VII., VIII. and IX. As in the two long series of readings of tartaric acid, filtered solutions (made up volumetrically) were used to facilitate the reading of the more difficult wave-lengths; their exact concentrations were then determined by comparing the readings for Hg 5461 with those made with unfiltered solutions, prepared gravimetrically from samples of the various salts in which the proportion of moisture had been checked by analysis. In the case of the ammonium salt, which decomposes on drying even at moderate temperatures, standard solutions for the determination of concentrations were made by adding the calculated amounts of a titrated solution of ammonia to weighed amounts of tartaric acid in a stoppered flask and diluting the solution to a known weight. Densities of all the solutions were also determined. The data used in these calculations are shown in Table X., where also are given a number

* Average values.

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of molecular rotations for sodium light, by means of which a comparison may be made with rotations interpolated from the earlier data of THOMSEN (' Jour. Prakt. Chem.,' 1886, new series, vol. 34, p. 74) and of PATTERSON (' Trans. Chem. Soc.,' 1904, vol. 85, p. 1120).

Our measurements of the molecular rotations of the tartrates show a close general agreement with the requirements of BIOT'S law, but with small deviations of a different type from those recorded by KRECKE. Thus whilst his values for $[M]\lambda^2$ always passed through a minimum in the central portion of the spectrum, ours either pass through a maximum as in Table VI., or rise progressively as the wave-length diminishes as in Tables VII., VIII. and IX. In the case of sodium tartrate (22.54 gr. of $\text{Na}_2\text{H}_4\text{C}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ in 100 c.c. of solution, Table VI. (a)) the agreement of our numbers with the requirements of BIOT'S law is remarkably close; thus the product $[M]\lambda^2$ has the value 20.29 in the visible red region at wave-lengths 6708 to 6438, and the value 20.31 in the extreme violet at wave-lengths 4072 to 4005, rising in the intermediate region to a shallow maximum 20.68 in the blue at wave-length 4678; if all the 22 readings are considered the average value of $[M]\lambda^2$ is 20.40, the maximum errors are +0.28 and -0.23, and the average error is only ± 0.11 or 0.5 per cent.

In view of the smallness of the deviations from BIOT'S law, it seemed probable that a complete agreement might be obtained between the observed and calculated values by using a "simple" dispersion formula containing a second arbitrary constant. In each case, therefore, the constants of the "simple" formula $[M] = k/(\lambda^2 - \lambda_0^2)$ were calculated in the usual way from the rotations for the two dominant mercury lines Hg_{5461} and Hg_{4358} , as shown in Table XI.

Special attention should be given to the values of the "dispersion-ratio" $\alpha_{4358}/\alpha_{5461}$, shown in the last column of Table XI., which increases and diminishes with the magnitude of the "dispersion-constant" λ_0^2 . The latter constant being the square of a real quantity must always be positive, so that the smallest value for this dispersion-ratio is that given by BIOT'S law, where $\lambda_0^2 = 0$, namely,

$$\frac{\alpha_{4358}}{\alpha_{5461}} = \frac{(5461)^2}{(4358)^2} = 1.570.$$

The ratios shown above come nearer to this minimum than in any case hitherto investigated, and in one of the solutions of sodium tartrate, where λ_0^2 falls to 0.00032, this minimum is almost attained. Some of the lowest values previously recorded are shown in Table XII.

These figures show that the dispersion-ratio rarely falls below 1.630 or the dispersion-constant below 0.018; in other words, the absorption-band which determines the position of the vertical asymptote of the dispersion-curve may be pushed out so far as $\lambda = \sqrt{0.018} = 0.135\mu$ or 1350 Å.U., but it never goes much beyond this, even in the case of the most transparent of the substances quoted in Table XII. When dealing

with the natural rotatory power of optically active liquids, the asymptote rarely goes beyond $\lambda = \sqrt{0.024} = 0.15\mu$ or 1500 Å.U. In view of this strict limitation of transparency, in carbon-compounds generally as well as in water and in silica, it seemed improbable that the metallic tartrates could be transparent to light of excessively short wave-length, especially as the magnetic rotations in ethyl tartrate are controlled by an absorption-band in exactly the same position as in the simple alcohols. The validity of the simple formula, therefore, lay open to suspicion, on account of the extreme smallness of the dispersion-constant, and it appeared much more probable that the dispersion-ratios in the tartrates had been brought down into close proximity with the minimum value 1.570 by the influence of a second (negative) term in DRUDE'S equation, similar to that which brings the dispersion-ratios in tartaric acid down below this minimum and gives rise to the anomalous dispersion of the acid.

[The evidence which first convinced us that the simple dispersion-formula, like BIOT'S law, is merely an approximate expression of the rotatory dispersion in the tartrates, is shown in Tables VI. (a) and (b). In these two tables a "simple" formula is shown which has been calculated to fit the experimental values for the green and violet mercury lines. The average error is only a fraction of 1 per cent.; but without exception, all the errors between the green and violet lines are positive in sign, whilst all those beyond the violet are negative; below the green, the errors are again negative in eight out of ten cases. This regular distribution of the errors, which was confirmed in the case of ammonium tartrate, Table IX., for 14 out of 15 visual readings in one series and for 12 out of 13 in a second series which has not been reproduced, proves clearly that the deviations are not accidental but systematic, calling for some further modification of the formula used to express the observations.

When once it has been recognised that the dispersion curves for the alkali-tartrates cannot be represented by the "simple" formula $\alpha = k/(\lambda^2 - \lambda_0^2)$, no difficulty is experienced in securing a satisfactory agreement between the observed and calculated rotations, by using a DRUDE equation with one positive and one negative term, as is shown in the last columns of Tables VI., VII., VIII. and IX., where the errors in the visual readings are seen to be small and for the most part distributed quite irregularly. On account of the smallness of the deviations from the simple law, it is difficult to determine the exact magnitude of the two additional constants which serve to express them in the equation. The dispersion-constants selected for these calculations were $\lambda_1^2 = 0.038$, $\lambda_2^2 = 0.06$, but since the sum of these two constants 0.098 is almost identical with the sum of the constants $0.030 + 0.074 = 0.104$ used in the case of tartaric acid, there can be little doubt that the latter pair would have given equally satisfactory results.

The negative rotation-constants, k_2 , as set out in Table XIII., are larger than might have been expected, approaching almost to one-half of the values for the positive rotation-constant k_1 . This is due to the fact that the dispersion-constant λ_2^2 of the negative term is but little greater than the dispersion-constant λ_1^2 of the positive term; the

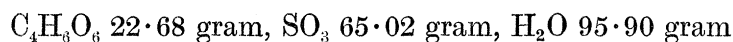
negative term must therefore be weighted somewhat heavily to produce any marked alteration in the form of the curve.

8. NEGATIVE ROTATIONS IN SOLUTIONS OF *d*-TARTARIC ACID AND ITS SALTS.

Although the common form of tartaric acid, and the tartrates derived from it, are usually dextrorotatory, negative rotations are occasionally observed, especially at high concentrations and low temperatures, and in the more refrangible portions of the spectrum. BIOT, who had predicted this phenomenon in 1838 ('Mém. Acad. Sci.,' 1838, vol. 16, p. 269), detected it twelve years later in the cold, glassy acid ('Ann. Chim. Phys.,' 1850, vol. 28, p. 353); the more elaborate work of BRUHAT ('Trans. Faraday Soc.,' 1914, vol. 10, p. 89) on the rotatory power of the anhydrous acid has shown that, whilst the rotations are positive in the red and yellow regions of the spectrum, they become negative for wave-lengths less than 5600 at 15° C. None of the aqueous or alcoholic solutions examined by BIOT gave negative rotations, but LEPESCHKIN ('Ber. Deutsch. Chem. Gesell.,' vol. 32, p. 1180–1184) detected a negative rotation $[\alpha]_{4482}^{20} = -1.22^\circ$ in the dark blue region of the spectrum when working with a supersaturated aqueous solution containing 66.5 per cent. by weight of tartaric acid. Our own observations include negative readings in the violet region for unsaturated solutions containing 50 grams of tartaric acid in 100 c.c. of solution; and NUTTING ('Physical Review,' vol. 17, p. 11) has observed very large negative rotations, up to $[\alpha]_{2750}^{19} = -296.8^\circ$, in the ultra-violet, in a solution containing 28.62 grams per cent. of tartaric acid. GROSSMANN ('Trans. Faraday Soc.,' 1914, vol. 10, p. 63) observed only positive rotations in methyl alcohol, but negative values have been recorded by ARNDTSEN ('Ann. Chim. Phys.,' 1858, vol. 54, p. 415) for more concentrated solutions. GROSSMANN showed, however, that solutions in ethyl alcohol, even at a concentration as low as 5 per cent., give negative rotations in the blue region beyond 4700, whilst similar solutions in propyl alcohol are levorotatory beyond 5200. Negative rotations for sodium light have been observed in solutions of tartaric acid in acetone mixed with ether or with chloroform (LANDOLT, 'Ber.,' 1880, vol. 13, p. 2333), in water mixed with butyl alcohol (PRIBRAM, 'Monatshefte,' 1888, vol. 9, p. 485) and in alcohol mixed with benzene, toluene, chlorobenzene or ethyl bromide (PRIBRAM, 'Ber.,' 1889, vol. 22, pp. 6–11).

This depression of rotatory power and ultimate reversal of sign may be regarded as a result of getting the tartaric acid into solution in much the same condition as that in which it exists in the anhydrous amorphous state, without developing the great increase of dextrorotatory power which results from hydration, or the lesser increase which results from interaction with the lowest members of the series of alcohols. A similar depression of dextrorotatory power is produced by formic acid, acetic acid, and especially propionic acid (GROSSMANN, *loc. cit.*, p. 65) as well as by mineral acids. In the special case of sulphuric acid, BIOT found that the addition of 20 per cent. of the strong acid to an aqueous solution of tartaric acid lowered its specific rotatory power by about one-third

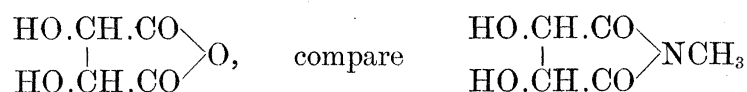
from $\alpha_{\text{RED}} = 15.4$ to 10.90 ('Mém. Acad. Sci.,' 1838, vol. 16, p. 280); but a concentrated solution containing



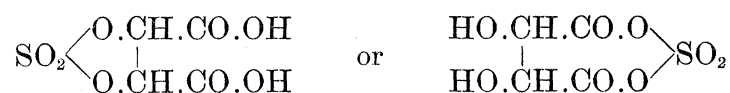
gave a much lower rotation and a novel type of dispersion in which the maximum disappeared into the infra-red, whilst a reversal of sign occurred in the blue region, giving rise to lævorotations in the violet thus :

$$\text{red } +2.200^\circ, \text{ yellow } +0.850^\circ, \text{ green } +0.550^\circ, \text{ violet } -4.950^\circ$$

(*ibid.*, p. 301). GROSSMANN has recently examined solutions of tartaric acid in sulphuric acid of higher concentrations (including the anhydrous acid containing 100 per cent. H_2SO_4), and has shown that lævorotations are found for violet light of wave-length 4620 from 45 to 75 per cent. of sulphuric acid only; when sulphuric acid containing less than 35 per cent. of water is used as a solvent, the tartaric acid increases again in rotatory power, and finally gives a specific rotation from $3\frac{1}{2}$ to 7 times as great as in aqueous solutions ('Trans. Faraday Soc.,' 1914, vol. 10, p. 67). This case is of special interest on account of the clear evidence which it affords of the formation of some new chemical compound of high dextrorotatory power, perhaps an anhydride :



for which $[\alpha]_{\text{D}} = +124^\circ$, $[\text{M}]_{\text{D}} = +281^\circ$, or a sulphate :

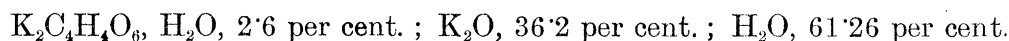


Of special interest is the fact, which is disclosed by plotting $1/\alpha$ against λ^2 , that, whatever the nature of this compound may be, it is sufficiently "fixed" to give rise to a rotatory dispersion which, in the case of five readings out of six, appears to obey the "simple" law $\alpha = k/(\lambda^2 - \lambda_0^2)$. In view of the importance of these observations we made several attempts to repeat them, in order to test the validity of the "simple" dispersion law by means of fresh data extending over a wider range and including a larger number of wave-lengths; but, up to the present, we have not succeeded in preparing solutions sufficiently clear to use for such a test.

