

THE DEPENDENCE OF ROTATION ON TEMPERATURE, DILUTION, NATURE OF SOLVENT, AND WAVE-LENGTH OF LIGHT.

Dr. T. S. Patterson read a Paper on "The Dependence of Rotation on Temperature, Dilution, Nature of Solvent, and Wave-length of Light."

Some twenty years ago the general opinion in regard to the influence of temperature on the rotation of an optically active substance probably was that the rotation, as in the case of a substance like ethyl tartrate, tended towards a constant value at higher temperatures, that the temperature-rotation curve became asymptotic to the axis of temperature. In 1896, however, it was shown by Frankland and Wharton in the case of ethyl dibenzoyl tartrate* that a minimum rotation could exist, and some years later Winther,† in an investigation connected with rotation-dispersion, fitted a parabolic expression to a number of temperature-rotation curves and made the assumption that since the parabola has a maximum therefore the rotation of these substances should also pass through a maximum value. Somewhat later still the present writer showed‡ that this maximum actually exists, although at a different temperature from that deduced by Winther, and showed also that the maximum, instead of occurring at a constant temperature in a series of homologous compounds, or on dilution of an active substance with an indifferent solvent, moves gradually through a range of temperature. Thus in nitrobenzene, for instance, the maximum rotation of ethyl tartrate, which occurs at a temperature of about 175° , moves rapidly towards a lower value as the solution becomes more dilute, the rotation, at the same time, becoming gradually greater. It thus becomes immediately clear why the rotation of a dilute solution of ethyl tartrate in nitrobenzene diminishes with rise of temperature whilst the rotation of the ester itself and of its more concentrated solutions in nitrobenzene increases on heating; in the former case the ordinary temperature is on one side of the maximum, whilst in the latter case it is on the other. The temperature coefficients of all solutions of ethyl tartrate in nitrobenzene are less than that for the pure ester; nitrobenzene at the ordinary temperature has a powerful elevating effect on the rotation of this particular active compound. A number of other substances, however, of which acetylene tetrabromide may be taken as the best example, have an opposite effect. These substances have a considerable power to depress the rotation of the ester, and in agreement with this it is found that the temperature coefficient of all solutions made up of ethyl tartrate and that

* *Trans. Chem. Soc.*, 1896, **69**, 1587.

† *Zeitsch. Phys. Chem.*, 1902, **41**, 176.

‡ *Trans. Chem. Soc.*, 1908, **93**, 1843.

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solvent have temperature coefficients which are greater than that of the pure ester. It may therefore be inferred that in these cases the maximum rotation would persist but would move towards a still higher temperature, which in this particular case has not yet been actually observed.*

Further, it has been found that other solvents produce effects of a closely similar kind in such a way that if, for instance, a solution in water and one in nitrobenzene have one and the same rotation at some given temperature, then the temperature-rotation curves of the two solutions will be closely similar, although the concentrations may be entirely different. Thus the curve for a number of different solvents at various concentrations blend into a diagram remarkably like that for one single solvent at a number of concentrations, and it would seem as if we might almost eliminate from consideration the nature of the inactive solvent and the concentration since the course of the temperature-rotation curve is apparently defined by the rotation at any given temperature.† When the influence of a particular solvent appears to be exhausted—that is, when its maximum influence has been reached in a dilute solution—the influence may be taken up, as it were, and carried on by another one more powerful. Thus α -nitronaphthalene, $p = 25$, has approximately the same effect as nitrobenzene, $p = 5$, so that the α -nitronaphthalene at $p = 25$ appears to pick up the influence of the nitrobenzene at that point and carry it farther.

