

Optical Rotatory Dispersion.<sup>1</sup>

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## 1.—Introduction.

THE discovery of optical rotatory dispersion may be said to have preceded rather than followed the discovery of optical rotatory power, since it was the unequal rotation of the plane of polarisation of lights of different wave-lengths which gave rise to the sequence of beautiful colours which Arago described in 1811 as being produced by the interposition of quartz plates between a polariser and analyser set to extinction. These colours were shown by Biot in 1812 to be due to a rotation of the plane of polarisation which increased with the thickness of the quartz plate and with change of colour from red to violet. When, therefore, a beam of polarised light had passed through a quartz plate it was impossible any longer to extinguish all the colours simultaneously with any one setting of the analyser.

Two features of Biot's work deserve special attention. In the first place, all his measurements of optical rotatory power included observations of rotatory dispersion; the custom of observing the rotatory power of a substance for light of only one wave-length and thus recording a single point on a curve of unknown form is of comparatively recent origin, and marks a distinct retrogression from the more thorough methods of the earlier workers. The second characteristic was the exact quantitative character of the work. Although he had no source of monochromatic light except a ruby glass which gave a red light of average wave-length about 6530, Biot made a quantitative study of the influence of wave-length and of other physical conditions on rotatory power, expressing his results, whenever this was possible, by means of mathematical equations and diagrams.

Two of Biot's diagrams retain their interest even at the present time. The first shows, by means of a series of straight lines, the influence of dilution with water on the rotatory power of tartaric acid. This diagram enabled Biot to predict that dextro-tartaric acid when in the anhydrous glassy form would actually become lævorotatory at the red end of the spectrum at all temperatures below 23° C., a bold prediction that was verified experimentally ten years later.

The second of these diagrams was used by Biot to illustrate his discovery that the rotation of the plane of polarisation of light in quartz was inversely proportional to the square of the wave-lengths, using the figures determined by Newton for corresponding regions of the spectrum. In this diagram the thickness of quartz required to produce a given rotation was plotted against the square of the wave-length, and the result was a series of straight lines. Biot recognised that some of the readings differed from the calculated rotations by 2 or 3 per cent., but he was not in a position to decide whether these deviations were due to experimental errors or to some inaccuracy in his formula. Our own measurements have shown that Biot's diagram represents almost exactly the

rotatory dispersion in quartz if the lines are drawn through a point a little to the right of the origin, and there can be little doubt that if more accurate methods of measurements had been available Biot's line of thought and method of representation would have led him almost inevitably to the simple formula for rotatory dispersion which has come into general use in recent years after the lapse of nearly a century.

## 2.—Simple Rotatory Dispersion.

As the accuracy of polarimetric work increased, the deviations from Biot's law of inverse squares became too important to be overlooked. The result was unfortunate, since those who destroyed the original formula had not got the skill to replace it by one that was more exact. For half a century, therefore, work on rotatory dispersion was limited to the occasional plotting of a curve of unknown form to represent the relationship between rotatory power and wave-length. As a natural result interest in the study of rotatory dispersion diminished, and (following the discovery of the Bunsen burner in 1866) the D line of the sodium flame acquired almost a monopoly as a source of light for the investigation of optical rotatory power.

During this period corrected formulæ were put forward by Boltzmann, who wrote  $\alpha = A/\lambda^2 + B/\lambda^4$ , and by Stefan, who wrote  $\alpha = A + B/\lambda^2$ ; but these proved to be of little value, since they could not readily be made to fit the curves, and, being obviously empirical in character, could be used only as a means of interpolation between the experimental values.

This period of retrogression came to an end with Drude's application to optics of the electronic theory at the close of the nineteenth century. His theoretical investigations led to the enunciation of a somewhat elaborate formula for optical rotatory dispersion which (when approximate results only were required) could be used in the simplified form shown in the equation,

$$\alpha = \sum \frac{k_n}{\lambda^2 - \lambda_n^2},$$

where the dispersion-constants  $\lambda_1^2, \lambda_2^2, \dots, \lambda_n^2$ , could be deduced from the refractive power of the medium, while  $k_n$  represented a series of arbitrary constants depending on the rotatory power of the medium. A similar formula, which actually included the refractive index, was put forward to express the influence of wave-length on magnetic rotatory power. Drude tested his formula for optical rotatory dispersion in the case of quartz, whilst that for magnetic rotatory dispersion was tested in the case of carbon disulphide and of creosote; but for some years both formulæ remained almost barren so far as practical applications to measurements of rotatory dispersion were concerned. In particular, it may be noted (i) that a complete knowledge of the curve of refractive dispersion was required before either formula could be applied to measurements of rotatory dispersion, and (ii) that even the approximate formula for optical rotatory dispersion contained an indefinite number of arbitrary