In quite a different category must be placed BIOT'S observation that aluminium tartrate, which is strongly dextrorotatory in dilute solutions, becomes lævorotatory when the solution is concentrated ('Comptes Rendus,' 1835, vol. 1, p. 459; 'Mém. Acad. Sci.,' 1838, vol. 16, Tables 12, 13, 14, at end of volume). It is possible that trivalent aluminium behaves in some respects like boron or antimony, and that concentration is accompanied by a change of structure analogous with that which is produced

by the addition of an excess of potash to tartar emetic (see below, p. 285). A detailed investigation of the aluminium tartrates from this point of view would be of great interest, but was not undertaken in the course of the present research.*

Confirmation has, however, been obtained of BIOT'S observation that the alkali-tartrates become lævorotatory when dissolved in an excess of strong alkali; thus whilst the rotatory power of potassium hydrogen tartrate in dilute solutions is about twice as great as that of the free acid, and the rotatory power of the neutral potassium salt is about three times as great, the further addition of potash (perhaps producing some displacement of hydrogen by potassium in the two hydroxyl-groups) causes the rotatory power to diminish and finally to become reversed in sign. BIOT found ('Mém. Acad. Sci.,' 1838, vol. 16, p. 345, and Table 6, facing p. 338) that a solution containing



was lævorotatory and gave the remarkable dispersion shown by the following readings,

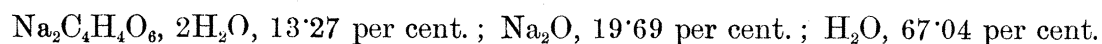
$$\text{red } -0\cdot433^\circ, \text{ yellow } -0\cdot617^\circ, \text{ green } -0\cdot2^\circ,$$

where the shallow maximum is of opposite sign to that observed in tartaric acid. Our own observations on a similar, but more concentrated, solution containing



in about 60 c.c. (density 1·504) gave a series of very small negative readings from which the molecular rotations shown in Table XIV. (a) may be deduced. The dispersion is obviously not simple, and the high value of the dispersion ratio $\alpha_{4358}/\alpha_{5461} = 3\cdot3$ suggests that the rotation would become positive in the infra-red. BIOT'S reversed maximum is not confirmed by our observations.

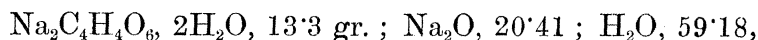
Sodium tartrate is more readily soluble both in water and in strong alkali. BIOT (*ibid.*, p. 364, and Table 8 at end of volume) found that a solution containing



gave the following rotations :—

$$\text{red } -2\cdot675^\circ, \text{ yellow } -4^\circ, \text{ green } -4\cdot700^\circ.$$

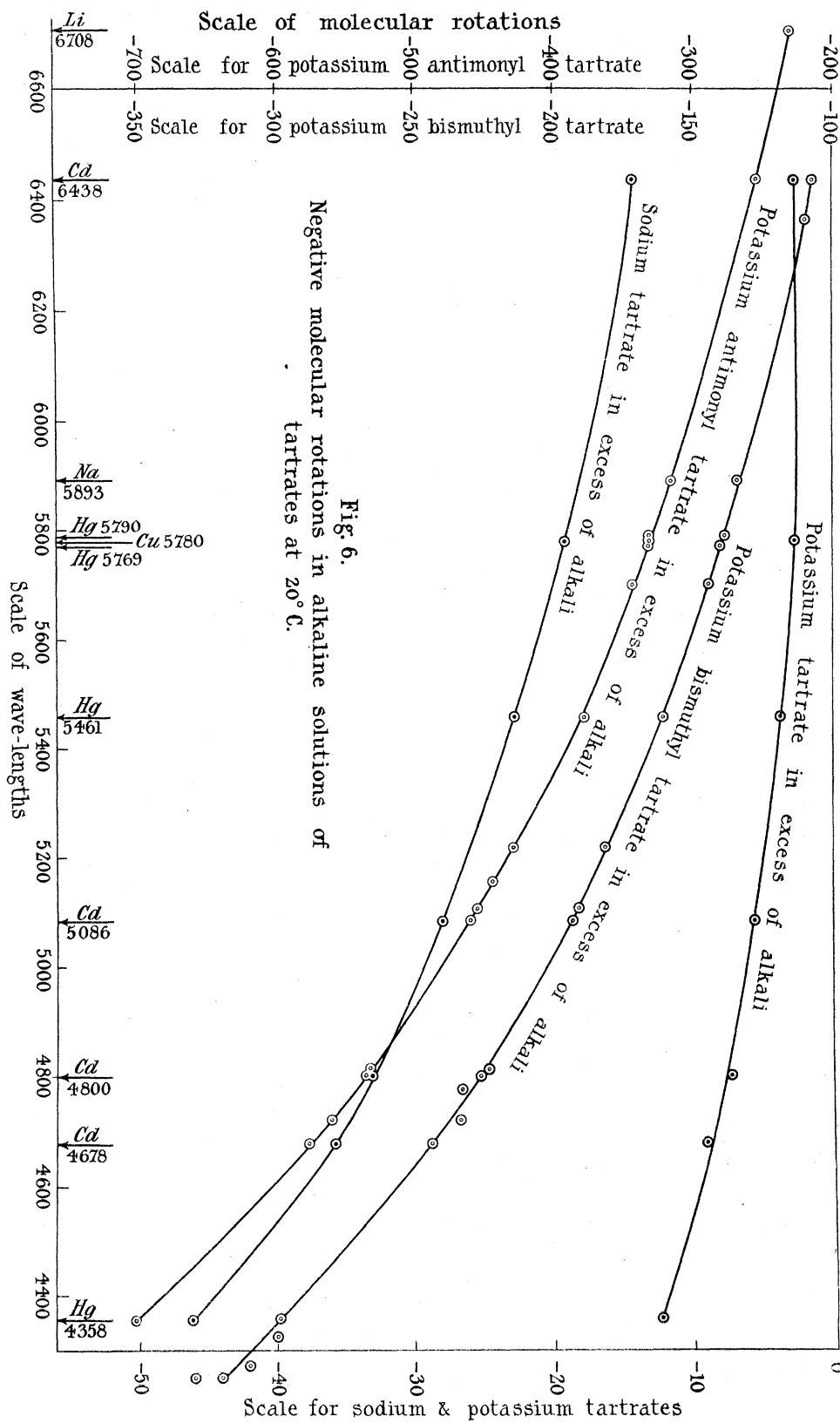
Our own observations on a stronger solution containing



in about 66 c.c. (density 1·4093) gave the very substantial negative readings shown in Table XIV (b). These readings are large enough to give smooth values (fig. 6) for the molecular rotatory power of the dissolved salt. They confirm the increase of lævorotatory power with diminishing wave-length already recorded by BIOT, but they do not

* This investigation is now being carried out by Miss GRAHAM (26.1.22).

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conform to BIOT'S law since $[M]\lambda^2$ increases from -3.9 at Cd 6438 to -5.7 at Hg 4358; and they cannot be expressed by the simple DRUDE formula $\alpha(\lambda^2 - \lambda_0^2) = \text{const.}$, since the line obtained by plotting $1/\alpha$ against λ^2 has a perfectly definite though very slight curvature.

The effects produced by the addition of a few molecular proportions only of alkali to aqueous solutions of potassium and sodium tartrates are shown in Table XV. (a) and (b). The molecular rotations are a little lower than in Tables VI. and VII., but the solutions are still dextrorotatory, and the dispersions, though certainly complex, can be expressed very closely by a "simple" formula, which, in the case of the sodium salt, is identical with BIOT'S law; the readings are, however, too small to reveal the complexity first disclosed in Table VI. (a).

9. TARTAR EMETIC.

Tartar emetic, $K(\text{SbO}) \text{C}_4\text{H}_4\text{O}_6, \frac{1}{2}\text{H}_2\text{O}$, although one of the most interesting of the tartrates, does not appear to have been examined by BIOT. The rotatory dispersion in tartar emetic was measured, apparently for the first time, in 1872 by KRECKE ('Arch. Néerland., 1872, vol. 7, p. 114), who observed a very close agreement with the requirements of BIOT'S law. Thus he gives for $[\alpha]\lambda^2$ the following numbers:—

	C	D	E	b	F
At 0°	52,405	51,253	50,966	51,308	53,142
At 100°	48,436	45,193	45,796	45,851	49,307

He calls attention to the fact that "the specific rotatory power of tartar emetic is extraordinarily great, and diminishes with rise of temperature," and includes this salt in his general statement that "the tartrates examined follow the law of BIOT."* Even more interesting than the high rotatory power of the salt is the fact discovered by GROSSMANN ('Zeitschr. Physikal. Chem.,' 1907, vol. 57, pp. 533-556) that when sodium hydroxide is added, the specific rotation of the salt assumes a large negative value, probably because "in the alkaline solution an antimony alkali tartrate is present, in which the hydrogen atoms of the alcoholic hydroxyl groups are also displaced."

Our own experiments give no support to KRECKE'S view that tartar emetic obeys BIOT'S law. Thus the first preliminary series of observations gave for the product $[M]\lambda^2$ values which increased progressively from 156.17 at wave-length 6708 to 203.85 at wave-length 3917. But a "simple" dispersion formula $[M] = 140.67/(\lambda^2 - 0.0477)$, based upon the readings for the two dominant mercury lines, showed an agreement that was very satisfactory, especially in view of the fact that the observed rotations had been multiplied by nearly 12 to convert them into molecular rotations. Moreover, the

* For further observations on tartar emetic, see LONG, 'Amer. Journ. Sci.,' 1889, series (3), vol. 38, p. 264; 1890, vol. 40, p. 275.

magnitude of the dispersion-constant 0.0477 did not present the same grounds for suspicion as in the case of the tartrates of the alkali metals. In view, however, of our experience with these tartrates, we considered it necessary to make a series of measurements at least as complete and as extensive as that which had disclosed the real complexity of the rotatory dispersion in sodium tartrate. The solution used for these measurements was made up to be approximately M/60 or 5.53 grams of tartar emetic per 100 c.c.; a comparison with the rotations of unfiltered solutions made up gravimetrically, Table X., gave the concentration as 5.32 grams per 100 grams of solution of density 1.0368, or 5.516 grams per 100 c.c., and this figure was adopted in calculating the molecular rotations. The rotations of this solution are set out in Table XVI., which gives the results of visual readings for 18 lines and photographic readings for five lines, as compared with 16+6 readings in the case of sodium tartrate. Although the observed rotations are multiplied by 10 in order to convert them into molecular rotations, their agreement with the calculated values is very satisfactory; even in the photographic region the largest error is only 1 per cent., and all the errors appear to be distributed quite casually, without any of the long series of positive or negative errors observed in the case of the alkali-tartrates. We therefore conclude that the rotatory dispersion in tartar emetic is definitely "simple" in character, and that in this compound we have for the first time succeeded in eliminating completely that complexity which is so strongly developed in the acid and its esters.

Similar remarks may be applied to the alkaline solutions of tartar emetic. The preliminary series of observations for seven lines in the visible spectrum showed that $[M]\lambda^2$ increased from -105.8 at wave-length 6438 to -133.3 at wave-length 4358, but that the dispersion could be represented satisfactorily by a simple formula. The simplicity of the rotatory-dispersion was, however, confirmed by a series of 17 visual readings as shown in Table XVII. Photographic readings are not included, as the solutions are not stable and show a marked diminution of rotatory power on keeping; the visual readings could be taken before any serious alteration had occurred, but the photographic readings would have occupied too much time for this to be done successfully.

10. COMPOUNDS OF ARSENIC AND BISMUTH.

The arsenyl compounds $H(AsO)C_4H_4O_6$, $K(AsO)C_4H_4O_6$, $Na(AsO)C_4H_4O_6$, corresponding with tartar emetic were examined by LANDOLT ('Ber. Deutsch. Chem. Gesell., 1873, vol. 6, p. 1077, and "Optical Rotatory Power," tr. 1902, p. 553). No measurements of dispersion were made, but the data showed that the arsenyl compounds have much the same rotatory power as the simple alkali-salts and do not exhibit any of the special qualities of tartar emetic. GROSSMANN (*loc. cit.*) states that the addition of sodium hydroxide to sodium arsenyl tartrate appeared to cause complete decomposition of the salt into neutral disodium tartrate and optically-inactive sodium arsenite. Our own observations on the rotatory dispersion in an alkaline solution of the arseno-tartrate,

Table XVIII. (*a*), are in agreement with GROSSMANN'S view. The rotations are positive and of the same order of magnitude as in the case of an alkaline solution of the potassium salt. The dispersion shows the same rough conformity with BIOT'S law, and the same close approximation to the requirements of a simple formula with an abnormally small dispersion-constant, as in Table XV. (*a*), but the observed rotations are too small in magnitude and too few in number to provide conclusive evidence of the complexity of the dispersion. In the absence of an alkali, the formation of an arseno-tartaric acid is indicated by the increase of rotatory power, Table XVIII. (*b*), which is produced by saturating a solution of tartaric acid with arsenious oxide and filtering off the excess of arsenic. The dispersion-curve is not "simple," like that of tartar emetic, since the dispersion-ratio $\alpha_{4358}/\alpha_{5461} = 1.476$ is less than the minimum value 1.570 for $\lambda_0^2 = 0$; it is probable, therefore, that the arseno-tartaric acid is already partially dissociated, and that the addition of an excess of alkali merely completes the hydrolysis already initiated by the water in the solution.