Another matter of interest in connection with the relation between temperature and rotation is the following. It has been found that certain substances, such as ethyl tartrate, show a maximum rotation, whereas some derivatives of that compound, for instance ethyl ditrichloroacetyl tartrate, show on the contrary a temperature of minimum rotation, and a reconciliation of this exactly opposite behaviour must obviously present some difficulty. Possibly, however, the reconciliation may be effected in this way. It is known that the substitution of an alkyl radicle, such as *n*-propyl, *iso*-butyl, etc., for ethyl, in ethyl tartrate, moves the maximum rotation towards a lower temperature whilst at the same time the actual value of the rotation is increased,‡ and it seems reasonable to suppose that the very much greater change involved in the replacement of the hydroxylic hydrogen by the trichloroacetyl group should produce a correspondingly greater shifting of the temperature of maximum rotation. The maximum may, in fact, be shifted out of the region of ordinary temperatures altogether and the portion of the curve for the ditrichloroacetyl derivative may correspond with some part of the graph for ethyl tartrate, a part with which we are unacquainted, only because we are not able at present to investigate the problem over a sufficient range of temperature. An examination of some of the data which have been obtained by various observers in the investigation of certain active substances over a fairly wide range of temperature strongly supports this view, for it is found that not only do maxima and minima exist in different curves, but that in the same curve not infrequently a maximum or a minimum together with a point of inflection may be observable.

No investigation has yet been carried out over a sufficient range of temperature to reveal both a maximum and a minimum.§

The temperature-rotation curve of an active compound is thus probably

* Such evidence as exists in regard to this question will be found in a paper in the *Transactions of the Chemical Society* for 1913, 103, 145, especially, perhaps, p. 171.

† See Fig. 3, *Trans. Chem. Soc.*, 1908, 93, 1846.

‡ *Trans. Chem. Soc.*, 1913, 103, 148.

§ This question has been fairly fully discussed elsewhere (*Trans. Chem. Soc.* 1913, 103, 151).

periodic, that is, may show several maxima and minima, and it seems probable that the influence of a solvent is simply to shift the complete curve of the homogeneous substance in one direction or another, but, of course, probably with minor alterations. Thus for ethyl tartrate the influence of nitrobenzene seems to be to shift the whole curve simultaneously towards a lower temperature and a higher rotation.

Rotation Dispersion.—Another very interesting question relates to the position of the maximum rotation for different colours of light. This is a subject which has been thoroughly investigated in only very few cases, but it would appear from the results which have been obtained that the maximum does not necessarily occur at the same temperature for different colours of light. Only two substances have been examined, ethyl tartrate and *n*-propyl tartrate, and in both the maximum rotation moves towards a higher temperature as the wave-length of the light becomes less.* The temperature-rotation curve for violet light is thus apparently retarded on the temperature-rotation curve for yellow or for red light.

This is chiefly important in connection with what is called rotation dispersion. It is well known, of course, that the rotation of an active substance usually depends on the wave-length of the light used, and it is often stated that the rotation for violet light is greater than that for red. If, on the diagram showing the temperature-rotation curves for different colours of light in the case of ethyl tartrate, a vertical line be drawn through the temperature 160° it will cut the temperature-rotation curves† in the order violet, blue, green, yellow, red, and if these values be plotted on a new diagram relative to wave-length a graph will be obtained which is always, so far as the writer is aware, a curved line. If the line be drawn, however, at a temperature of say, 80° , it would cut the temperature-rotation curves in the order, blue, green, violet, yellow, red, and on plotting these values of rotation against wave-length a dispersion graph would be obtained rising from red to a maximum at blue and descending again to violet. Such a curve is generally said, without any proper reason, to be abnormal. At some wave-length intermediate between the extremes there is a rotation maximum. If now a line be drawn through the temperature -40° the sequence of the rotation values will be the same as at first, but the violet light gives the lowest rotation, a negative rotation being regarded as less than a positive rotation. This is, however, a purely accidental circumstance and is solely due to the fact that the temperature-rotation curves for ethyl tartrate happen to pass through the point of inactivity in the neighbourhood we are considering, otherwise the values for violet would be numerically less than for red. It is quite essential that in discussing rotation-dispersion some method must be devised which shall eliminate the sign of the rotation, and it would seem desirable to designate the dispersion on one side of the region of intersection of these curves as positive and that on the other as negative.