<sup>1</sup> Abridged from the Bakerian Lecture delivered before the Royal Society on June 2, 1921.

constants. Drude himself did not apply his formula to a single member of the vast array of optically active liquids and solutions, which have been prepared and studied more especially from the time of Pasteur onwards, and he can, perhaps, scarcely be blamed for this omission, in view of the fact that the rotatory power of the great majority of these media had been determined for one wave-length only. It was therefore not until the problem of rotatory dispersion had been taken up afresh and new series of exact measurements had been accumulated that the unique merit of Drude's formula was established.

The results of these new tests were most striking. Fifty series of measurements of magnetic and optical rotatory dispersion were made and classified into groups with similar rotatory dispersion, in order to minimise individual errors of observation. It was then found (Lowry and Dickson, *Trans. Chem. Soc.*, vol. 103, p. 1067, 1913) that the whole of these readings could be expressed within the limits of experimental error by using a single term of Drude's equation, involving only two arbitrary constants—namely, a "rotation-constant,"  $k$ , and a "dispersion-constant,"  $\lambda_0^2$ , as set out in the equation  $a = k/(\lambda^2 - \lambda_0^2)$ .

The substances examined at this stage were nearly all compounds of simple structure—*e.g.* secondary alcohols of the aliphatic series; but the two methyl glucosides, each containing five asymmetric carbon atoms, were proved to obey the same simple law (Lowry and Abram, *Trans. Faraday Soc.*, vol. 10, p. 112, 1914). A somewhat dramatic vindication of Drude's formula, in the case of compounds of much greater complexity, has, however, been provided by the more recent work of Prof. Rupe, of Basel, who published in 1915 (*Ann. der Chem.*, vol. 409, p. 327, 1915) a series of measurements of the rotatory power for four different wave-lengths of some forty compounds of the terpene series. In order to determine the mathematical form of the dispersion-curves he plotted  $a$  against  $\lambda$ ,  $\log a$  against  $\lambda$ ,  $\log a$  against  $1/\lambda$ ,  $a$  against  $1/\lambda$ ,  $a$  against  $1/\lambda^2$  (to test Biot's equation and Stefan's equation), and  $a\lambda^2$  against  $1/\lambda^2$  (to test Boltzmann's equation); but in no case was there any indication of a linear relationship. The results obtained by plotting  $1/a$  against  $\lambda^2$ , in order to test the validity of the one-term Drude equation (Lowry and Abram, *Trans. Chem. Soc.*, vol. 115, p. 300, 1919), are, however, most remarkable, since thirty-seven of the forty substances studied by Rupe give straight lines, and only three show any marked curvature. It is, moreover, noteworthy that two of these exceptional compounds agree in containing the group,  $C : C(C_6H_5)_2$ , although it is not clear why this group should be associated with the occurrence of abnormal optical properties.

Further work by Pickard and others has confirmed the fact that the rotatory dispersion of a vast range of organic compounds can be represented by the simple formula  $a = k/(\lambda^2 - \lambda_0^2)$ , and that a satisfactory classification of optically active compounds can be made by distinguishing between "simple rotatory dispersion," where this law holds good within the limits of experimental error, and "complex rotatory dispersion," where marked deviations from the law are found.

### 3.—Complex and Anomalous Rotatory Dispersion.

Amongst the substances which do not obey the simple law of rotatory dispersion, tartaric acid and its derivatives have been conspicuous ever since Biot in 1837 directed attention to the peculiar behaviour of the acid in aqueous and in alcoholic solutions. The principal anomaly noted by Biot was the fact that the rotation, instead of increasing continuously with decreasing wave-length, rose to a maximum in the green, and then diminished again in the blue, indigo, and violet to values almost as low as those observed in the red region of the spectrum; but the extreme sensitiveness of the rotatory power of the acid to changes of temperature and concentration, as well as to the influence of solvents and of chemical agents, was in Biot's opinion at least as important an anomaly as the maximum in the curve of rotatory dispersion.