The dispersion of the corresponding compounds of bismuth do not appear to have been investigated hitherto*, but we have been able to prepare an alkaline solution of a bismuthyl compound which shows all the characteristics of alkaline solutions of tartar emetic. Its rotatory power is strongly negative, though less than in the case of tartar emetic, and its rotatory dispersion, as set out for 21 wave-lengths in Table XIX., agrees very well with a simple dispersion formula $[M] = -37.414/(\lambda^2 - 0.0645)$. The dispersion-constant in this formula agrees closely with the value 0.06275 given by an alkaline solution of tartar emetic; it is therefore clear that in alkaline solutions bismuth yields a levorotatory compound with tartaric acid of exactly the same type as the compound formed from tartar emetic, and that both compounds differ from the acid and from its simple salts in giving simple rotatory dispersion. The simple dispersion in these more complex tartrates is indeed the most striking discovery that we have made in the course of the present investigation.

11. BORO-TARTARIC ACID.

Boric acid was mentioned in BIOT'S sealed communication of August 25, 1834, as a substance which (like the alkalis) combined with tartaric acid, giving dextrorotatory solutions which obeyed the general laws of rotatory dispersion as they had been established in the case of quartz and of several optically-active liquids ('Comptes Rendus,' 1835, vol. 1, p. 458; compare 'Mém. Acad. Sci.,' 1838, vol. 16, p. 271). The action of boric acid was described in detail ten years later ('Ann. Chim. Phys.,' 1844, vol. 11, pp. 82-112; see also 1860, vol. 59, pp. 229-256) in a long memoir "On the Employment of Polarised Light to Study Various Questions of Chemical Mechanics." The acid produced a marked increase in the dextrorotatory power of tartaric acid; and this could be represented by a hyperbolic formula tending to a constant value when the

* For rotations of sodium light in potassium bismuthyl tartrates, see ROSENHEIM, VOGELSANG, and GROSSMANN, 'Zeitschr. für anorg. Chem.,' 1906, vol. 48, p. 209.

boric acid was in large excess, or less exactly by a linear formula representing a tangent to the hyperbola. This linear formula was found to apply also to the enhancement of rotatory power in a glassy mixture of amorphous tartaric and boric acids; four such mixtures gave rotations (for the neutral tint) ranging from $+31^\circ$ to $+13^\circ$, and these when extrapolated gave for pure glassy tartaric acid a negative rotation -2.9° , agreeing closely with the value -3.28° observed experimentally ('Ann. Chim. Phys.,' 1850, vol. 28, p. 374).

Preliminary experiments on an equimolecular mixture of tartaric and boric acids (15 grams of tartaric acid and 6.2 grams of boric acid in 100 c.c. of solution) showed that the dispersion did not fulfil the requirements of BIOT'S law, but could be expressed by a simple formula with a normal dispersion constant $[M] = 24.835/(\lambda^2 - 0.0271)$. A more exact series, Table XX.(a), including readings for 18 lines in the visual and five lines in the photographic region of the spectrum, showed, however, that the simple formula was again only an approximation; but the negative term in the complex formula is very small (only about $\frac{1}{20}$ of the positive term), and would probably disappear altogether if a sufficient quantity of boric acid were used to convert the tartaric acid wholly into boro-tartaric acid. Table XX.(b), which shows the effect of $1\frac{1}{2}$ mols. of boric acid on tartaric acid of half the strength used for Table XX.(a) affords further justification for this view; the dispersion is here so nearly simple that the only hint of complexity is that given by a few negative errors in the red and in the extreme violet region of the spectrum.

The study of boro-tartaric acid, like that of tartar emetic, illustrates in a very striking manner the way in which the complex rotatory dispersion of tartaric acid is simplified when it is converted into "fixed" derivatives, even when these are more complex in their chemical structure. The actual structure of these derivatives has been the subject of much speculation, and must be regarded as still very uncertain; but we hope to be able to carry out a chemical study of this problem, which will form a suitable sequel to the physical investigations which are described in the present paper.

12. SUMMARY.

1. The rotatory power of tartaric acid for a series of 9 wave-lengths has been determined in aqueous solutions of 11 different concentrations ranging from 5 to 55 per cent. by weight, and also for 21 and 26 wave-lengths respectively at 2 other concentrations.

2. The optical rotatory power of tartaric acid, like that of its methyl and ethyl esters, is expressed to a close degree of approximation by the formula

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} - \frac{k_2}{\lambda^2 - \lambda_2^2}.$$

3. The rotatory power of sodium tartrate agrees very closely with BIOT'S law, $\alpha = k/\lambda^2$, but requires for its exact expression a two-term formula similar to that

used for tartaric acid. Potassium and ammonium tartrates and Rochelle salt give similar dispersion curves, but deviate more widely from BIOT'S law.

4. A number of solutions which give negative rotations have been examined for a range of wave-lengths, and the corresponding dispersion-curves have been plotted.

5. In presence of an excess of boric acid the rotatory dispersion of tartaric acid is no longer complex but simple, and can be expressed over a wide range of wave-lengths by the equation

$$\alpha = \frac{k}{\lambda_2 - \lambda_0^2}.$$

Tartar emetic also gives a simple dispersion curve.

6. When tartar emetic is dissolved in an excess of potassium hydroxide, or when a corresponding solution is prepared with bismuth in place of antimony, strongly lævo-rotatory solutions are obtained, but these are again characterised by a simple rotatory dispersion.

7. It is suggested that *d*-tartaric acid, like nitro-camphor, exists in solution in two labile isomeric forms, and that the anomalous dispersion of the acid and of many of its derivatives is due to the presence of two isomeric compounds of opposite rotatory power and unequal dispersion. Derivatives which give simple rotatory dispersion are assumed (like the salts of nitro-camphor) to be fixed in one of these forms.

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- XX. Rotatory Dispersion of Boro-tartaric Acid in Aqueous Solutions at 20° C.

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Density*	1·2987.						1·2658.					
Concentration in (a) grams per 100 grams.	55·0.						50·0.					
(b) grams per 100 c.c.	71·43.						63·29.					
λ .	i.	ii.	iii.	Mean.	[α].	[M].	i.	ii.	iii.	iv.	v.	Mean.
Cd 6438	25·73	25·73	25·73	25·73	6·004	9·005	25·60	25·61	25·56	25·54	25·55	25·57
Na 5893	27·88	—	27·84	27·86	6·501	9·751	27·90	28·00	27·99	27·98	28·00	27·97
Hg 5790	28·16	28·10	28·16	28·14	6·566	9·849	28·37	28·40	28·36	28·32	28·30	28·35
Hg 5769	28·20	28·15	28·21	28·19	6·577	9·866	28·45	28·46	28·44	28·42	28·40	28·43
Hg 5461	28·35	28·31	28·37	28·34	6·613	9·919	29·09	29·08	29·05	29·08	29·02	29·06
Cd 5086	26·71	26·71	26·75	26·72	6·235	9·352	28·41	28·41	28·41	28·40	28·39	28·40
Cd 4800	22·93	22·92	22·91	22·92	5·348	8·022	25·70	25·73	25·73	25·80	25·78	25·75
Cd 4678	20·31	20·31	20·31	20·31	4·739	7·108	23·65	23·69	23·70	23·72	23·76	23·70
Hg 4358	7·92	—	—	7·92	1·848	2·772	13·75	13·80	13·82	13·95	13·80	13·82

To face p. 288.]

			1·2352.						1·2052.					
			45·0.						40·0.					
			55·58.						48·21.					
n.	[α].	[M].	i.	ii.	iii.	Mean.	[α].	[M].	i.	ii.	iii.	iv.	Mean.	
57	6·734	10·100	24·79	24·76	24·71	24·75	7·421	11·132	23·34	23·31	23·37	23·37	23·35	8
37	7·366	11·049	27·45	27·39	27·39	27·41	8·219	12·328	26·05	26·03	26·07	26·08	26·06	9
35	7·466	11·198	—	27·78	27·79	27·78	8·331	12·497	26·47	26·46	26·53	26·54	26·50	9
43	7·487	11·230	—	27·83	27·84	27·83	8·346	12·519	26·56	26·52	26·58	26·60	26·56	9
36	7·653	11·479	28·85	28·80	28·85	28·83	8·645	12·967	27·77	27·72	27·74	27·77	27·75	9
40	7·479	11·218	28·98	28·88	28·87	28·91	8·668	13·003	28·28	28·25	28·33	28·34	28·30	9
75	6·781	10·171	27·18	27·17	27·19	27·18	8·150	12·225	27·24	27·23	27·33	27·30	27·27	9
70	6·241	9·362	25·75	25·63	25·73	25·70	7·707	11·560	26·12	26·15	26·29	26·22	26·19	9
32	3·631	5·446	18·15	17·97	18·11	18·08	5·421	8·132	20·32	20·29	20·36	20·32	20·32	7

TABLE I.—Specific and Molecular Rotatory Power of Tartaric Acid in

Length of Tube = 6 dm.

		1·1760.					1·1476.						
		35·0.					30·0.						
		41·16.					34·43.						
[α].	[M].	i.	ii.	iii.	iv.	Mean.	[α].	[M].	i.	ii.	iii.	Mean.	[α].
8·073	12·109	21·63	21·53	21·52	21·54	21·55	8·728	13·092	19·23	19·28	19·22	19·24	9·3
9·010	13·514	24·26	24·21	24·22	24·10	24·20	9·799	14·699	21·65	—	21·63	21·64	10·5
9·162	13·742	24·71	24·63	24·62	24·58	24·63	9·975	14·963	22·15	22·19	22·14	22·16	10·7
9·184	13·776	24·81	24·73	24·75	24·64	24·73	10·014	15·021	22·19	22·29	22·20	22·23	10·7
9·594	14·391	26·03	25·99	26·01	26·02	26·01	10·532	15·798	23·51	23·56	23·52	23·53	11·4
9·784	14·676	26·93	26·84	26·83	26·83	26·86	10·876	16·314	24·54	24·61	24·58	24·58	11·9
9·430	14·144	26·56	26·43	26·46	26·39	26·46	10·714	16·071	24·40	24·47	24·46	24·44	11·8
9·056	13·584	25·81	25·70	25·79	25·70	25·75	10·427	15·640	24·03	24·03	24·04	24·03	11·6
7·025	10·538	21·31	21·31	21·36	21·35	21·33	8·637	12·956	20·87	20·91	20·86	20·88	10·1

* The densities shown in this table were read off from a sensitive curve plotted from our own readings and the

n Aqueous Solutions at 20° C.

		1·1201.						1·0942.					
		25·0.						20·0.					
		28·00.						21·88.					
[α].	[M].	i.	ii.	iii.	Mean.	[α].	[M].	i.	ii.	iii.	iv.	Mean.	[α].
·336	14·003	16·66	16·59	16·59	16·61	9·886	14·829	13·76	13·73	13·73	13·71	13·73	10·45
·500	15·750	18·83	—	18·83	18·83	11·207	16·811	15·68	15·69	15·71	15·67	15·69	11·94
·752	16·129	19·29	19·33	19·24	19·29	11·481	17·222	16·06	16·01	16·02	15·97	16·01	12·19
·786	16·180	19·39	19·43	19·33	19·38	11·535	17·302	16·12	16·09	16·07	16·03	16·08	12·24
·417	17·126	20·58	20·56	20·53	20·56	12·237	18·355	17·13	17·16	17·19	17·13	17·15	13·06
·927	17·890	21·71	21·70	21·64	21·68	12·904	19·355	18·23	18·27	18·29	18·21	18·25	13·89
·859	17·788	21·95	21·89	21·85	21·89	13·032	19·547	18·53	18·61	18·68	18·56	18·59	14·16
·660	17·490	21·81	21·83	21·72	21·79	12·969	19·453	18·34	18·49	18·51	18·45	18·45	14·05
·131	15·197	19·41	19·47	19·45	19·44	11·570	17·356	17·02	17·10	17·15	17·13	17·10	13·02

ose of PRIBRAM (' Sitzungsber. Wien. Akad.,' II., vol. 107, p. 148.)