The rotation-dispersion is often defined as the ratio of the rotations for various colours of light to the rotation for one given colour of light such as red or yellow, but it has been carefully pointed out by Winther‡ that this is a very unsatisfactory procedure giving most misleading values for rotation-dispersion as in the case of methyl tartrate. This point has been overlooked quite recently by Armstrong and Walker and by Pope and Winmill. The latter authors have measured the rotation, for three different lines of the spectrum, of derivatives of tetrahydroquinoline, and in regard to the *o*-nitrobenzoyl

* *Trans. Chem. Soc.*, 1913, **103**, 165, 166.

† *Trans. Chem. Soc.*, 1913, **103**, p. 165, Fig. 7.

‡ *Zeitschr. Phys. Chem.*, 1902, **41**, 205.

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derivative state* that this substance exhibits quite abnormal rotation constants, whilst with regard to the 2-nitrotoluene-4-sulphonyl derivative † they say, "The considerable variation of rotatory dispersion of the latter substance with the solvent used is noteworthy."

Armstrong and Walker comment on what they term the abnormal dispersive power of these substances and remark, ‡ "It is obvious that a special explanation is required to account for the peculiar behaviour of the two compounds mentioned." The rotatory dispersive power of these substances is, however, not more abnormal than is that of any of the other compounds examined by Pope and Winmill. The explanation, in the first case at least, is in fact merely arithmetical, the cause of any anomaly that exists being identical with that discussed by Winther in the case of methyl tartrate already referred to, namely, that in certain of the solvents used, the rotation of the active compound passes through the point of inactivity, and that by applying an arithmetical process by a purely rule of thumb method to numbers sometimes negative and sometimes positive, one is bound to obtain quotients also sometimes positive and sometimes negative, but this only indicates that the abnormality ought not to be laid at the door of the substance examined.

The second of these two cases is, however, of considerable interest and will be referred to farther on because it raises an interesting question in connection with normal rotation-dispersion, but before dealing with it we may revert for a moment to the case of ethyl tartrate in regard to abnormal rotation-dispersion. We have seen that at a temperature of about 80° the dispersion-rotation curve shows a maximum in the neighbourhood of the blue light, but that if the temperature be 160° there is no such maximum for these particular colours and that the same is the case if the temperature be about -40°. To say, however, as is often done, that the rotation-dispersion at the high and low temperatures is normal whereas at the intermediate temperature it is abnormal seems very arbitrary. It must be clear that if the other two curves were extrapolated so as to include in the former case light of wave-length considerably less than violet, a maximum would be very likely to appear in the curve, whilst at the lower temperature of -40°, if the rotation-dispersion curve were extrapolated, a maximum would occur, with equal probability, for light of greater wave-length than red. The term abnormal, if it is to be used at all, should be applied, not merely to the temperature-rotation curve at one temperature, but to the temperature-rotation curves for all temperatures, in fact, to the substance itself. The reason for abnormal rotation-dispersion in the light of what has already been said as regards the maximum in temperature-rotation curves seems simple. The whole curve for violet light is retarded on that for blue, that for blue is retarded on that for green and so on, the result being that the maximum passes to a higher temperature as the wave-length of the light decreases. In the same way, since the whole curve is displaced, and since, as appears to be the case, the sweep of these curves is the same also, they intersect one another at different points, not all at one point, and this gives rise to the phenomenon of anomalous rotation-dispersion.

It may be remarked in this connection that attention has often been drawn to the fact that abnormal rotation-dispersion occurs in substances the rotation of which alters rapidly with temperature-change. The reason for this seems clear from what has just been said. It is at a distance from a maximum—roughly speaking, midway between a maximum and a minimum—that rotation changes most rapidly with alteration of temperature, and it is just in this

* *Trans. Chem. Soc.*, 1912, 101, 2311.

† *Loc. cit.*, 2316.

