CCXX.—*Rotatory Dispersion : Intersections of Dispersion Curves and of Temperature–Rotation Curves.*

By CHARLES EDMUND WOOD and SYDNEY DIGGARY NICHOLAS.

IT is well known that the temperature–rotation curves for methyl, ethyl, propyl, butyl, heptyl, and octyl *d*-tartrates show maxima in the positive region of rotation and that such maxima are displaced to a higher temperature with decrease of wave-length. The esters thus exhibit similar phenomena (Patterson, J., 1916, **109**, 1139, etc.; Frankland and Garner, J., 1919, **115**, 636; Winther, *Z. physikal. Chem.*, 1902, **41**, 161; Walden, *Ber.*, 1905, **38**, 366). A maximum in a temperature–rotation curve for a particular wave-length corresponds to the particular wave-length point on a dispersion curve, this point being situated vertically above points for the same wave-length on all other dispersion curves both for lower and higher temperatures.

Under certain conditions a maximum is defined by the point of intersection of two dispersion curves, the wave-length corresponding to the point of intersection having maximum rotation between the limits of temperature of the two dispersion curves—the closer the temperature limits, the more accurately is the maximum rotation defined for the wave-length of intersection. In general, maxima in temperature–rotation curves indicate intersection in dispersion curves except in cases of simplicity. The movement of maxima is indicated by a particular type of intersection.

Manner of Intersection of Dispersion Curves showing Maxima of Positive Rotation.—Intersections of the dispersion curves occur in a definite order. The diagrammatic dispersion curves (Fig. 1) represent maxima of rotation for different wave-lengths and their movement in the positive region. The lower-temperature dispersion curve (for 60°) is cut by the steeper higher-temperature curve (for 80°) at λ_1. The intersection indicates (i) a maximum in the temperature–rotation curves for λ_1, (ii) maxima for all wave-lengths greater than λ_1, more pronounced definition of the maxima occurring the greater the wave-length, and (iii) no maxima for all wave-lengths less than λ_1, less pronounced approach to maxima occurring the smaller the wave-length. Therefore the maxima for different wave-lengths are moving into the blue region of the spectrum with increase of temperature. The important point to note is that decrease of rotation causing maxima originates in the red. The movement of maxima is shown clearly when the higher-temperature dispersion curve cuts the lower and becomes the dispersion curve of *highest rotational value* towards the blue.* This intersection depends upon a relatively large temperature rotation movement of the maxima, or if small, the experimental determination of dispersion curves of only small temperature differences in the region of intersection.

The steepest (100°) dispersion curve cuts the lower-temperature curves in the following order: 40°, 60°, 80°, and finally becomes the curve of highest rotational value in the blue, *i.e.*, on decreasing

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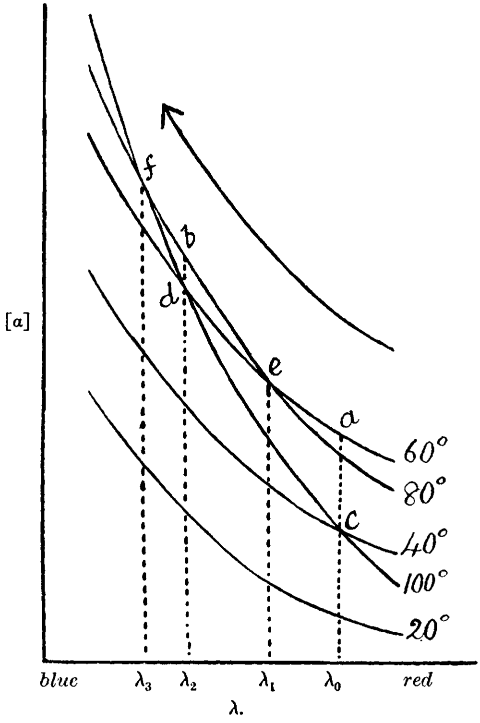
* Secondary intersections (as *c*, *d*, Fig. 1) indicate also the type of intersection.

the wave-length the dispersion curve for 100° intersects other dispersion curves in the order of increasing temperature, and thus at the intersection of the 100° and 80° curves the maximum rotation is carried to a higher temperature in the blue.

This order of intersection and origination of maxima in the red occurs in those derivatives of *d*-tartaric and *l*-lactic acids which show movements of maximum rotation for different wave-lengths in the positive region. If the following condition obtained—that the 100° curve intersected the dispersion curves in the irregular order, 40°, 80°, 60°—a discontinuity would be noted resulting in an irregularity, a depression, in the temperature–rotation curves.

Fig. 1.