		1·0692.							1·0448.				
		15·0.							10·0.				
		16·04.							10·45.				
[.].	[M].	i.	ii.	iii.	iv.	Mean.	[α].	[M].	i.	ii.	iii.	iv.	Mean.
457	15·685	10·62	10·64	10·62	10·64	10·63	11·047	16·570	7·27	7·35	7·30	7·29	7·30
949	17·924	12·16	12·18	12·16	12·16	12·165	12·642	18·963	8·37	8·29	8·37	8·32	8·34
197	18·295	12·52	12·44	12·42	12·47	12·46	12·948	19·423	8·52	8·55	8·66	8·58	8·58
246	18·370	12·52	12·48	12·47	12·50	12·49	12·980	19·469	8·52	8·55	8·66	8·58	8·58
361	19·592	13·42	13·45	13·36	13·38	13·40	13·925	20·888	9·22	9·20	9·31	9·23	9·24
399	20·849	14·27	14·34	14·28	14·29	14·295	14·855	22·283	9·90	9·94	10·01	9·91	9·94
162	21·243	14·77	14·68	14·70	14·74	14·72	15·297	22·945 ₅	10·20	10·35	10·39	10·29	10·31
051	21·077	14·82	14·75	14·76	14·79	14·78	15·359	23·039	10·34	10·38	10·40	10·39	10·38
023	19·535	13·90	13·88	13·97	14·00	13·94	14·486	21·730	9·98	9·99	10·02	10·02	10·00

1·0211.								
5·0.								
5·10.								
Mean.	[α].	[M].	i.	ii.	iii.	Mean.	[α].	[M]
7·30	11·645	17·467 ₅	3·75	3·74	3·73	3·74	12·209	18·314
8·34	13·304	19·956	4·30	4·32	4·30	4·31	14·070	21·105
8·58	13·687	20·530	4·47	4·45	4·45	4·45	14·527	21·790
8·58	13·687	20·530	4·47	4·45	4·45	4·45	14·527	21·790
9·24	14·740	22·109	4·80	4·81	4·80	4·80	15·669	23·504
9·94	15·856	23·784	5·14	5·31	5·22	5·22	17·040	25·561
10·31	16·446	24·670	5·38	5·59	5·49	5·49	17·922	26·883
10·38	16·558	24·837	5·45	5·67	5·55	5·56	18·150	27·226
10·00	15·952	23·928	5·42	5·46	5·46	5·45	17·791	26·687

TABLE II.—Specific Rotatory Power of Tartaric Acid, Observed and Calculated.

e = proportion by weight of water.

$[\alpha]$ = observed specific rotation.

$[\alpha_0]$ = $A_0 + B_0 e$ (linear law, correct at $e = 0$, for Hg 4358 only).

$[\alpha_1]$ = $A_1 + B_1 e$ (linear law, correct at $e = 0.55$ and 0.85).

$[\alpha_2]$ = $A_2 + B_2 e + C_2 e^2$ (parabolic law, correct at $e = 0.55, 0.70$ and 0.85).

λ .	$e = 0$.	0.45	0.50	0.55	0.60	0.65	0.70	0.75	0.80	0.85	0.90	0.95	Constants of Equations.
Cd red 6438	$[\alpha]$	+2.000	6.734	7.421	8.073	8.728	9.336	9.886	10.457	11.047	11.645	12.209	$A_1 = +0.7753$
	$[\alpha_1]$	+0.773	6.817	7.421	8.025	8.630	9.234	9.838	10.443	11.047	11.651	12.256	$B_1 = +12.0867$
	$[\alpha_2]$	-1.346	6.737	7.421	8.082	8.720	9.336	9.929	10.499	11.047	11.572	12.074	$A_2 = -1.3460$
	$[\alpha] - [\alpha_1]$	+1.227	-0.208	-0.083	+0.048	+0.098	+0.102	+0.048	+0.014	-0.006	-0.006	-0.047	$B_2 = +18.4333$
	$[\alpha] - [\alpha_2]$	+3.346	-0.027	-0.003	-0.009	+0.008	+0.008	±	-0.043	-0.042	+0.073	+0.135	$C_2 = -4.5353$
Na yellow 5893	$[\alpha]$	+1.600	+6.501	7.366	8.219	9.010	9.799	10.500	11.207	11.949	12.642	13.304	$A_1 = +0.1100$
	$[\alpha_1]$	+0.110	+6.745	7.482	8.219	8.956	9.693	10.431	11.168	11.905	12.642	13.379	$B_1 = +14.7433$
	$[\alpha_2]$	-1.329	+6.623	7.429	8.219	8.996	9.755	10.500	11.229	11.943	12.642	13.324	$A_2 = -1.3292$
	$[\alpha] - [\alpha_1]$	+1.490	-0.244	-0.116	+0.054	+0.106	+0.106	+0.069	+0.039	+0.044	±	-0.075	$B_2 = +19.0610$
	$[\alpha] - [\alpha_2]$	+2.929	-0.122	-0.063	+0.014	+0.044	+0.044	±	-0.022	+0.006	±	-0.020	$C_2 = -3.0888$
Hg yellow 5790	$[\alpha]$	—	+6.566	7.466	8.331	9.162	9.975	10.752	11.481	12.197	12.948	13.687	$A_2 = -2.4710$
	$[\alpha_2]$	—	+6.592	7.474	8.331	9.163	9.970	10.752	11.509	12.241	12.948	13.630	$B_2 = +22.3900$
	$[\alpha] - [\alpha_2]$	—	-0.026	-0.008	-0.001	+0.005	+0.005	±	-0.028	-0.044	±	+0.057	$C_2 = -5.0000$
Hg yellow 5769	$[\alpha]$	—	+6.577	7.487	8.346	9.184	10.014	10.786	11.535	12.246	12.980	13.687	$A_2 = -2.7054$
	$[\alpha_2]$	—	+6.583	7.480	8.346	9.187	10.000	10.786	11.545	12.276	12.980	13.657	$B_2 = +23.1000$
	$[\alpha] - [\alpha_2]$	—	-0.006	+0.007	-0.003	+0.014	+0.014	±	-0.010	-0.030	±	+0.030	$C_2 = -5.4666$
Hg yellow (mean) 5780	$[\alpha]$	+1.500	+6.571	7.476	8.338	9.173	9.994	10.769	11.508	12.221	12.964	13.687	$A_1 = -0.1416$
	$[\alpha_1]$	-0.142	+6.796	7.567	8.338	9.109	9.880	10.651	11.422	12.193	12.964	13.735	$B_1 = +15.4183$
	$[\alpha_2]$	-2.588	+6.587	7.474	8.338	9.175	9.985	10.769	11.527	12.258	12.964	13.644	$A_2 = -2.5882$
	$[\alpha] - [\alpha_1]$	+1.642	-0.225	-0.091	+0.064	+0.114	+0.114	+0.118	+0.086	+0.028	±	-0.048	$B_2 = +22.7450$
	$[\alpha] - [\alpha_2]$	+4.088	-0.016	+0.002	-0.002	+0.009	+0.009	±	-0.019	-0.037	±	+0.043	$C_2 = -5.2333$

TABLE II. (continued).

λ .	$e = 0$.	0.45.	0.50.	0.55.	0.60.	0.65.	0.70.	0.75.	0.80.	0.85.	0.90.	0.95.	Constants of Equations.
Hg green 5461	$[a]$	+0.700	7.653	8.645	9.594	10.532	11.417	12.237	13.061	13.925	14.740	15.669	$A_1 = -1.0350$
	$[a_1]$	-1.035	7.765	8.645	9.525	10.405	11.285	12.165	13.045	13.925	14.805	15.685	$B_1 = +17.6000$
Cd green 5086	$[a_2]$	+3.778	7.662	8.645	9.598	10.522	11.417	12.282	13.118	13.925	14.702	15.450	$A_2 = -3.7780$
	$[a] - [a_1]$	+1.735	-0.112	\pm	+0.069	+0.127	+0.132	+0.072	+0.016	\pm	-0.065	-0.016	$B_2 = +25.8134$
	$[a] - [a_2]$	+4.478	-0.009	\pm	-0.004	+0.010	\pm	-0.045	-0.057	+0.038	+0.038	+0.219	$C_2 = -5.8666$
	$[a]$	-1.000	7.479	8.668	9.784	10.876	11.927	12.904	13.899	14.855	15.856	16.846	$A_1 = -2.6736$
Cd blue 4800	$[a_1]$	-2.674	7.637	8.668	9.700	10.731	11.762	12.793	13.824	14.855	15.886	16.917	$B_1 = +20.6220$
	$[a_2]$	-6.107	7.509	8.668	9.791	10.878	11.927	12.940	13.916	14.855	15.758	16.623	$A_2 = -6.1069$
	$[a] - [a_1]$	+1.674	-0.371	\pm	+0.084	+0.145	+0.165	+0.111	+0.075	+0.030	-0.030	+0.123	$B_2 = +30.9038$
	$[a] - [a_2]$	+5.107	-0.030	\pm	-0.007	-0.002	\pm	-0.036	-0.017	+0.098	+0.098	+0.417	$C_2 = -7.3444$
Cd blue 4678	$[a]$	-3.300	6.781	8.150	9.430	10.714	11.859	13.032	14.162	15.297	16.446	17.922	$A_1 = -4.9528$
	$[a_1]$	-4.953	6.959	8.150	9.341	10.532	11.723	12.915	14.106	15.297	16.488	17.679	$B_1 = +23.8233$
	$[a_2]$	-7.768	6.853	8.150	9.416	10.653	11.859	13.035	14.181	15.297	16.383	17.438	$A_2 = -7.7682$
	$[a] - [a_1]$	+1.653	-0.178	\pm	+0.089	+0.182	+0.136	+0.117	+0.056	+0.056	-0.042	+0.243	$B_2 = +32.2544$
Cd blue 4678	$[a] - [a_2]$	+4.468	-0.072	\pm	+0.014	+0.061	\pm	-0.003	-0.019	\pm	+0.063	+0.484	$C_2 = -6.0222$
	$[a]$	-4.500	6.241	7.707	9.056	10.427	11.660	12.969	14.051	15.359	16.558	18.150	$A_1 = -6.3217$
	$[a_1]$	-6.322	6.432	7.707	8.982	10.258	11.533	12.808	14.084	15.359	16.634	17.910	$B_1 = +25.5067$
	$[a_2]$	-8.960	6.333	7.707	9.053	10.370	11.660	12.921	14.154	15.359	16.535	17.684	$A_2 = -8.9605$
Hg violet 4358	$[a] - [a_1]$	+1.822	-0.191	\pm	+0.074	+0.169	+0.127	+0.161	-0.033	\pm	-0.076	+0.240	$B_2 = +33.4088$
	$[a] - [a_2]$	+4.460	-0.092	\pm	+0.003	+0.057	\pm	+0.048	-0.103	\pm	+0.023	+0.466	$C_2 = -5.6444$
	$[a]$	-10.600	3.631	5.421	7.025	8.637	10.131	11.570	13.023	14.486	15.952	17.791	$A_0 = -10.6000$
	$[a_0]$	-10.600	4.164	5.641	7.117	8.594	10.070	11.547	13.023	14.499	15.976	17.452	$B_0 = +29.5288$
Hg violet 4358	$[a_1]$	-11.198	3.910	5.421	6.932	8.443	9.953	11.464	12.975	14.486	15.997	17.508	$A_1 = -11.1982$
	$[a_2]$	-14.886	3.772	5.421	7.031	8.601	10.131	11.622	13.074	14.486	15.859	17.192	$B_1 = +30.2167$
	$[a] - [a_0]$	\pm	-0.533	-0.220	-0.092	+0.043	+0.061	+0.023	\pm	-0.013	-0.024	+0.339	$A_2 = -14.8860$
	$[a] - [a_1]$	+0.598	-0.279	\pm	+0.093	+0.194	+0.178	+0.106	+0.048	+0.048	-0.045	+0.283	$B_2 = +41.2610$
Hg violet 4358	$[a] - [a_2]$	+4.286	-0.141	\pm	-0.006	+0.036	\pm	-0.052	-0.051	\pm	+0.093	+0.599	$C_2 = -7.8890$

ON OPTICAL ROTATORY DISPERSION.

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TABLE III.—Rotatory Dispersion of Tartaric Acid in Aqueous Solutions at 20° C.