‡ *Proc. Roy. Soc.*, 1913, A, 88, 391.

region that the temperature-rotation curves intersect and give rise to abnormal rotation-dispersion.

The question now arises, what is normal rotation-dispersion? or, to put it otherwise, do any substances exist which differ in their behaviour from ethyl tartrate? This is a question which cannot be settled at the present time, since, although a considerable amount of material has been collected, it scarcely touches the main question because the all-important matter of temperature-change has been left out of account. Nevertheless, very many statements may be found in the literature to the effect that this substance or that has normal rotation-dispersion, and the idea seems generally to be that if the dispersion coefficient varies comparatively little, perhaps when the compound is mixed with a solvent or when its temperature is altered slightly, then the rotation-dispersion is to be considered as normal. An example in which the temperature-change was very considerable is afforded by the dispersion data obtained by Pickard and Kenyon.* But it is, nevertheless, difficult to decide whether these substances really have normal rotation-dispersion or not. The matter may be considered in this way. It will probably be granted that the rotation of a substance for any colour of light varies at least to some extent as the temperature changes, as is the case, for instance, with the rotation of the alcohols prepared by Pickard and Kenyon. Now let us imagine that the rotation for a given substance for violet light at a temperature t is A , and for red light is B , then the dispersion coefficient is

$\frac{A}{B}$ †; now suppose the temperature to change to t' and the rotation for violet light at this temperature to be A' , and suppose that this is less than A , that is, that the rotation diminishes as the temperature falls, let us say, from t to t' , then in order that the dispersion coefficient may be the same as before we must have $\frac{A'}{B'} = \frac{A}{B}$, B' being the rotation for the red light at the temperature

t' . Now it will be obvious that this ratio can only be preserved provided the two temperature-rotation curves for violet light and for red light are such that they intersect at the point at which the rotation for both colours of light is zero, and that beyond the temperature at which this occurs they proceed again in a similar manner, but with negative, instead of positive, rotations. From such examples as we know it is impossible to decide whether this behaviour will be, in any way, general—whether temperature-rotation curves will cut in a single point just where the rotation is zero—and it seems to the writer that the apparent normality of certain rotation-dispersions is to be ascribed to the fact that these dispersion coefficients have been measured on substances the temperature-rotation curves of which happen to have a maximum value in the neighbourhood of ordinary temperatures, ‡ and are not due, or at least not necessarily due, to any inherent peculiarity of the substances themselves. But, of course, Pickard and Kenyon's alcohols may represent a class of substances conforming exactly to the type for which the temperature-rotation curves meet exactly at zero rotation.

Nevertheless, it may, after all, be essential to distinguish between two different classes of compounds. We have seen already that the family of temperature-rotation curves for a substance such as ethyl tartrate do not all cut in one point, and this, we have seen, was due to the fact that the maxi-

* *Trans. Chem. Soc.*, 1913, **103**, 1933.

† This is the ordinary way of looking at the matter. Winther's method is much better, but for reasons which cannot be entered on here it also would probably fail if applied over a wide range of temperature.

‡ As is the case with Pickard and Kenyon's alcohols.

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mum rotations for the different colours lie at different temperatures. Now it is quite possible that in certain other cases the maximum rotation for different colours of light may perhaps lie at the same temperature, in which case, if the sweep of the different curves were the same, the whole family of curves would cut in a single point, but of course it does not follow in any way that the rotation corresponding with the points in which they cut should be zero. No such instance as this has quite definitely been observed, but perhaps the data obtained by Pickard and Kenyon for optically active alcohols may represent a case of this sort, which would account for the comparative constancy over a wide range of temperature of the dispersion coefficients, which happen to lie more or less in the neighbourhood of the maximum rotation. It is even more probable that the data already referred to, obtained by Pope and Winmill for 2-nitrotoluene-4-sulphonyl *l*-tetrahydroquinoline, may be of the same sort. From a study of their data for this substance, it seems very likely that, if a solvent could be found in which the active compound would have a rotation of about -85° , the rotation would be identical at least for the three colours of light which they used, and perhaps it might be identical even for a wider range of colours than this.