The values *e* and *f* may be regarded as the maximum rotations attained by the wave-lengths λ_1 and λ_3, respectively, under the experimental conditions investigated. Similarly the values for *a* and *b* may be regarded as maxima. The secondary intersection *c* (intersection of dispersion curves for wider temperature limits than the primary intersection) gives two equal rotational values, one for

40° on one side, and the other for 100° on the other side, of the maximum rotation a for λ_0.

Curve of Maximum Dispersion.—The curve *fba* into the red region is an infinite number of intersecting dispersion curves which intersect systematically (without irregularity of the type of intersection, the intersections passing gradually out of the red into the blue region) and give rise to a curve of maximum dispersion developing in the direction red–blue (Fig. 1). The curve will lie just above a primary intersection, and will coincide with the two intersecting curves, *viz.*, the low-temperature dispersion curve on the side of the intersection directed towards the red, and the high-temperature curve on the side directed towards the blue. This curve is interesting, for it has direction and shows clearly the variation of maximum rotation with change of wave-length. Further the generation of this curve, *i.e.*, the type of intersection, shows how dispersion curves pass over the maximum of a surface into a non-anomalous region where increase of temperature causes a decrease of rotation and where there is no access to the negative region with decrease of rotation. The only way of gaining the zero axis is by a passage back over the maximum into the anomalous region.

Intersection of Dispersion Curves.

Ethyl Tartrate.—The intersections of the α–λ dispersion curves * for ethyl tartrate have been studied and the measurements are given below.

λ.	Temp. 120°.	140°.	152°.	162·4°.	173°.
7214	+11·87	11·94	11·90	11·82	11·71
7006	12·14	12·20	12·15	12·08	11·99
6707	12·85	12·97	12·94	12·88	12·78
6364		14·10	14·10	14·05	13·96
6152		14·83	14·85	14·82	14·73
5893		15·86	15·92	15·90	15·82
5590		17·08	17·16	17·15	17·08
5461		17·63	17·71	17·72	17·66
5219			18·75	18·82	18·78
5154				19·11	19·13
5086				19·39	19·43
4964				19·89	19·95

(The rotations were taken in a 3-dcm. tube. Densities determined: $d_{4^\circ}^{149\cdot9^\circ}$ 1·0720; $d_{4^\circ}^{181\cdot3^\circ}$ 1·0386.)

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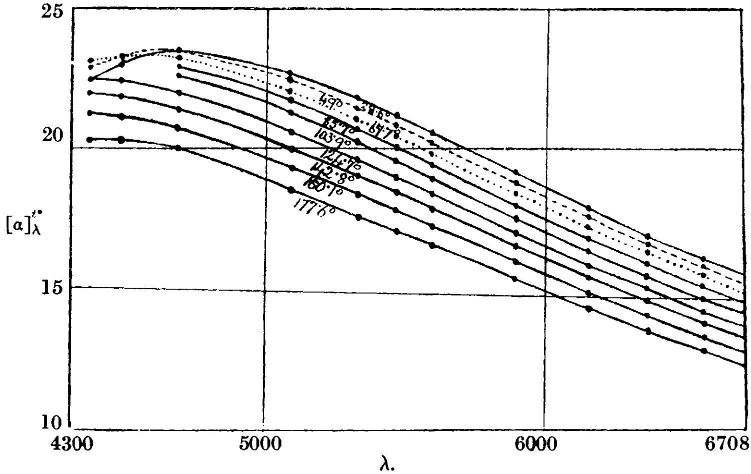
* The authors recognise that the returning of the α–λ dispersion curves is open to criticism. To obtain intersection of the $[\alpha]$–λ curves, it is necessary to work at over 200° (compare Patterson, *loc. cit.*), which is difficult. They have not observed change in the mode of intersection of the α–λ dispersion curves to that present in the final $[\alpha]$–λ curves in any compound yet examined; it is a good guide to the probability of intersection of the $[\alpha]$–λ curves at higher temperatures.

From the above measurements the 152° dispersion curve intersects the 140° curve at $\lambda = 6364$; the 162·4° curve intersects the 140° curve at about $\lambda = 6152$ and the 152° curve between λ 5590 and λ 5461; finally, the 173° curve intersects the 140° curve at $\lambda = 5590$, the 152° curve between $\lambda = 5461$ and λ 5219, and the 162·4° curve between λ 5219 and 5154, becoming the dispersion curve of highest rotational value towards the blue. A curve of maximum dispersion (α, λ) originating in the red can be drawn touching the family of curves, which curve may be looked upon as an envelope of the family.

Ethyl Monobenzoyltartrate.—The dispersion curves (Fig. 2*a*) of this derivative are interesting. They are remarkably parallel and

FIG. 2*a*.