(a) 54.1 gr. tartaric acid in 100 gr. solution, or 69.9 gr. „ „ in 100 c.c. Density = 1.2920. Length of tube = 6 dm. $[M_1] = \frac{17.188}{\lambda^2 - 0.030} - \frac{12.080}{\lambda^2 - 0.074}$					(b) 41.34 gr. tartaric acid in 100 gr. solution, or 50.15 gr. „ „ in 100 c.c. Density = 1.2132. Length of tube = 6 dm. $[M_1] = \frac{17.960}{\lambda^2 - 0.030} - \frac{11.869}{\lambda^2 - 0.074}$			
λ .	α obs.	[M] obs.	[M ₁].	[M]—[M ₁].	α obs.	[M] obs.	[M ₁].	[M]—[M ₁].
Li 6708	+24.35	8.71	8.80	—0.09	+22.40	11.17	11.20	—0.03
Cd 6438	25.55	9.14	9.22	—0.08	23.51	11.71	11.85	—0.14
Na 5893	27.78	9.94	9.97	—0.03	26.43	13.18	13.18	±
Cu 5782	28.52	10.20	10.07	+0.13	26.94	13.43	13.43	±
Hg 5780	28.12	10.08	10.08	±	26.94	13.43	13.43	±
Cu 5700	28.67	10.25	10.14	+0.11	27.32	13.62	13.60	+0.02
Hg 5461	28.53	10.20	10.20	±	28.14	14.03	14.03	±
Cu 5219	27.75	9.93	10.02	—0.09	28.55	14.24	14.27	—0.03
Ag 5209	27.41	9.80	10.00	—0.20	—	—	—	—
Cu 5154	27.51	9.82	9.90	—0.08	28.61	14.26	14.28	—0.02
Cu 5105	27.18	9.72	9.80	—0.08	28.62	14.26	14.27	—0.01
Cd 5086	26.97	9.64	9.75	—0.11	28.78	14.34	14.27	+0.07
Zn 4811	23.54	8.42	8.60	—0.18	—	—	—	—
Cd 4800	23.30	8.33	8.53	—0.20	27.41	13.67	13.74	—0.07
Zn 4722	21.91	7.84	7.98	—0.14	—	—	—	—
Zn 4680	20.73	7.41	7.63	—0.22	—	—	—	—
Cd 4678	20.69	7.40	7.61	—0.21	26.51	13.22	13.17	+0.05
Fe 4580	—	—	—	—	25	12.5	12.5	±
Fe 4440	—	—	—	—	22	11.0	11.1	—0.1
Hg 4358	9.13	3.26	3.26	±	19.9	9.92	9.92	±
Fe 4228	0	0	+0.2	—0.2	—	—	—	—
Fe 4275	—	—	—	—	17	8.5	8.5	±
Fe 4209	—	—	—	—	14	7.0	7.0	±
Fe 4146	—	—	—	—	11	5.5	5.5	±
Fe 4110	—10	—3.6	—3.5	—0.1	—	—	—	—
Fe 4096	—	—	—	—	8	4.0	3.8	+0.2
Fe 4046	—	—	—	—	5	2.5	2.0	+0.5
Fe 4023	—	—	—	—	3	1.5	1.1	+0.4
Fe 4005	—20	—7.1	—8.0	+0.9	2	1.0	+0.4	+0.6
Fe 4000	—	—	—	—	*1	+0.5	—0.1	+0.6
Fe 3967	—	—	—	—	—1	—0.5	—1.3	+0.8
Fe 3941	—	—	—	—	—4	—2.0	—2.6	+0.6

TABLE IV.—Molecular Rotatory Power of Tartaric Acid in Aqueous Solutions (Observed and Calculated).

e = proportion of water present.
 $[M]$ = molecular rotation observed.
 $[M_1]$ = molecular rotation calculated.

e .	λ .	Cd 6438	Na 5893	Hg 5790	Hg 5769	Hg 5461	Cd 5086	Cd 4800	Cd 4678	Hg 4358
0.45	$[M]$	9.005	9.751	9.849	9.866	9.919	9.352	8.022	7.108	2.772
	$[M_1]$	9.028	9.730	9.819	9.834	9.919	9.414	8.143	7.204	2.772
	$[M]-[M_1]$	-0.023	+0.021	+0.030	+0.032	\pm	-0.062	-0.121	-0.096	\pm
0.50	$[M]$	10.100	11.049	11.198	11.230	11.479	11.218	10.171	9.362	5.446
	$[M_1]$	10.106	11.041	11.183	11.210	11.479	11.251	10.249	9.445	5.446
	$[M]-[M_1]$	-0.006	+0.008	+0.015	+0.020	\pm	-0.033	-0.078	-0.083	\pm
0.55	$[M]$	11.132	12.328	12.497	12.519	12.967	13.003	12.225	11.560	8.132
	$[M_1]$	11.117	12.281	12.477	12.514	12.967	13.028	12.307	11.655	8.132
	$[M]-[M_1]$	+0.015	+0.047	+0.020	0.005	\pm	-0.025	-0.082	-0.095	\pm
0.60	$[M]$	12.109	13.514	13.742	13.776	14.391	14.676	14.144	13.584	10.538
	$[M_1]$	12.107	13.484	13.726	13.775	14.391	14.699	14.223	13.684	10.538
	$[M]-[M_1]$	+0.002	+0.030	+0.016	+0.001	\pm	-0.023	-0.079	-0.100	\pm
0.65	$[M]$	13.092	14.699	14.963	15.021	15.798	16.314	16.071	15.640	12.956
	$[M_1]$	13.079	14.667	14.959	15.016	15.798	16.360	16.129	15.712	12.956
	$[M]-[M_1]$	+0.013	+0.032	+0.004	+0.005	\pm	-0.046	-0.058	-0.072	\pm
0.70	$[M]$	14.003	15.750	16.129	16.180	17.126	17.890	17.788	17.490	15.197
	$[M_1]$	14.004	15.788	16.124	16.192	17.126	17.919	17.912	17.606	15.197
	$[M]-[M_1]$	-0.001	-0.038	+0.005	-0.012	\pm	-0.029	-0.124	-0.116	\pm
0.75	$[M]$	14.829	16.811	17.222	17.302	18.355	19.355	19.547	19.453	17.356
	$[M_1]$	14.846	16.817	17.196	17.274	18.355	19.376	19.593	19.400	17.356
	$[M]-[M_1]$	-0.017	-0.006	+0.026	+0.028	\pm	-0.021	-0.046	+0.053	\pm
0.80	$[M]$	15.685	17.924	18.295	18.370	19.592	20.849	21.243	21.077	19.535
	$[M_1]$	15.693	17.854	18.275	18.361	19.592	20.845	21.287	21.208	19.535
	$[M]-[M_1]$	-0.008	+0.070	+0.020	+0.009	\pm	+0.004	-0.044	-0.131	\pm
0.85	$[M]$	16.570	18.963	19.423	19.469	20.888	22.283	22.945	23.039	21.730
	$[M_1]$	16.595	19.045	19.412	19.507	20.888	22.369	23.030	23.060	21.730
	$[M]-[M_1]$	-0.025	-0.082	+0.011	-0.038	\pm	-0.086	-0.085	-0.021	\pm
0.90	$[M]$	17.467	19.956	20.530	20.530	22.109	23.784	24.670	24.837	23.928
	$[M_1]$	17.423	19.966	20.474	20.577	22.109	23.824	24.719	24.869	23.928
	$[M]-[M_1]$	+0.044	-0.010	+0.056	-0.047	\pm	-0.040	-0.049	-0.032	\pm
0.95	$[M]$	18.314	21.105	21.790	21.790	23.504	25.561	26.883	27.226	26.687
	$[M_1]$	18.333	21.105	21.666	21.781	23.504	25.527	26.742	27.058	26.687
	$[M]-[M_1]$	-0.019	\pm	+0.124	+0.009	\pm	+0.034	+0.141	+0.168	\pm

The highest number in each series of molecular rotations is shown in heavy type; the wave-lengths at which the true maxima occur are shown in Table V.

TABLE V.—Rotatory Dispersion in Aqueous Solutions of Tartaric Acid at 20° C.

Constants and Anomalies.

$$[M] = \frac{k_1}{\lambda^2 - \lambda_1^2} - \frac{k_2}{\lambda^2 - \lambda_2^2}.$$

P.	λ_1^2 .	λ_2^2 .	k_1 .	k_2 .	λ_σ (Inflexion).	λ_μ (Maximum).	λ_ρ (Reversal).
Per cent.							
55	0.03	0.074	17.127	12.093	<i>0.6571</i>	0.5527	<i>0.4239</i>
54.1	0.03	0.074	17.188	12.080	0.6533	0.5485	0.4220
50	0.03	0.074	17.485	12.043	0.6376	0.5373	0.4140
45	0.03	0.074	17.686	11.877	0.6197	0.5232	<i>0.4050</i>
41.25	0.03	0.074	17.960	11.869	0.6092	0.5150	0.3997
40	0.03	0.074	18.053	11.865	0.6058	0.5123	<i>0.3980</i>
35	0.03	0.074	18.367	11.812	0.5929	0.5022	<i>0.3915</i>
30	0.03	0.074	18.709	11.799	0.5822	0.4937	<i>0.3861</i>
25	0.03	0.074	18.936	11.714	0.5722	0.4859	<i>0.3812</i>
20	0.03	0.074	19.160	11.624	0.5628	0.4785	<i>0.3767</i>
15	0.03	0.074	19.485	11.605	0.5543	0.4720	<i>0.3726</i>
10	0.03	0.074	19.657	11.475	0.5458	0.4653	<i>0.3684</i>
5	0.03	0.074	19.592	11.108	0.5341	0.4562	<i>0.3628</i>

P = concentration in grammes of tartaric acid per 100 gr. of solution.

In the last three columns all values which lie outside the range of the observations are given in italics.

TABLE VI.—Rotatory Dispersion of Sodium Tartrate in Aqueous Solution at 20° C.

(a) *First Series*.—22·54 gr. $\text{Na}_2\text{H}_4\text{C}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ in 100 gr. aqueous solution,
or 25·72 gr. „ „ in 100 c.c.

Density = 1·1411.

Length of tube = 6 dm.

*Simple Formula.**Complex Formula.*

$$[\text{M}_1] = \frac{20 \cdot 152}{\lambda^2 - 0 \cdot 0029}$$

$$[\text{M}_2] = \frac{37 \cdot 445}{\lambda^2 - 0 \cdot 038} - \frac{18 \cdot 025}{\lambda^2 - 0 \cdot 06}$$

λ .	α .	$[\text{M}]$ obs.	$[\text{M}] \lambda^2$.	$[\text{M}_1]$.	$[\text{M}] - [\text{M}_1]$.	$[\text{M}_2]$.	$[\text{M}] - [\text{M}_2]$.
Li 6708	30·23	45·05	20·27	45·07	-0·02	44·67	+0·38
Cd 6438	32·88	49·00	20·31	48·96	+0·04	48·61	+0·39
Na 5893	39·22	58·45	20·30	58·52	-0·07	58·33	+0·12
Hg 5790	40·58	60·48	20·27 ₅	60·64	-0·16	60·50	-0·02
Cu 5782	40·91	60·97	20·38	60·80	+0·17	60·66	+0·31
Hg 5769	40·67	60·62	20·17	61·08	-0·46	61·24	-0·62
Cu 5700	41·95	62·52	20·31	62·58	-0·06	62·47	+0·05
Hg 5461	45·78	68·23	20·35	68·23	±	68·23	±
Cu 5219	50·41	75·13	20·46	74·78	+0·35	74·89	+0·24
Ag 5209	50·57	75·37	20·45	75·07	+0·30	75·18	+0·19
Cu 5154	51·77	77·16	20·50	76·70	+0·46	76·84	+0·32
Cu 5105	53·15	79·21 ₅	20·64 ₅	78·19	+1·02 ₅	78·36	+0·85 ₅
Cd 5086	53·44	79·65	20·60	78·79	+0·86	78·96	+0·69
Cd 4800	59·96	89·36 ₅	20·59	88·58	+0·78 ₅	88·84	+0·52 ₅
Cd 4678	63·41	94·51	20·68	93·32	+1·19	93·58	+0·93
Hg 4358	72·29	107·74	20·46	107·74	±	107·74	±
Fe 4271	75	111·8	20·39	112·3	-0·5	112·0	-0·2
Fe 4210	77	114·8	20·34	115·6	-0·8	115·2	-0·4
Fe 4154	79	117·7	20·32	118·8	-1·1	118·1	-0·4
Fe 4072	82	122·2	20·26	123·7	-1·5	122·6	-0·4
Fe 4033	84	125·2	20·36	126·1	-0·9	124·8	+0·4
Fe 4005	85	126·7	20·32	127·9	-1·2	126·4	+0·3

TABLE VI.—Rotatory Dispersion of Sodium Tartrate in Aqueous Solution at 20° C.
(continued).

(b) *Second Series*.—34·32 gr. $\text{Na}_2\text{H}_4\text{C}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ in 100 gr. aqueous solution,
or 41·97 gr. „ „ in 100 c.c.

Density = 1·2228.

Length of tube = 6 dm.

*Simple Formula.**Complex Formula.*

$$[M_1] = \frac{19 \cdot 537}{\lambda^2 - 0 \cdot 00032}.$$

$$[M_2] = \frac{37 \cdot 108}{\lambda^2 - 0 \cdot 038} - \frac{18 \cdot 348}{\lambda^2 - 0 \cdot 06}.$$

λ .	α .	[M] obs.	[M] λ^2 .	[M ₁].	[M]—[M ₁].	[M ₂].	[M]—[M ₂].
Cd 6438	51·50	47·04	19·50	47·17	−0·13	46·80	+0·24
Na 5893	61·42	56·10	19·48	56·31	−0·21	56·12	−0·02
Hg 5780	63·88	58·35	19·49	58·55	−0·20	58·40	−0·05
Hg 5461	71·80	65·58	19·56	65·58	±	65·58	±
Cd 5086	83·08	75·88	19·63	75·62	+0·26	75·80	+0·08
Cd 4800	93·10	85·04	19·59	84·91	+0·13	85·20	−0·16
Cd 4678	98·52	89·99	19·69	89·41	+0·58	89·69	+0·30
Fe 4425	110	100·5	19·67	99·9	+0·6	100·0	+0·5
Hg 4358	112·81	103·04	19·57	103·04	±	103·04	±
Fe 4218	120	109·6	19·50	110·0	−0·4	109·6	±
Fe 4031	130	118·7	19·29	120·5	−1·8	119·1	−0·4
Fe 3874	140	127·9	19·19	130·5	−2·6	127·4	+0·5

TABLE VII.—Rotatory Dispersion of Potassium Tartrate in Aqueous Solution at 20° C.