When, however, the quantitative basis for the study of rotatory dispersion had been destroyed, attention was no longer directed to the deviations from the law of inverse squares (which were then recognised as being universal), but to the qualitative peculiarities of the curves, which alone were regarded as justifying the use of the term "anomalous dispersion." The principal anomaly thus selected for special attention was the occurrence of a maximum; but a reversal of sign or a decrease of optical rotation with diminishing wave-length were sometimes included as anomalies of similar importance. The undue emphasis thus laid upon the qualitative anomalies has had some curious results; in particular, Winther not only adopted the view that the maximum is the sole criterion of anomalous rotatory dispersion, but actually insisted that this maximum must lie within the visible region of the spectrum. He therefore speaks of a dispersion-curve which "becomes normal in that the maximum passes into the ultra-violet," whilst a curve which cuts right across the axis is described as "normal with a maximum in the infra-red." A definition of anomalous dispersion which thus depends on the physiological properties of the eye, instead of on the physical properties of the medium, can scarcely be regarded as worthy of serious consideration, but it provides a suitable anticlimax to direct attention to the value of the more precise methods of treatment which prevailed when rotatory dispersion was first studied almost a century before.

A complete solution of the problem of anomalous rotatory dispersion has been found by returning to the mathematical methods of Biot and applying similar processes of analysis to curves plotted with the greater accuracy which modern physical apparatus has rendered possible. A series of dispersion-curves (Fig. 1) for aqueous solutions of tartaric acid of different concentrations will illustrate the typical forms of the curves that are encountered in studying the substances of this group.

These curves show clearly three principal anomalies—*inflexion*, *maximum*, and *reversal of sign*—appearing at various points on the experimental curves as the concentration of the solutions is altered.

Similar curves, but covering a wider range, are obtained when the esters of tartaric acid—*e.g.* methyl tartrate and ethyl tartrate (Fig. 2)—are examined a

homogeneous liquids at different temperatures or in a series of different solvents (Lowry and Dickson, *Trans. Chem. Soc.*, vol. 107, p. 1183, 1915; Lowry and Abram, *ibid.*, p. 1193).

Careful mathematical analysis has shown that all

It should be noted that in this series of compounds the negative term always has a higher dispersion-constant than the positive term, so that the asymptote of the negative hyperbola is nearer to the visible region of the spectrum than that of the positive hyperbola.

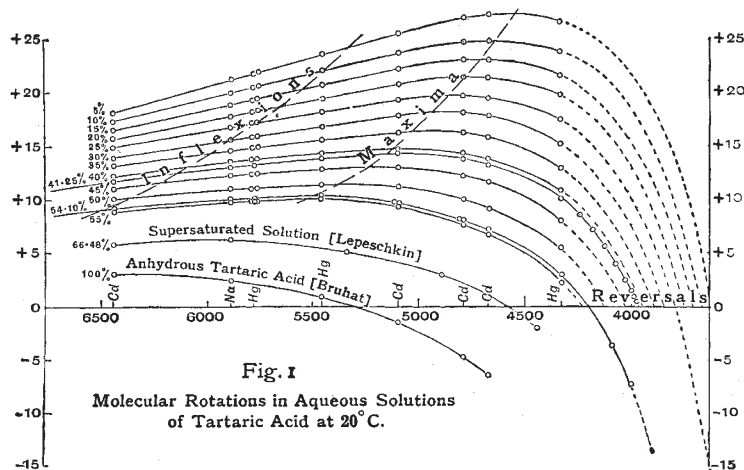


Fig. 1  
Molecular Rotations in Aqueous Solutions of Tartaric Acid at 20°C.

these curves can be expressed by two terms of Drude's equation, of opposite sign and with unequal dispersion-constants—*e.g.*

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

The agreement is particularly good in the case of the esters. In the case of aqueous solutions of tartaric acid the ionisation of the acid appears to introduce an additional factor of complexity giving rise to small but systematic deviations from the values calculated by means of a two-term formula.