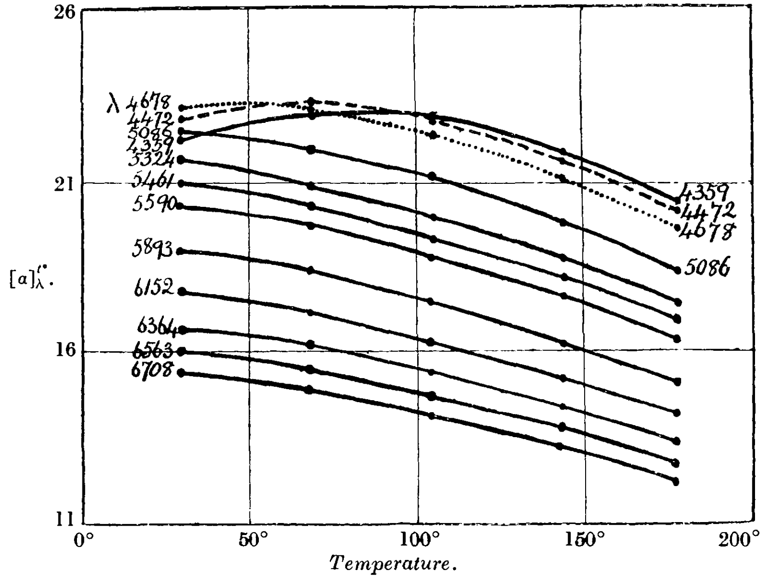
Rotatory dispersion curves for ethyl monobenzoyltartrate.

show maxima for the low temperatures, but only approaches to maxima for the high temperatures. Intersections taking place in the blue and the violet in the usual manner give rise to the maxima as shown in the temperature–rotation diagram (Fig. 2*b*) (Wood and Nicholas, this vol., p. 1671).

These dispersion curves lie almost wholly (except those for wave-lengths in the blue and violet for the lower temperatures) on a descending surface, where increase of temperature, though decreasing the rotation, removes them from the region of anomaly. The temperature–rotation curves make this point clear, for they (λ 5086—λ 6708) are on a surface to the right of the maxima; a point of importance is that to the right of the maxima the curves show no tendency to converge and intersect. Curves for temperatures higher than 160·1° may not be trustworthy owing to slight decomposition in the compound, but up to 190° there was no indication of minima (see curve for 177·6°).

Frequently in experimental work intersecting dispersion curves are obtained as represented diagrammatically in Fig. 3. From a consideration of these curves it is clear that the temperature–rotation curves show no definite movement of the maxima with temperature, maxima for all wave-lengths being situated apparently at 80°; nevertheless, the higher-temperature dispersion curve is the steepest, the inference being that the maxima for different wave-lengths exhibit small movement in the neighbourhood of 80° to a higher temperature and higher rotation as the wave-length decreases. The range of temperature for investigating the movement of maxima has not been selected appropriately. It may so happen that the 100° dispersion curve is coincident or almost coincident with the 80° curve, definite intersection being within experimental error. This is owing to the parallelism of the dispersion curves.

Fig. 2*b*.

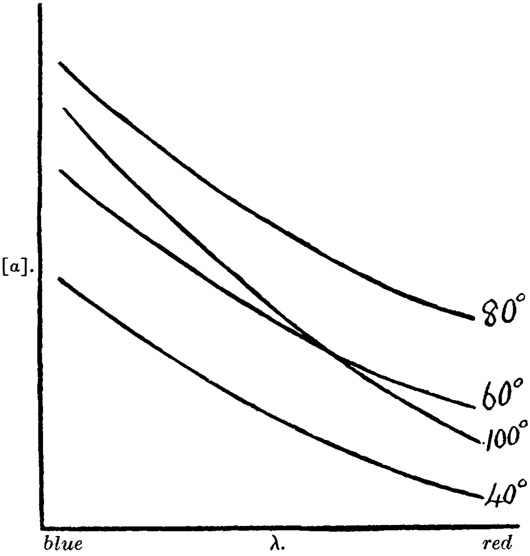


*Rotation–temperature curves for ethyl monobenzoyl-*d*-tartrate.*

A Dispersion–Temperature Relationship for Two Enantiomorphs.