(a) *First Series*.—33·60 gr. $K_2H_4C_4O_6 \cdot \frac{1}{2}H_2O$ in 100 gr. aqueous solution,
or 41·647 gr. „ in 100 c.c.

Density = 1·2395.

Length of tube = 6 dm.

*Simple Formula.**Complex Formula.*

$$[M_1] = \frac{23\cdot225}{\lambda^2 - 0\cdot0065}$$

$$[M_2] = \frac{41\cdot75}{\lambda^2 - 0\cdot038} - \frac{19\cdot255}{\lambda^2 - 0\cdot06}$$

λ .	α .	[M] obs.	[M] λ^2 .	[M ₁].	[M]—[M ₁].	[M ₂].	[M]—[M ₂].
Li 6708	54·66	51·92	23·36	52·37	—0·45	51·96	—0·04
Cd 6438	59·49	56·51	23·42	56·93	—0·42	56·58	—0·07
Na 5893	71·55	67·96	23·60	68·15	—0·19	67·96	±
Hg 5790	74·33	70·60	23·67	70·65	—0·05	70·50	+0·10
Cu 5782	74·49	70·75	23·65	70·85	—0·10	70·71	+0·04
Hg 5769	74·77	71·02	23·64	71·17	—0·15	71·03	—0·01
Cu 5700	76·76	72·91	23·69	72·94	—0·03	72·83	+0·08
Hg 5461	83·81	79·61	23·74	79·61	±	79·61	±
Cu 5219	92·28	87·65	23·87 ₅	87·35	+0·30	87·47	+0·18
Cu 5154	94·74	89·91	23·90 ₅	89·62	+0·29	89·77	+0·14
Cu 5105	96·50	91·66	23·89	91·40	+0·26	91·57	+0·09
Cd 5086	97·26	92·39	23·90	92·10	+0·29	92·28	+0·11
Zn 4811	109·20	103·72	24·01	103·24	+0·48	103·51	+0·21
Cd 4800	109·55	104·06	23·97 ₅	103·73	+0·33	104·00	+0·06
Zn 4722	113·50	107·81	24·04	107·29	+0·52	107·55	+0·26
Zn 4680	115·25	109·50	23·98	109·29	+0·21	109·55	—0·05
Cd 4678	115·42	109·63	23·99	109·38	+0·25	109·65	—0·02
Hg 4358	133·30	126·61	24·05	126·61	±	126·61	±
Fe 4326	136	129·2	24·12	128·6	+0·6	128·5	+0·7
Fe 4187	145	137·7	24·15	137·6	+0·1	137·1	+0·6
Fe 4110	150	142·5	24·07	143·0	—0·5	142·1	+0·4
Fe 4046	155	147·2	24·10	147·7	—0·5	146·5	+0·7

TABLE VII.—Rotatory Dispersion of Potassium Tartrate in Aqueous Solution at 20° C. (continued).

(b) *Second Series.*—32·68 gr. $K_2H_4C_4O_6 \cdot \frac{1}{2}H_2O$ in 100 gr. aqueous solution,
or 40·255 gr. „ in 100 c.c.

Density = 1·2318.

Length of tube = 6 dm.

*Simple Formula.**Complex Formula.*

$$[M_1] = \frac{22\cdot93}{\lambda^2 - 0\cdot0068}$$

$$[M_2] = \frac{41\cdot108}{\lambda^2 - 0\cdot038} - \frac{18\cdot886}{\lambda^2 - 0\cdot06}$$

λ .	α .	[M] obs.	[M] λ^2 .	[M] ₁ .	[M]—[M] ₁ .	[M] ₂ .	[M]—[M] ₂ .
Cd 6438	57·34	55·79	23·12	56·25	—0·46	55·91	—0·12
Na 5893	69·07	67·20	23·34	67·50	—0·30	67·18	+0·02
Hg 5790	71·50	69·57	23·32	69·82	—0·25	69·68	—0·11
Cu 5782	71·95	70·01	23·40	70·01	±	69·88	+0·13
Hg 5769	72·10	70·15	23·35	70·34	—0·19	70·21	—0·06
Cu 5700	74·05	72·05	23·41	72·08	—0·03	71·98	+0·07
Hg 5461	80·88	78·69	23·47	78·69	±	78·69	±
Cu 5219	89·00	86·59	23·59	86·34	+0·25	86·46	+0·13
Cu 5154	91·40	88·93	23·62	88·58	+0·35	88·74	+0·19
Cu 5105	93·15	90·63	23·62	90·34	+0·29	90·52	+0·11
Cd 5086	93·80	91·26	23·61	91·04	+0·22	91·23	+0·03
Zn 4811	105·65	102·79	23·79	102·06	+0·73	102·34	+0·45
Cd 4800	105·67	102·81	23·69	102·55	+0·26	102·82	—0·01
Zn 4722	109·75	106·78	23·81	106·07	+0·71	106·34	+0·44
Cd 4678	111·17	108·68	23·78	108·14	+0·54	108·42	+0·26
Hg 4358	128·70	125·22	23·78	125·22	±	125·22	±
Fe 4337	130	126·5	23·79	126·5	±	126·4	+0·1
Fe 4308	132	128·4	23·84	128·2	+0·2	128·1	+0·3
Fe 4271	134	130·4	23·78	130·6	—0·2	130·4	±
Fe 4251	136	132·3	23·91	131·8	+0·5	131·6	+0·7

TABLE VIII.—Rotatory Dispersion of Rochelle Salt in Aqueous Solution at 20° C.

44·63 gr. $\text{NaKH}_2\text{C}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ in 100 gr. aqueous solution,
or 55·93 gr. „ in 100 c.c.

Density = 1·2533.

Length of tube = 6 dm.

*Simple Formula.**Complex Formula.*

$$[M_1] = \frac{21 \cdot 150}{\lambda^2 - 0 \cdot 0051}$$

$$[M_2] = \frac{38 \cdot 513}{\lambda^2 - 0 \cdot 038} - \frac{18 \cdot 066}{\lambda^2 - 0 \cdot 06}$$

λ .	α .	[M] obs.	[M] λ^2 .	[M] ₁ .	[M]—[M] ₁ .	[M] ₂ .	[M]—[M] ₂ .
Cd 6438	61·27	51·49	21·34	51·67	—0·18	51·33	+0·16
Na 5893	73·46	61·72	21·43	61·82	—0·10	61·64	+0·08
Hg 5790	76·31	64·12	21·49	64·07	+0·05	63·93	+0·19
Cu 5782	76·42	64·21	21·47	64·25	—0·04	64·11	+0·10
Hg 5769	76·71	64·45	21·45	64·55	—0·10	64·42	+0·03
Cu 5700	78·76	66·18	21·50	66·14	+0·04	66·04	+0·14
Hg 5461	85·88	72·16	21·52	72·16	±	72·16	±
Cu 5219	94·52	79·42	21·63	79·14	+0·28	79·25	+0·17
Cu 5154	97·19	81·66	21·69	81·18	+0·48	81·32	+0·34
Cu 5105	99·02	83·20	21·68	82·78	+0·42	82·95	+0·25
Cd 5086	99·63	83·72	21·65	83·42	+0·30	83·59	+0·13
Zn 4811	111·47	93·66	21·68	93·44	+0·22	93·70	—0·04
Cd 4800	112·36	94·41	21·75	93·89	+0·52	94·15	+0·26
Zn 4722	116·07	97·53	21·74	97·09	+0·44	97·34	+0·19
Zn 4680	118·07	99·21	21·73	98·88	+0·33	99·15	+0·06
Cd 4678	118·35	99·44	21·76	98·96	+0·48	99·72	—0·28
Hg 4358	136·20	114·45	21·73	114·45	±	114·45	±
Fe 4286	140	117·6	21·61	118·4	—0·8	118·3	—0·7
Fe 4271	142	119·3	21·76	119·3	±	119·1	+0·2
Fe 4135	152	127·7	21·84	127·5	+0·2	126·8	+0·9
Fe 4055	155	130·3	21·42	132·8	—2·5	131·6	—1·3

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TABLE IX.—Rotatory Dispersion of Ammonium Tartrate in Aqueous Solution at 20° C.

32·10 gr. $(\text{NH}_4)_2\text{H}_4\text{C}_4\text{O}_6$ in 100 gr. aqueous solution,
or 37·075 gr. „ in 100 c.c.

Density = 1·1550.

Length of tube = 6 dm.

*Simple Formula.**Complex Formula.*

$$[\text{M}_1] = \frac{22\cdot173}{\lambda^2 - 0\cdot0094}$$

$$[\text{M}_2] = \frac{38\cdot676}{\lambda^2 - 0\cdot038} - \frac{17\cdot117}{\lambda^2 - 0\cdot06}$$

λ .	α .	$[\text{M}]$ obs.	$[\text{M}] \lambda^2$.	$[\text{M}_1]$.	$[\text{M}] - [\text{M}_1]$.	$[\text{M}_2]$.	$[\text{M}] - [\text{M}_2]$.
Cd 6438	65·57	54·24	22·48	54·74	-0·50	54·44	-0·20
Na 5893	79·10	65·43	22·72	65·63	-0·20	65·47	-0·04
Hg 5790	82·07	67·88	22·76	68·05	-0·17	67·93	-0·05
Cu 5782	82·45	68·20	22·80	68·24	-0·04	68·12	+0·08
Hg 5769	82·49	68·23	22·71	68·56	-0·33	68·45	-0·22
Cu 5700	85·00	70·31	22·84	70·28	+0·03	70·19	+0·12
Hg 5461	92·81	76·77	22·89	76·77	±	76·77	±
Cu 5219	101·99	84·36	22·98	84·32	+0·04	84·42	-0·06
Cu 5154	104·77	86·66	23·02	86·53	+0·13	86·66	±
Cu 5105	106·75	88·30	23·01	88·27	+0·03	88·41	-0·11
Cd 5086	107·73	89·10	23·05	88·95	+0·15	89·10	±
Zn 4811	120·88	99·98	23·14	99·85	+0·13	100·09	-0·11
Cd 4800	121·52	100·51	23·16	100·33	+0·18	100·57	-0·06
Zn 4722	125·75	104·01	23·19	103·82	+0·19	104·06	-0·05
Zn 4680	128·20	106·04	23·22	105·78	+0·26	106·01	+0·03
Cd 4678	128·28	106·11	23·22	105·87	+0·24	106·11	±
Hg 4358	148·50	122·83	23·33	122·83	±	122·83	±
Fe 4271	155	128·2	23·39	128·2	±	128·0	+0·2
Fe 4199	160	132·3	23·34	132·8	-0·5	132·5	-0·2
Fe 4144	165	136·5	23·44	136·6	-0·1	136·0	+0·5
Fe 4085	170	140·6	23·46	140·8	-0·2	139·9	+0·7
Fe 4046	172·5	142·7	23·36	142·7	±	142·6	+0·1
Fe 4025	175	144·7	23·45	145·3	-0·6	144·1	+0·6
Fe 3970	180	148·9	23·47	149·6	-0·7	148·0	+0·9
Fe 3919	185	153·0	23·50	153·8	-0·8	151·7	+1·3

TABLE X.—Molecular Rotatory Power of Tartrates.

Salt.	Percentage of water.		P.	<i>d</i> .	C.	α_{5461} .	[M] _D .	
	Obs.	Calc.						
Na ₂ H ₄ C ₄ O ₆ .2H ₂ O ...	15.66	15.65	22.05	1.1379	25.09	44.75	58.45	58.35 (Thomsen)
	15.70	—	<i>22.54</i>	<i>1.1411</i>	<i>25.72</i>	45.78		
			23.02	1.1443	26.34	46.79		
			34.04	1.2207	41.55	71.09		
			<i>34.32</i>	<i>1.2228</i>	<i>41.97</i>	71.80	56.10	56.36 (Thomsen)
K ₂ H ₄ C ₄ O ₆ .½H ₂ O ...	3.94	3.83	34.99	1.2278	42.96	73.50		
	lost at 150°	—	32.00	1.2263	39.24	78.76		
	3.54	—	32.68	1.2318	40.255	80.86	67.20	
	lost at 120°	—	33.60	<i>1.2395</i>	<i>41.647</i>	83.81	67.96	
			35.44	1.2542	44.45	89.48		
NaKH ₄ C ₄ O ₆ .4H ₂ O ...	25.53	25.53	37.12	<i>1.2678</i>	<i>47.06</i>	95.07		
			44.50	1.2523	55.73	85.47		
			<i>44.63</i>	<i>1.2533</i>	<i>55.93</i>	85.88	61.72	
			44.68	1.2536	56.01	86.01		
			45.01	1.2557	56.52	86.69		
(NH ₄) ₂ H ₄ C ₄ O ₆ ...	—	—	27.60	1.1333	31.28	77.87		
			30.38	1.1466	34.83	87.16		
			32.00	1.1548	36.95	92.50		
			<i>32.10</i>	<i>1.1550</i>	<i>37.075</i>	92.81	65.43	
			33.79	1.1637	39.32	99.03		
KSbOH ₄ C ₄ O ₆ .½H ₂ O...	—	—	5.53	1.0382	5.74	59.61		
			5.32	1.0368	5.516	57.20	573.7	

P = grammes of salt in 100 gr. of solution.

d = density.