These two classes of substances may be illustrated by two of the diagrams in the paper by Armstrong and Walker* already referred to. In that paper these authors have arrived at the conclusion that change of rotation, both with alteration of temperature and of solvent, is to be ascribed to a variation in the relative proportions of dynamic isomerides. Limitations of space render it impossible to point out the enormous objections which could immediately be brought against any such idea. It need only be remarked here that Armstrong and Walker's diagram on p. 398 is only another method of representing rotation-dispersion, in which the values of the rotation are plotted relative to the rotation instead of relative to wave-length, and that they do not necessarily have anything whatever to do with the presence or absence of dynamic isomerides. Since this diagram therefore merely represents dispersion data in a new way, the deductions which can be made from it are exactly those which could be made from ordinary dispersion-rotation curves, but inasmuch as the diagram depends upon a purely arbitrary assumption, it is of course of less value. It is to be noted that the lines for the different colours drawn on their diagram intersect practically at a single point, and that the diagram differs from those on p. 397 for methyl and ethyl tartrate exactly in this respect.

These two diagrams of Armstrong and Walker represent the same thing as is shown in the diagram Fig. 7 of a paper by the present writer† for ethyl tartrate, where there is also an intersection of temperature-rotation graphs throughout a certain range. It may possibly be that substances really exist in two classes, those for which the temperature-rotation curves or Armstrong and Walker's dispersion curves cut in a single point and those for which they cut over a range of temperature or rotation, but this is likely to be the only difference which can be discovered in regard to rotation-dispersion between various active compounds. Whether it will be wise to label one as normal and the other as abnormal remains to be seen.

Only one further matter need be referred to, namely, rotation-dispersion in solution. It has been shown by the present writer that the temperature of maximum rotation of a substance such as ethyl tartrate moves to a different temperature as the concentration is varied. Very few substances have been examined for different colours of light in various solvents and at several

* *Proc. Roy. Soc.*, 1913, A, **88**, 388.

† *Trans. Chem. Soc.*, 1913, **103**, 165.

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concentrations, but it appears very clearly from the data which have been collected by Winther for tartaric acid in water and in alcohol, that the period of intersection of the temperature-rotation curves is very similar in solution to what it is for the homogeneous substance, and further, that on dissolving the compound in a liquid this period of intersection shifts its position on a diagram in exactly the same kind of way that the maximum rotation shifts its position.* It seems, therefore, extremely probable, in fact it seems certain, that the so-called normality of the rotation-dispersion of, say, tartaric acid in water is solely to be ascribed to the fact that the influence of the solvent is to move the maximum of the temperature-rotation curves into the ordinary temperature, and at the maximum rotation the so-called dispersion coefficient appears to be normal. This greater normality is, however, altogether imaginary, since the abnormality has merely been shifted to a different region of temperature. It is for a similar reason that the rotation-dispersion of the alkali tartrates appears to be normal.

It may perhaps be mentioned in conclusion that by the adoption of the point of view advocated in this paper and in *Trans. Chem. Soc.*, 1913, **103**, 145, a survey of all the phenomena of optical activity may be made and a comprehension of the interdependence and interrelationship of these phenomena be obtained, and in addition it may be observed that this advantage is gained independently of any theory as to the ultimate causes of the phenomena discussed. The writer's own working hypothesis as to the mechanism of these changes has been detailed in various papers, and it is perhaps only necessary to say here that the statement by Pope and Winmill,† which is prominently quoted by Armstrong and Walker,‡ to the effect "that he has abandoned the view that internal pressure is an operative factor in connection with variations in the rotatory power," is incorrect.

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* See *Trans. Chem. Soc.*, 1913, **103**, 167, Fig. 9.

† *Trans. Chem. Soc.*, 1912, **101**, 2313.

‡ *Proc. Roy. Soc.*, 1913, A, **88**, 390.