Ethyl *d*-tartrate is anomalous in the positive region. Its dispersion curves show crossing of the axis in a definite manner, maxima, inflexion, and intersection of a particular type. Its temperature–rotation curves show crossing of the axis ($d\alpha/dT$ positive), intersection, and maxima of positive rotation moving in the manner indicated above. With the exception of the passage of curves from the negative to the positive region of rotation, these characteristics occur only in the positive region. It is inferred that such characteristics are definite criteria for a compound of *d*-configuration. For instance none of the *n*-alkyl *l*-lactates (methyl to nonyl inclusive) exhibits visible anomaly in the homogeneous condition, but certain of the esters (including *iso*butyl *l*-lactate) show definite movement of maxima (temperature–rotation curves) to a higher temperature with decreasing wave-length.

FIG. 3.



l-α-Naphthylmethylcarbinol (Pickard and Kenyon, J., 1914, **105**, 1115) is anomalous in the negative region of rotation, and its temperature–rotation curves exhibit movement of maxima to a higher temperature with decreasing wave-length. Since the intersection of its dispersion curves takes place in the negative region and is of similar general character to the method of intersection of the dispersion curves of ethyl *d*-tartrate situated in the positive region, it is inferred that the alcohol exhibits *maxima* of negative rotation and is related configuratively to *l*-tartaric acid. If temperature–rotation curves showing maxima and their movement be drawn diagrammatically for a compound of *d*-configuration, then the maxima and their movement for a compound of *l*-configuration may be represented by a mirror image situated in the negative region. This method of ascertaining the configuration of a compound by maxima of positive or negative rotation is dependent on the following conditions : (1) The crossing of the axis, $d\alpha/dT$, is positive for a compound of *d*-configuration and negative for a compound of *l*-configuration on the temperature–rotation diagram, provided that the maxima are to the right of the region of anomaly ; (2) maxima move in the manner indicated, provided that the region of anomaly is to the left of the maxima. If the region of anomaly is to the right of the maxima, then crossing of the axis $d\alpha/dT$ is negative (compound of *d*-configuration) or positive (compound of *l*-configuration). The maxima will move to a lower temperature with decrease in wave-length. This follows from the convention of plotting temperature in one direction only, without reference to the singular way of crossing the axis in the dispersion diagram. [Compare the esters of *d*-benzylmethylcarbinol (Kenyon and Pickard, J., 1914, **105**, 2271), in which increase of temperature causes a decrease in rotation.]

" *Negative* " *Minima.*

The temperature–rotation curves to be considered are situated in the negative region and are concave towards the axis of zero rotation. In these respects they are similar to the temperature–rotation curves showing maxima of negative rotation (compound of *l*-configuration). The former for sodium light were first investigated by Frankland and Wharton (J., 1896, **69**, 1587) and the curve obtained for ethyl dibenzoyl-*d*-tartrate was described as " the passage through a maximum in the change of rotation brought about by change of temperature." Patterson (*loc. cit.*), however, describes such curves as showing minima of rotation, rotation being considered in an absolute sense. They are considered here as true minima and are termed " negative " minima.

The dispersion diagram for ethyl dibenzoyl-*d*-tartrate exhibits the following main features : (1) Increase of temperature increases the rotation until a definite temperature is reached, after which further increase of temperature decreases the rotation ; (2) dispersion curves intersecting in the order of increasing temperatures ; (3) a curve of minimum dispersion originating, in the visible spectrum, in the violet. The minima in temperature–rotation curves therefore move to a lower temperature with decrease of wave-length.

A number of unrecorded intersecting dispersion curves were obtained for this compound—one curve had rotation $[\alpha]_{6708}^{66\cdot9^\circ} = -43\cdot71^\circ$ and $[\alpha]_{4678}^{66\cdot9^\circ} = -126\cdot85^\circ$ (compare experimental portion of preceding paper)—all of which definitely exhibited the movement. These results are in agreement with the investigation of Patterson on *iso*butyl dibenzoyl-*d*-tartrate (*Proc. Roy. Soc. Edin.*, 1918, **39**, 18).

The movement of negative minima (compound of *d*-configuration) is in a direction opposite to the movement of maxima of negative rotation (compound of *l*-configuration). This movement holds for those minima which have been investigated. Cases may arise where it is not easy to distinguish negative minima from maxima of negative rotation. It has been mentioned that maxima move in one direction only provided that such maxima are plotted on the temperature–rotation diagram to the right of the crossing of the axis and region of anomaly. If minima are plotted to the left of the crossing of the axis, $d\alpha/dT$ positive, only then is it possible to distinguish clearly negative minima by their movement from maxima of negative rotation (in absence of anomaly) and hence the configuration of the compound.