C = grammes of salt in 100 c.c. of solution.

Values obtained by interpolation are shown in italics.

TABLE XI.—Dispersion-constants and Dispersion-ratios.

Salt.	Concentration.		k .	λ_0^2 .	$\frac{\alpha_{4358}}{\alpha_{5461}}$
	gr./100 gr.	gr./100 c.c.			
Sodium tartrate (dihydrate)	{ (a) 22·54	25·72	20·152	0·0029	1·579
	{ (b) 34·32	41·97	19·537	0·00032	1·571
Potassium tartrate (hemihydrate)	{ (a) 33·60	41·65	23·225	0·0065	1·591
	{ (b) 32·68	40·26	22·930	0·0068	1·591
Rochelle salt (tetrahydrate)	44·63	55·93	21·150	0·0051	1·586
Ammonium tartrate (anhydrous)	32·10	37·075	22·173	0·0094	1·600

TABLE XII.—Dispersion-constants and Dispersion-ratios.

	λ^2 .	$\frac{\alpha_{4358}}{\alpha_{5461}}$
Quartz (opt.-mag.)	0·0173	1·627
Ethyl alcohol (mag.)	0·0170	1·626
Methyl alcohol (mag.)	0·0164	1·624
Other alcohols (mag.)	0·0182	1·630
Water (mag.)	0·0222	1·645
Nine methyl carbinols (opt.)	0·0237	1·651

TABLE XIII.—Constants of DRUDE'S Equation.

	k_1 .	k_2 .	λ_1^2 .	λ_2^2 .
Sodium tartrate—				
(a) 25·72 grams in 100 c.c.	37·445	18·025	0·038	0·060
(b) 41·97 grams in 100 c.c.	37·108	18·348	0·038	0·060
Potassium tartrate—				
(a) 41·647 grams in 100 c.c.	41·750	19·255	0·038	0·060
(b) 40·255 grams in 100 c.c.	41·108	18·886	0·038	0·060
Rochelle salt—				
55·93 grams in 100 c.c.	38·513	18·066	0·038	0·060
Ammonium tartrate—				
37·075 grams in 100 c.c.	38·676	17·117	0·038	0·060

TABLE XIV.—Rotatory Dispersion of Potassium and Sodium Tartrates at 20° C. in presence of an excess of Alkali.

(a) 2·6 gr. of potassium tartrate + 36·43 gr. of potassium oxide (K_2O) in 90·32 gr. of aqueous solution, or 4·329 gr. potassium tartrate in 100 c.c. Length of tube = 6 dm. Density = 1·504.			(b) 13·3 gr. of sodium tartrate + 20·41 gr. of sodium oxide (Na_2O) in 92·891 gr. of aqueous solution, or 20·178 gr. sodium tartrate in 100 c.c. Length of tube = 6 dm. Density = 1·4093.	
λ .	α .	[M].	α .	[M].
Cd 6438	-0·29	- 2·62	- 7·54	-14·32
Na 5893	-0·30	- 2·71	—	—
Hg 5780	-0·30	- 2·71	-10·09	-19·17
Hg 5461	-0·41	- 3·71	-11·87	-22·55
Cd 5086	-0·61	- 5·52	-14·61	-27·75
Cd 4800	-0·80	- 7·24	-17·43	-33·11
Cd 4678	-0·99	- 8·96	-18·87	-35·85
Hg 4358	-1·34	-12·12	-24·29	-46·14

TABLE XV.—Rotatory Dispersion of Potassium and Sodium Tartrates at 20° C. in presence of Alkali.

(a) 4.7 gr. (0.02 mol.) $K_2H_4C_4O_6 \cdot \frac{1}{2}HO$ in 100 c.c. Length of tube = 6 dm. <i>Simple Formula.</i> $[M_1] = \frac{17.298}{\lambda^2 - 0.013}$						(b) 4.6 gr. (0.02 mol.) $Na_2H_4C_4O_6 \cdot 2H_2O$ in 100 c.c. Length of tube = 6 dm. <i>Simple Formula.</i> $[M_1] = \frac{18.56}{\lambda^2 - 0}$				
λ .	α .	[M] obs.	[M ₁] calc.	[M]—[M ₁].	[M] λ^2 .	α .	[M] obs.	[M ₁] calc.	[M]—[M ₁].	[M] λ^2 .
Cd 6438	+5.13	42.7	43.1	—0.4	17.72	+5.23	43.6	44.8	—1.2	18.08
Hg 5780	6.47	53.9	53.9	±	18.01	6.66	55.5	55.5	±	18.54
Cu 5782	6.46	53.8	53.8	±	18.00	6.65	55.4	55.5	—0.1	18.52
Cu 5700	6.55	54.6	55.4	—0.8	17.74	6.76	56.3	57.1	—0.8	18.29
Hg 5461	7.37	61.4	60.7	+0.7	18.31	7.49	62.4	62.2	+0.2	18.61
Cu 5219	8.12	67.7	66.7	+1.0	18.43	8.25	68.7	68.2	+0.5	18.70
Cu 5154	8.23	68.6	68.5	+0.1	18.21	8.40	70.0	69.9	+0.1	18.59
Cu 5105	8.34	69.5	69.9	—0.4	18.11	8.51	70.9	71.2	—0.3	18.48
Cd 5086	8.50	70.8	70.4	+0.4	18.32	8.61	71.7	71.7	±	18.56
Zn 4811	9.60	80.0	79.2	+0.8	18.52	9.65	80.4	80.2	+0.2	18.61
Cd 4800	9.53	79.4	79.6	—0.2	18.29	9.66	80.5	80.6	—0.1	18.55
Zn 4722	9.84	82.0	82.4	—0.4	18.29	10.05	83.7	83.2	+0.5	18.68
Cd 4678	10.08	84.0	84.0	±	18.38	10.08	84.0	84.8	—0.8	18.38
Hg 4358	11.68	97.3	97.8	—0.5	18.48	11.85	98.7	97.7	+1.0	18.75
Fe 4242	—	—	—	—	—	13	108	103	+5	19.5

TABLE XVI.—Rotatory Dispersion of Tartar Emetic in Aqueous Solution at 20° C.

5·32 gr. $\text{KSbOH}_4\text{C}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ in 100 gr. of solution,
or 5·516 gr. „ „ in 100 c.c.

Density = 1·0368.

Length of tube = 6 dm.

Simple Formula.

$$[M_1] = \frac{142\cdot78}{\lambda^2 - 0\cdot04936}$$

λ .	α .	[M] obs.	[M ₁] calc.	[M]—[M ₁].	[M] λ^2 .	$\frac{[M] \times}{(\lambda^2 - 0\cdot04936)}$.
Li 6708	35·70	358·1	356·4	+1·7	161·1	143·5
Cd 6438	38·87	389·9	391·1	—1·2	161·6	142·4
Zn 6364	40·00	401·3	400·6	+0·7	162·5	142·7
Na 5893	47·95	481·0	479·3	+1·7	167·0	143·3
Hg 5790	49·70	498·6	499·4	—0·8	167·1	142·5
Cu 5782	49·82	499·8	501·1	—1·3	167·1	142·4
Hg 5769	50·07	502·3	503·7	—1·4	167·2	142·4
Cu 5700	51·60	517·6	518·2	—0·6	168·2	142·6
Hg 5461	57·19	573·7	573·7	±	171·1	142·8
Cu 5219	63·78	639·8	640·2	—0·4	174·3	142·7
Cu 5154	65·70	659·1	660·2	—1·1	175·1	142·6
Cu 5105	67·25	674·6	675·9	—1·3	175·8	142·5
Cd 5086	68·00	682·2	682·2	±	176·5	142·8
Zn 4811	78·15	784·0	784·1	—0·1	181·5	142·8
Cd 4800	78·67	789·2	788·7	+0·5	181·8	142·9
Zn 4722	82·00	822·6	822·4	+0·2	183·4	142·8
Cd 4678	83·98	842·5	842·5	±	184·4	142·8
Hg 4358	101·26	1015·8	1015·8	±	192·9	142·8
Fe 4228	110	1103	1103	±	197·3	142·8
Fe 4160	115	1154	1154	±	199·6	142·7
Fe 4113*	120	1204	1192	+12	203·6	144·2
Fe 4035	125	1254	1258	—4	204·2	142·3
Fe 3984	130	1304	1306	—2	207·0	142·6

* This reading appears to be incorrect, but has been retained in the table.

TABLE XVII.—Rotatory Dispersion of Tartar Emetic in presence of excess of Alkali at 20° C.

5·53 gr. ($\frac{1}{60}$ mol.) $\text{KSbOH}_4\text{C}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ + 11·2 gr. ($\frac{1}{5}$ mol.) KOH in 100 c.c. of solution.

Length of tube = 6 dm.

Simple formula.

$$[M_1] = \frac{-89\cdot48}{\lambda^2 - 0\cdot06275}$$

λ .	α .	[M] obs.	[M ₁] calc.	[M]—[M ₁].	[M] λ^2 .
Li 6708	—22·90	—229·0	—231·1	+2·1	—103·0
Cd 6438	—25·38	—253·8	—254·4	+0·6	—105·2
Na 5893	—31·37	—313·7	—314·5	+0·8	—108·9
Hg 5790	—32·88	—328·8	—328·4	—0·4	—110·2
Cu 5782	—32·91	—329·1	—329·5	+0·4	—110·0
Hg 5769	—33·13	—331·3	—331·3	±	—110·3
Cu 5700	—34·11	—341·1	—341·3	+0·2	—110·8
Hg 5461	—38·04	—380·4	—380·0	—0·4	—113·4
Cu 5218	—42·72	—427·2	—426·8	—0·4	—116·4
Cu 5153	—44·12	—441·2	—441·2	±	—117·2
Cu 5105	—45·32	—453·2	—452·2	—1·0	—118·1
Cd 5086	—45·78	—457·8	—456·7	—1·1	—118·4
Zn 4811	—53·11	—531·1	—530·4	—0·7	—122·9
Cd 4800	—53·43	—534·3	—533·7	—0·6	—123·1
Zn 4722	—55·82	—558·2	—558·5	+0·3	—124·5
Cd 4678	—57·43	—574·3	—573·2	—1·1	—125·7
Hg 4358	—70·20	—702·0	—703·6	+1·6	—133·2

TABLE XVIII.—Rotatory Dispersion of Potassium and Hydrogen Arsenyl Tartrates at 20° C.

Length of tube = 6 dm.

(a) 2.5 gr. ($\frac{1}{80}$ mol.) tartaric acid + 1.65 gr. ($\frac{1}{60}$ mol.) As_2O_3 + 14 gr. ($\frac{1}{4}$ mol.) KOH in 100 c.c.						(b) 15 gr. ($\frac{1}{10}$ mol.) tartaric acid in 100 c.c. Solution saturated with arsenious acid by boiling.	
<i>Simple Formula.</i>							
$[\text{M}_1] = \frac{20.148}{\lambda^2 - 0.017}$							
λ .	α .	[M].	[M] λ^2 .	[M ₁].	[M] - [M ₁].	α .	[M] approx.
Cd 6438	+5.10	51.0	21.14	50.7	+0.3	+20.81	34.68
Na 5893	—	—	—	—	—	24.93	41.55
Hg 5790	+6.28	62.8	21.06	63.3	-0.5	25.72	42.87
Hg 5769	6.38	63.8	21.23	63.8	±	25.87	43.12
Hg 5461	7.22	72.2	21.53	71.7	+0.5	28.70	47.83
Cd 5086	8.38	83.8	21.68	83.4	+0.4	32.60	54.33
Cd 4800	9.55	95.5	22.00	94.4	+1.1	36.21	60.35
Cd 4678	9.90	99.0	21.66	99.8	-0.8	37.81	63.02
Fe 4378	11.75	117.5	22.10	115.3	+2.2	—	—
Hg 4358	11.49	114.9	21.82	116.5	-1.6	42.37	70.62
Fe 4259	12.25	122.5	22.22	122.5	±	—	—

TABLE XIX.—Rotatory Dispersion of Potassium Bismuthyl Tartrate in presence of excess of Alkali at 20° C.

2.5 gr. ($\frac{1}{60}$ mol.) tartaric acid + 2.16 gr. ($\frac{1}{120}$ mol.) of $\text{Bi}(\text{OH})_3$ + 14 gr. ($\frac{1}{4}$ mol.) KOH in 100 c.c. of solution.

Length of tube = 6 dm.