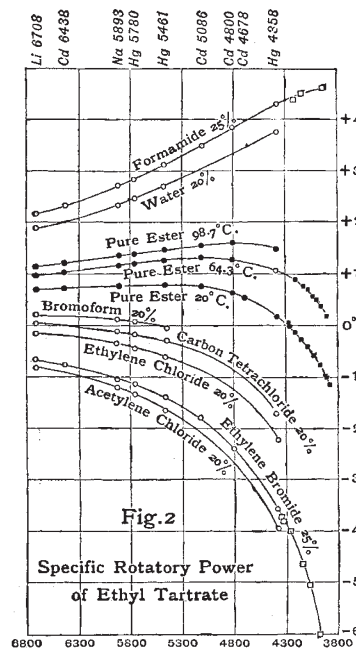


Fig. 2  
Specific Rotatory Power of Ethyl Tartrate

up of the sum of two such rectangular hyperbolas, lying on opposite sides of a common horizontal asymptote, but working up to two different vertical asymptotes. These simple hyperbolas lie beyond the curves for solutions in formamide and in acetylene chloride, which are the highest and lowest of the series shown in Fig. 2, but every curve in this figure can be represented as a weighted mean of two such hyperbolas.

All the positive rotations are therefore drawn over towards the negative side as the wave-length diminishes, as in the top curve of Fig. 2, which shows a reversal of curvature on the extreme right. The curves in the upper part of Fig. 2 must therefore show, not merely one, but *all* of the features which are usually regarded as characteristic of anomalous rotatory dispersion—namely, (i) an inflexion, (ii) a maximum, (iii) a diminution of rotatory power with decreasing wave-length, (iv) a reversal of sign.

On the other hand, the curves at the bottom of Fig. 2 are negative throughout, since the positive term is always smaller than the negative term of the equation. There is therefore no inflexion, maximum, or reversal of sign.

The curves obtained by plotting  $\alpha$  against  $\lambda^2$  are, however, not rectangular hyperbolas, but the weighted means of two hyperbolas, and require two terms of the Drude formula to represent them. Although, therefore, these curves are not anomalous, they are not "simple," and must be classed with the anomalous curves as "complex."

It should be noted that a small alteration in the numerical values of the constants of the equation for a complex curve may suffice to introduce the whole range of anomalies, or alternatively to remove them, whereas, to render a complex curve simple, one of the two terms in the complex equation must be made to disappear altogether. The difference between simple and complex dispersion is therefore probably of more significance than that between normal and anomalous dispersion, in spite of the more picturesque character of the latter contrast.

4.—The Origin of Anomalous Rotatory Dispersion.

It has been shown above that the curves of rotatory dispersion of organic compounds may be of three types—(i) simple, as in the case of the vast majority of the alcohols, acids, sugars, terpenes, etc., to which reference has already been made; (ii) complex, but without anomalies, as in the case of the tartaric esters when dissolved in solvents such as acetylene tetrachloride; (iii) anomalous, as in the case of tartaric acid and its esters. What, then, is the origin of the complexities seen in classes (ii) and (iii)? Mathematically they depend on the same fundamental factor—namely, the introduction into the equation of rotatory dispersion of a second term of opposite sign, which is absent in class (i). From the chemical point of view it is difficult to avoid the conclusion that the complexities expressed by the two-term formula are due to the presence in these liquids of two kinds of optically active molecules, differing in sign and in dispersive power, but each characterised by a simple rotatory dispersion corresponding with one term of the equation.



This suggestion is far from new. Biot himself, as long ago as 1836, produced an artificial anomaly when he attempted to compensate the optical rotatory power of lævorotatory turpentine by means of a column of dextrorotatory oil of lemon. Similar results were obtained with artificial mixtures of turpentine and camphor; and so long ago as 1858 Arndtsen, after establishing by his own measurements the unequal dispersive power of optically active compounds, made the following suggestions:—

“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 increases (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 could then regard tartaric acid as a mixture of two substances differing only in their optical properties, of which one would have a negative, and the other a positive, rotatory power, and of which the rotations would vary in different proportions with the refrangibility of the light.”