Considering minima, it is necessary to ascertain that no intersection of the temperature–rotation curves occurs in the negative region, and further, that crossing of the axis and region of anomaly, provided these points can be investigated accurately by extrapolation, are to the right of the plotted curves in the temperature–rotation diagram. Considerable information on these points is given by a characteristic diagram (Patterson, J., 1916, **109**, 1139). An important point with regard to compounds showing negative minima is that, although solvents alter the rotation to some extent, yet the effect is not great, and in certain solvents the minima persist (Patterson, *Proc. Roy. Soc. Edin.*, 1918, **39**, 18), which is not the case, as a rule, with compounds exhibiting maxima.

The fourth case—positive minima (compound of *l*-configuration)—situated in the positive region of rotation, has not been investigated so far as we are aware. This case may be looked upon as being, in general character, a mirror image of the minima discussed: further, it is assumed that the occurrence and movement of minima is a dispersion–temperature relationship for two enantiomorphs, and that such movement differentiates them from maxima.

In illustration of a few points as to the nature of the region from minima to crossing of the axis, the results obtained from the investigation of methyl diacetyl-*d*-tartrate may be mentioned. The dispersion curves lie in the negative region except for the highest temperature, when crossing of the zero axis occurs. The temperature–rotation curves show approach to minima, convergence on proceeding towards the axis but no intersection, and crossing of the axis to the right of the probable minima for the curves of longer wave-length. Since anomaly is in the positive region and crossing of the axis ($d\alpha/dT$) is positive, it is inferred that the temperature–rotation curves are approaching to negative minima of a similar type to those exhibited by ethyl dibenzoyltartrate. Had the compound possessed the reverse temperature coefficient with regard to rotation, the temperature–rotation curves would cross the axis to the left of the minima; it is necessary, therefore, to consider the region of anomaly or other characteristics mentioned.

Ethyl *d*-dichlorosuccinate exhibits simple rotatory dispersion in the visible spectrum and negative minima in the temperature–rotation curves. Definite indication of movement of the minima could not be obtained owing to the remarkable parallelism of the dispersion curves. If the movement of minima occurs, it is over a very close range of temperature and is within experimental error. In this connexion it is interesting to note that ethyl dibenzoyl-*d*-tartrate is complex.

Minima of Positive Rotation.

*iso*Butyl diacetyl-*d*-tartrate, investigated by Patterson (*loc. cit.*), shows minima of positive rotation which move to a higher temperature and lower rotation with increase of wave-length. Intersection and consequent development of a dispersion enveloping curve of minimum rotation in the direction violet ⟶ red occurs, which is characteristic of those *d*-tartrates which show negative minima and movement of minima in the negative region.

It is assumed that minima of negative rotation may be represented, in general character, by the mirror image of the case considered.

Although several cases of minima and possible minima (temperature–rotation curves convex towards the axis of zero rotation) are known, little definite information is available regarding the movement of such minima, and no conclusion can be reached, at this stage, as to whether there are two or four cases of convexity (minima and maxima). If there are only two, representing enanticmorphic relationship, the minima mentioned above, then the rotation region of occurrence indicates the configuration; further, the movement, provided movement of minima occurs, indicates the position of the minima, *viz.*, to the right or the left of the anomalous region on the temperature–rotation diagram.*

If it were shown that a compound of d-*configuration* in its temperature–rotation curves exhibited what *appeared*, on a cursory

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* With respect to the position of the minima of positive rotation and the anomalous region, compare Patterson (*loc. cit.*).

glance, to be minima of negative rotation (curves convex to the axis in the *negative* region) though *actually* maxima, then it would be necessary to differentiate this phenomenon * from minima of negative rotation before a criterion, based on minima and maxima (curves convex to the axis), could be established for determining configuration.

The temperature–rotation curves for ethyl thionyl-*d*-tartrate lie in the negative region and are of small curvature, slightly convex to the axis of zero rotation. The investigation of this compound at higher temperatures than those recorded yielded no information as to the possibility of a second type of convexity ascending to a *maximum* in the negative region.

d-Ethyl-*n*-decylcarbinol may be cited as a case of a compound showing minima of positive rotation; and *l*-ethyl-*n*-nonylcarbinol and *l*-ethyl-*n*-dodecylcarbinol (Pickard and Kenyon, J., 1913, **103,** 1934) as showing minima of negative rotation. The presence of these minima in the positive and negative regions, respectively, does not prove the configurations of the alcohols conclusively.

Intersection of Temperature–Rotation Curves.

Intersection takes place in a definite order, and indicates under certain conditions the precise region of a maximum in the dispersion curve for a particular temperature; it always indicates anomaly.