Simple Formula.

$$[M_1] = \frac{-37.414}{\lambda^2 - 0.0645}.$$

λ .	α .	[M] obs.	[M ₁] calc.	[M]—[M ₁].	[M] ($\lambda^2 - 0.0645$).
Cd 6438	−10.64	−106.4	−106.9	+0.5	−37.24
Zn 6364	−10.93	−109.3	−109.9	+0.6	−37.22
Na 5893	−13.22	−132.2	−132.2	±	−37.38
Hg 5790	−13.78	−137.8	−138.2	+0.4	−37.31
Cu 5782	−13.90	−139.0	−138.7	−0.3	−37.50
Hg 5769	−13.98	−139.8	−139.4	−0.4	−37.51
Cu 5700	−14.39	−143.9	−143.7	−0.2	−37.47
Hg 5461	−15.99	−159.9	−160.1	+0.2	−37.37
Cu 5219	−18.04	−180.4	−180.2	−0.2	−37.50
Cu 5154	−18.60	−186.0	−186.1	+0.1	−37.41
Cu 5105	−19.01	−190.1	−190.8	+0.7	−37.28
Cd 5086	−19.26	−192.6	−192.6	±	−37.40
Zn 4811	−22.23	−222.3	−224.0	+1.7	−37.12
Cd 4800	−22.55	−225.5	−225.5	±	−37.35
Zn 4722	−23.28	−232.8	−236.1	+3.3	−36.89
Cd 4678	−24.34	−243.4	−242.5	−0.9	−37.57
Hg 4358	−29.89	−298.9	−298.4	−0.5	−37.49
Fe 4326	−30	−300	−305	+5	−36.79
Fe 4271	−31	−310	−317	+7	−36.55
Fe 4251	−32	−320	−322	+2	−37.19
Fe 4249	−33	−330	−322	−8	−38.28

TABLE XX.—Rotatory Dispersion of Boro-tartaric Acid in Aqueous Solutions at 20° C.

(a) 15 gr. (0.10 mol.) tartaric acid + 6.2 gr. (0.10 mol.) boric acid in 100 c.c. solution.					(b) 7.5 gr. (0.05 mol.) tartaric acid + 4.65 gr. (0.075 mol.) boric acid in 100 c.c. solution.				
<i>Complex Formula.</i>					<i>Simple Formula.</i>				
$[M_1] = \frac{25.7}{\lambda^2 - 0.03} - \frac{1.249}{\lambda^2 - 0.065}$					$[M_2] = \frac{24.08}{\lambda^2 - 0.02458}$				
λ .	α .	[M] obs.	[M ₁].	[M]—[M ₁].	λ .	α .	[M] obs.	[M ₂].	[M]—[M ₂].
Li 6708	+34.66	57.8	57.9	—0.1	Li 6708	+16.76	55.9	56.6	—0.7
Cd 6438	37.79	63.0	63.3	—0.3	Cd 6438	18.40	61.3	61.8	—0.5
Na 5893	46.00	76.7	76.6	+0.1	Na 5893	22.43	74.8	74.6	+0.2
Hg 5790	47.83	79.7	79.6	+0.1	Hg 5790	23.24	77.5	77.5	±
Cu 5782	47.90	79.8	79.8	±	Cu 5782	23.39	78.0	77.7	+0.3
Hg 5769	48.06	80.1	80.2	—0.1	Hg 5769	23.42	78.1	78.1	±
Cu 5700	49.50	82.5	82.3	+0.2	Cu 5700	24.13	80.4	80.2	+0.2
Hg 5461	54.38	90.6	90.5	+0.1	Hg 5461	26.42	88.1	88.0	+0.1
Cu 5218	60.04	100.1	100.0	+0.1	Cu 5218	29.28	97.6	97.2	+0.4
Cu 5153	61.86	103.1	102.8	+0.3	Cu 5105	30.65	102.2	102.0	+0.2
Cu 5105	63.06	105.1	105.1	±	Cd 5086	30.92	103.1	102.9	+0.2
Cd 5086	63.52	105.9	106.0	—0.1	Zn 4811	35.09	117.0	116.4	+0.6
Zn 4811	72.11	120.2	120.1	+0.1	Cd 4800	35.17	117.2	117.0	+0.2
Cd 4800	72.30	120.5	120.7	—0.2	Zn 4722	36.50	121.7	121.4	+0.3
Zn 4722	75.30	125.5	125.3	+0.2	Cd 4678	37.24	124.1	124.0	+0.1
Zn 4680	76.50	127.5	127.8	—0.3	Hg 4358	43.62	145.4	145.6	—0.2
Cd 4678	76.85	128.1	128.0	+0.1	Fe 4353	44	147	146	+1
Hg 4358	90.10	150.2	150.7	—0.5	Fe 4288	45	150	151	—1
Fe 4242	96	160	161	—1	Fe 4261	46	153	153	±
Fe 4182	99	165	166	—1	Fe 4210	47	156	158	—2
Fe 4123	102	170	172	—2	Fe 4178	48	160	161	—1
Fe 4072	105	175	177	—2	Fe 4100	50	167	168	—1
Fe 4046	107	178	180	—2					

TABLE I.—Specific and Molecular Rotatory Power of Tartaric Acid in Aqueous Solutions at 20° C.

Length of Tube = 6 dm.

Density*	1.2987.					1.2938.					1.2882.					1.2952.					1.1765.					1.1476.					1.1201.					1.0942.					1.0692.					1.0448.					1.0211.																							
	55.0.					60.0.					45.0.					40.0.					35.0.					30.0.					25.0.					20.0.					15.0.					10.0.					5.0.																							
Concentration in (a) grams per 100 grams.	71.48.					63.29.					55.58.					48.31.					41.16.					34.13.					23.00.					21.82.					16.04.					10.45.					5.10.																							
λ.	Mean. [α]. [M].					Mean. [α]. [M].					Mean. [α]. [M].					Mean. [α]. [M].					Mean. [α]. [M].					Mean. [α]. [M].					Mean. [α]. [M].					Mean. [α]. [M].					Mean. [α]. [M].					Mean. [α]. [M].																												
	i.	ii.	iii.	iv.	v.	i.	ii.	iii.	iv.	v.	i.	ii.	iii.	iv.	v.	i.	ii.	iii.	iv.	v.	i.	ii.	iii.	iv.	v.	i.	ii.	iii.	iv.	v.	i.	ii.	iii.	iv.	v.	i.	ii.	iii.	iv.	v.	i.	ii.	iii.	iv.	v.	i.	ii.	iii.	iv.	v.																								
Cd 6455	25.73	25.73	25.73	25.73	0.004	9.003	25.69	25.61	25.58	25.64	25.55	25.67	6.734	10.400	24.79	24.76	24.74	24.75	7.424	11.133	24.34	23.31	23.37	23.35	23.35	8.073	13.109	21.63	21.33	21.32	21.34	21.35	8.728	13.062	19.23	19.29	19.29	19.24	9.886	14.603	16.66	16.64	16.69	16.61	9.686	14.820	13.76	13.73	13.73	13.71	13.73	10.457	15.685	10.62	10.64	10.62	10.64	10.63	11.047	16.570	7.27	7.35	7.30	7.29	7.30	11.645	17.167	8.75	8.74	8.73	8.74	12.209	18.314	
Na 5893	27.28	27.28	27.28	27.28	0.571	9.761	27.99	28.10	27.99	27.96	28.00	27.97	7.868	11.049	27.45	27.59	27.59	27.41	5.219	12.832	26.08	26.03	26.07	26.06	26.06	9.010	13.514	24.26	24.21	24.22	24.10	24.20	8.799	14.899	21.65	—	21.03	21.64	10.000	16.750	16.83	—	18.83	18.83	11.207	16.811	15.68	15.60	15.71	15.67	15.69	11.949	17.924	12.16	13.12	12.16	12.16	12.16	12.165	12.642	13.963	6.37	8.29	8.37	8.33	8.34	13.304	18.956	4.80	4.92	4.80	4.81	14.070	21.106
Hg 5790	28.16	28.16	28.16	28.16	0.538	9.649	28.37	28.40	28.38	28.32	28.30	28.35	7.466	11.196	—	27.78	27.70	27.78	5.331	12.497	26.47	26.43	26.53	26.64	26.50	9.163	13.742	24.71	24.63	24.62	24.58	24.63	9.075	14.263	22.15	22.19	22.14	22.16	10.752	16.129	19.29	19.33	19.24	19.29	11.451	17.222	16.06	16.01	16.02	16.97	16.01	12.197	18.296	12.52	12.44	12.42	12.47	12.46	12.948	19.423	8.52	8.56	8.56	8.58	8.58	13.687	20.530	4.47	4.45	4.45	4.45	14.527	21.700	
Hg 5709	28.26	28.18	28.21	28.19	0.577	9.666	28.45	28.46	28.44	28.43	28.40	28.43	7.457	11.200	—	27.83	27.84	27.83	5.346	12.519	26.56	26.52	26.58	26.60	26.56	9.184	13.776	24.51	24.73	24.75	24.64	24.73	10.014	15.021	22.19	22.29	22.30	22.23	10.786	16.180	19.29	19.43	19.33	19.38	11.535	17.302	16.12	16.09	16.07	16.03	16.03	12.246	18.370	12.52	12.44	12.42	12.47	12.46	12.930	19.469	8.52	8.56	8.56	8.58	8.58	13.687	20.530	4.47	4.45	4.45	4.45	14.527	21.700	
Hg 5481	28.26	28.31	28.37	28.34	0.613	9.919	29.02	29.03	29.01	29.02	29.02	29.06	7.653	11.479	28.85	28.90	28.85	28.83	8.645	12.967	27.77	27.72	27.74	27.77	27.75	9.594	14.341	26.03	25.99	26.01	26.02	26.01	10.503	15.708	23.61	23.63	23.53	23.55	11.417	17.126	20.53	20.56	20.53	20.56	12.297	18.866	17.13	17.16	17.19	17.13	17.15	18.061	19.592	13.42	13.45	13.36	13.33	13.40	13.623	20.838	9.22	9.20	9.21	9.21	9.24	14.740	22.109	4.80	4.81	4.80	4.80	15.608	23.354	
Cd 5086	28.74	28.71	28.75	28.72	0.223	9.352	28.41	28.41	28.41	28.40	28.39	28.40	7.475	11.213	28.98	28.88	28.87	28.81	8.668	13.003	28.26	28.26	28.26	28.24	28.26	9.784	14.676	26.63	26.84	26.83	26.83	26.83	10.870	16.314	24.64	24.61	24.58	24.52	11.027	17.800	21.71	21.70	21.64	21.68	12.604	19.366	18.23	18.27	18.29	18.21	18.25	13.899	20.840	14.27	14.34	14.28	14.29	14.295	14.835	22.283	9.00	9.04	10.04	9.01	9.04	15.866	23.784	5.14	5.31	5.32	5.23	17.040	25.561	
Cd 4800	22.08	22.02	22.01	22.02	5.348	8.122	23.70	23.73	23.73	23.70	23.78	23.75	6.721	10.171	27.16	27.17	27.19	27.18	8.160	12.226	27.24	27.23	27.24	27.20	27.27	9.430	14.144	26.56	26.43	26.46	26.34	26.46	10.714	16.071	24.10	24.47	24.46	24.44	11.853	17.788	21.95	21.80	21.83	21.80	13.052	19.547	18.53	18.61	18.68	18.56	18.53	14.162	21.243	14.77	14.65	14.70	14.74	14.72	15.397	23.045	10.20	10.53	10.59	10.29	10.31	16.448	24.670	6.36	6.59	6.49	6.49	17.922	26.823	
Cd 4673	20.31	20.31	20.31	20.31	4.730	7.108	23.05	23.09	23.10	23.13	23.16	23.10	6.241	9.362	25.75	25.68	25.73	25.70	7.707	11.560	26.13	26.15	26.19	26.22	26.19	9.056	13.584	26.81	26.70	26.70	26.70	26.75	10.427	15.640	24.03	24.03	24.04	24.08	11.060	17.490	21.81	21.83	21.73	21.70	12.069	19.453	18.34	18.40	18.51	18.45	18.45	14.061	21.077	14.82	14.73	14.76	14.79	14.78	15.330	23.039	10.34	10.35	10.40	10.39	10.38	16.538	24.837	6.45	6.67	6.56	6.56	18.150	27.228	
Hg 4358	7.93	—	—	—	7.92	1.845	3.772	13.75	13.89	13.82	13.96	13.80	3.631	5.448	18.35	17.97	18.11	18.08	6.421	8.132	20.33	20.29	20.36	20.32	20.32	7.025	10.338	21.31	21.31	21.36	21.33	21.33	8.687	12.956	20.67	20.91	20.86	20.88	10.131	13.197	19.41	19.47	19.45	19.44	11.570	17.250	17.02	17.10	17.15	17.13	17.10	13.023	15.535	13.90	13.85	13.97	14.00	13.94	14.485	21.730	9.95	9.99	10.02	10.02	10.00	15.592	23.923	5.42	5.46	5.46	5.46	17.791	26.867	

* The densities shown in this table were read off from a sensitive curve plotted from our own readings and those of Pichuan (Sitzungsber. Wien. Akad., II., vol. 107, p. 145.)