This suggestion, made more than sixty years ago, can now be supported by two additional lines of argument: (i) the mathematical evidence that the rotatory dispersion of these substances is in fact the sum of two simple rotations—*e.g.* as expressed graphically by the fact that the complex curves obtained by plotting  $\alpha$  against  $\lambda^2$  are merely the weighted mean of two rectangular hyperbolas; (ii) the chemical evidence that mixtures of isomers do in fact exist, which fulfil the conditions laid down by Arndtsen. Of these optically active “dynamic isomerides” nitrocamphor was one

of the earliest examples to be studied, and it is still one of the best illustrations that can be given of this group of phenomena.

The existence of two forms of nitrocamphor was proved by the discovery of mutarotation—*i.e.* change of rotatory power with time in freshly prepared solutions of the compound; but a mere trace of a catalyst, such as piperidine at a concentration of M/10,000, is sufficient to speed up the isomeric change to such an extent that mutarotation can no longer be detected. In tartaric acid and its esters similar conditions of rapid interconversion appear to prevail, since careful observations have failed to detect any lag of rotatory power after dissolution, dilution, distillation, or fusion. As in the case of nitrocamphor, however, it is possible to recognise, in addition to the usual mixtures, a certain number of derivatives of a fixed or homogeneous character, and these are characterised by opposite rotatory powers and unequal simple dispersions, precisely as we have postulated for the two modifications of the parent acid. Thus (i) tartar emetic differs from the other tartrates not only in showing a much higher rotatory power, but also in giving a dispersion-curve of the “simple” type which is characteristic of the vast majority of optically active organic compounds; (ii) on adding an excess of alkali to tartar emetic a lævorotatory derivative is produced, but this also exhibits simple rotatory dispersion; (iii) boric acid also possesses the power of fixing tartaric acid in a dextrorotatory form with simple rotatory dispersion.

In view of these observations it is difficult to resist the conclusion that tartaric acid, like nitrocamphor, can exist in two forms and yield two types of derivatives, and that the presence of these two types is responsible for the complex rotatory dispersion of the acid and of so many of its derivatives. The molecular structure of these two types is a fascinating problem which still awaits investigation.

### Obituary.

DR. G. B. MATHEWS, F.R.S.

BRIEFLY recorded in NATURE a fortnight ago, the death of Dr. George Ballard Mathews occurred in a Liverpool nursing home on March 19.

Born in London (February 23, 1861), of a Herefordshire family, Mathews' versatile intellect showed itself during his schoolboy days at Ludlow Grammar School, where the then head master instructed his boys in Hebrew and Sanscrit as well as in Greek and Latin. After a year at University College, London, where he studied geometry under Henrici, and of which body he later became a fellow, he entered St. John's College, Cambridge, which offered him the senior scholarship of his year either in mathematics or classics. Carrying out his intention of reading for the Mathematical Tripos he became a private pupil of Mr. W. H. Besant of St. John's. The keen competition for leading places in the Tripos of this period had brought fame to Mr. E. J. Routh as a coach and all the abler candidates went to Routh as a matter of course, for Routh had a long series of senior wranglers to his credit. However, Mathews' name was read out first in the list of 1883, this being the only break in a succession of about thirty consecutive seniors trained by Routh.

In 1884 Mathews was appointed to the chair of mathematics in the then newly-constituted University College of North Wales at Bangor, his election to a fellowship at St. John's taking place the same year. His colleagues at Bangor were all of the same generation as himself and included such men as Professors Andrew Gray, James Dobbie, and the late Henry Jones under the leadership of Principal Harry Reichel (the last three named have all since been knighted). The Bangor chair was resigned in 1896, and shortly followed by Mathews' election into the Royal Society and by his return to Cambridge as University Lecturer in Mathematics. During this period he was mathematical secretary of the Cambridge Philosophical Society for a time and also served on the Council of the Royal Society and on that of the London Mathematical Society. Resigning the Cambridge appointment in 1906 he returned to Bangor and, since 1911, held a special lectureship in the North Wales University College. The honorary degree of LL.D. was conferred by Glasgow University in 1915, and he again acted as professor of mathematics in Bangor during the two College sessions 1917–19. Dr. Mathews himself attributed the distressing series of illnesses which clouded