The following points are summarised from the consideration of the temperature–rotation curves of ethyl *d*-tartrate and its mono- and di-acetyl and monobenzoyl derivatives, also of methyl *d*-tartrate and its mono-acetyl and -benzoyl derivatives :

(1) When intersection occurs, the temperature–rotation curve for a definite wave-length intersects (with increasing temperature)

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* Also there would be established four cases, and since each case may involve two types, according to the position of the region of anomaly, the problem would assume a more complex character, and it would be necessary to differentiate minima of positive rotation (*d*-enantiomorph) from maxima of positive rotation (*l*-enantiomorph); in both cases the curves would be convex to the zero axis and situated in the positive region. Similarly for the negative region, the other two cases of minima and maxima would have to be considered.

Expressed briefly, for a compound of *d*-configuration there may exist :

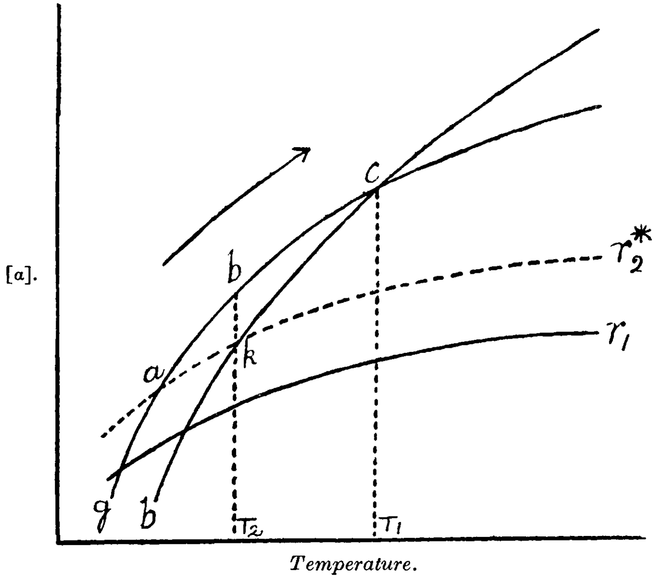
	Type of curves to the zero axis.	Region of rotation.	Example.
Minima of positive rotation.	Convex.	Positive.	*iso*Butyl diacetyl-*d*-tartrate.
Maxima of positive rotation.	Concave.	Positive.	Ethyl *d*-tartrate.
Negative minima.	Concave.	Negative.	Ethyl dibenzoyl-*d*-tartrate.
Maxima of negative rotation.	Convex.	Negative.	Not established.

other temperature–rotation curves in the order of decreasing wave-length, as illustrated in Fig. 4.

(2) A primary intersection *c*, originating from the intersection of two such curves for two wave-lengths not far apart, indicates a maximum in a dispersion curve—the nearer the wave-lengths the more accurately is the maximum in the dispersion curve defined for T_1.

(3) A secondary intersection *k* indicates two equal rotations on each side of a maximum *b* (which is situated on a curve of definite wave-length), provided that *b* is situated on a small intercept.

FIG. 4.



* Wave-length $r_1 > r_2$.

Of course, the two intersecting curves at *k* define the wave-lengths for the two equal rotations on either side of the maximum of the dispersion curve for temperature T_2.

(4) There is no irregularity in the order of intersection. Intersection occurs at a lower temperature between two temperature–rotation curves for wave-lengths in the red, and at a higher temperature between two curves for wave-lengths in the blue; thus intersections proceed from the red into the violet with increase of temperature. This is another statement of the well-known fact that maxima in dispersion curves move to decreasing wave-lengths with increase of temperature.

(5) A curve of maximum temperature–rotation may be drawn

lying above the intersections (as *a* and *c*) and coinciding with the intercepts (as *ac*). The curve originates in the red and develops in the direction red → blue as the temperature increases.

(6) Intersection of temperature–rotation curves is a phenomenon which occurs at a lower temperature than intersection (movement of maxima of temperature rotation curves) of dispersion curves in the compounds studied. The two phenomena are intimately associated.

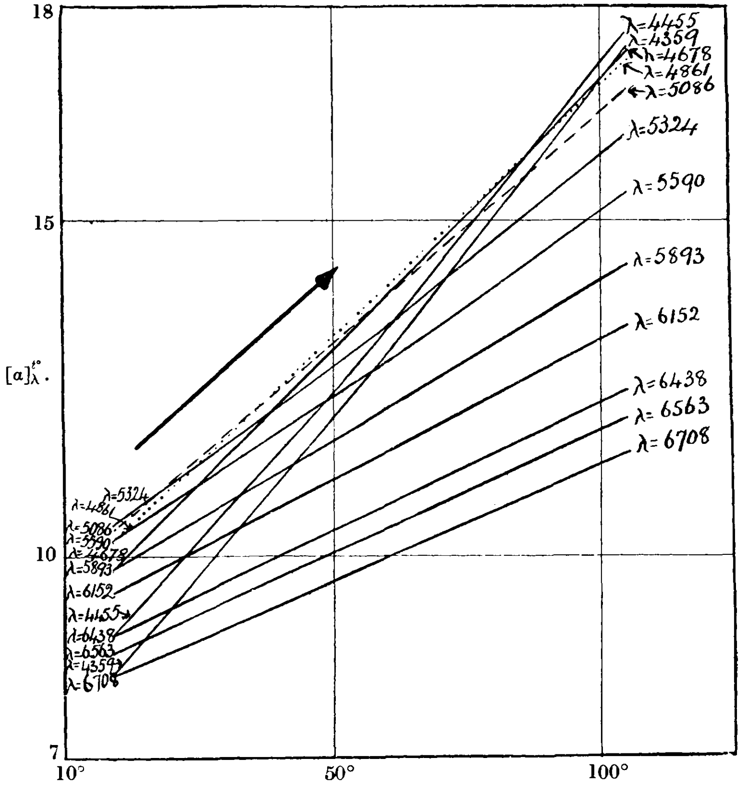
It is assumed that the zero axis and the maxima represent the limits of anomaly, and the presence of maxima without intersection suggests the probability of realising the region of anomaly by suitable choice of solvents, temperature, or derivatives.

The dispersion diagram is considered as a developing surface on a temperature–wave-length plane, having rotations as ordinates; the surface of access to the negative region of rotation confronts the observer, regions of non-access being more remote. The cross-section is a temperature–rotation diagram and shows part of a surface developing from the red into the violet. Reversal of the movement of the maxima, intersection, etc., in the temperature–rotation curves may take place with change in sign of the rotation temperature coefficient, the zero axis being crossed to the right of the maxima. The temperature–rotation diagram would then represent the cross-section of a surface developing from the blue into the red end of the spectrum, *i.e.*, the position of observation is reversed. The zero rotation–wave-length axis is perpendicular to the plane of Fig. 4, and on the left of the diagram. Consideration of this point reduces the two possible movements of the maxima to one movement; in fact, consideration of the three axes reduce the eight possible cases of maxima and minima (curves concave towards the temperature rotation zero axis) to four.

Intersection of the Temperature Rotation Curves of the Acetyl Derivatives of Ethyl Tartrate.

Figs. 5*a* and 5*b* exhibit a remarkable similarity. The important points to note are: (1) Temperature–rotation curves for λ 4359 intersect temperature–rotation curves for λ 6708, λ 6563, λ 6364, etc., with increase of temperature, without irregularity in the order of intersection. (2) The temperature–rotation curve for λ 4359 (monoacetyl derivative) intersects other temperature–rotation curves in order of decreasing wave-length, and finally becomes part of a curve or envelope of maximum temperature rotation, *above* the highest temperature investigated. Similar comments apply to the curve λ 4678 (diacetyl derivative); this curve becomes part of a curve or envelope of maximum rotation *below* the highest temperature investigated. (3) The arrow in both diagrams indicates the direction of formation of the envelope of maximum-temperature rotation, developing from the yellow-green into the violet. (4) In these derivatives of ethyl *d*-tartrate, intersection of the temperature–rotation curves takes place before the appearance of maxima. (5) The crossing of the axis (diacetyl derivative) is positive. The zero rotation–wave-length axis perpendicular to the plane of the diagram is to the left. (6) Both diagrams show temperature–rotation curves passing over the maximum of a surface—the nearer part of the surface being formed by temperature–rotation curves of longer wave-length (λ 6708, 6563, etc.), and the remoter part by curves of shorter wave-length (λ 4359, 4678, etc.). Considering the temperature–rotation curve for λ 4861—this curve for lower temperatures lies on a more remote part of a surface; on increase of temperature the curve passes over a maximum on to a nearer

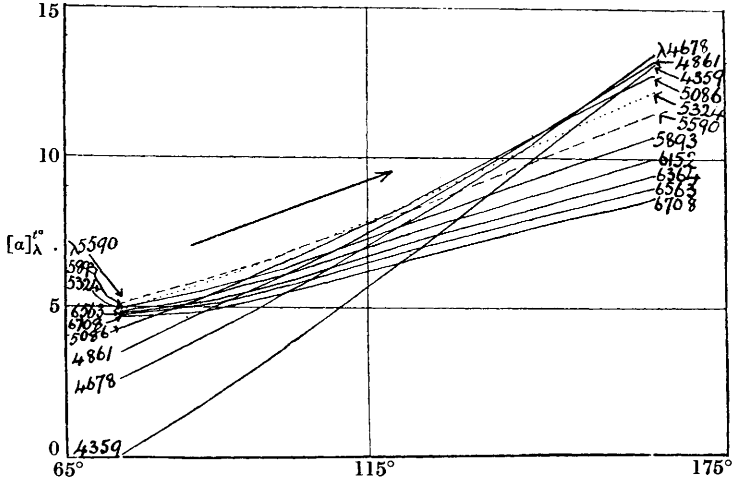
FIG. 5*a*.



*Rotation–temperature curves for ethyl monoacetyl-*d*-tartrate.*

part of the surface, so the passage of the curve over the maximum is observed from a position in the red end of the spectrum. (7) The effect of acetylating a single hydroxyl group of ethyl tartrate is to increase the rotation, to remove maxima to higher temperatures, and to remove crossings of the axis to lower temperatures. The effect of acetylating the hydroxyl group of the monoacetyl derivative is to decrease the rotation and to bring the crossings of the axis to a higher temperature. The temperature–rotation diagram (for 17·5° to 95°) for the monoacetyl derivative corresponds, in general character, to the diagram for the diacetyl derivative to the right of 122° (122° to 163°), *i.e.*, the diagram for the monoacetyl derivative has been removed as a whole to a higher temperature.

FIG. 5*b*.



Temperature.

Rotation–temperature curves for ethyl diacetyltartrate.

Maximum Temperature Rotation and the Movement of Maxima in Dispersion Curves.

Temp.	Ethyl mono-acetyltartrate. Max. rot., [α].	λ.	Temp.	Ethyl di-acetyltartrate. Max. rot., [α].	λ.
17·5°	+10·46°	5300	74·1°	+5·13°	5890
25·1	11·06	5170	87·5	5·83	5660
29·5	11·44	5100	101·3	6·68	5480
44·5	12·68	4950	122·2	8·44	5190
59·6	14·11	4830	142·8	10·62	4930
76·8	15·76	4700	162·8	13·39	4665
94·5	17·78	4540			

The above results, obtained by examination of the dispersion curves, show the variation of maximum rotation with temperature, and the wave-lengths at which maxima occur (dispersion diagram). In Fig. 5 the envelope of maximum rotation is derived from intersecting temperature–rotation curves for wave-lengths lying between λ 5300 and λ 4540 (approx.) (monoacetyl derivative) and for wave-lengths lying between λ 5890 and λ 4665 (approx.) (diacetyl derivative) and these wave-lengths indicate the movement of maxima in dispersion curves across the spectrum. An interesting observation for these two closely related compounds is the fact that over the same range of wave-length (λ 5300 to λ 4665) the increase of maximum rotation (5·75°) is, within experimental error, the same for both derivatives, the temperature range in the case of the monoacetyl derivative being 67° (84·2—17·5°), whilst that of the diacetyl compound is 49° (162·8—113·5°). It is difficult, however, to decide from the measurements and graphs the wave-length of maximum rotation for a particular temperature, and this is especially the case with methyl and ethyl tartrates, data for which are given below.

	Methyl tartrate.			Ethyl tartrate.	
Temp.	Max. rot., [α].	λ.	Temp.	Max. rot., [α].	λ.
17·7°	+2·36°	6590	0·8°	+ 5·31°	6150
34·9	3·49	6330	14·4	7·19	5700
59·8	4·75	6090	20·0	7·91	5590
81·2	5·68	5910	40·0	10·41	5310
95·3	6·21	5790	60·0	12·55	5090
100·8	6·43	5750	80·0	14·72	4860
124·9	7·22	5590	100·0	16·31	4710
144·8	7·75	5500	120·0	17·81	4590
162·1	8·15	5440	140·0	18·87	4490

The curvature of the $[\alpha]$–T curves is concave, and of the $[\alpha]$–λ curves convex towards the axis. Over the same range of wave-length, λ 6150—5440, the increase of maximum rotation in the case of methyl tartrate is 3·7°, and in the case of the ethyl ester 3·8°; in the former case the temperature range is approximately 109°, and in the latter 29·4°, which indicates the sensitiveness of the ethyl derivative to temperature change.

Summary.

1. The manner of intersection of dispersion curves is discussed.
2. An envelope of maximum dispersion develops in certain tartrates and lactates, with increase of temperature, in the direction red → blue, which indicates movement of maxima in temperature–rotation curves.
3. Movement of maxima of positive rotation (temperature–rotation diagram) is in one direction only, provided the crossing of the axis, $d\alpha/dT$, is positive. A definite movement is of value in deciding configuration. It is necessary to know, in absence of

anomaly, the direction of crossing the axis and the possibility of intersection of the temperature–rotation curves in the positive region. Two methods throw light on these points—effect of solvents, and extrapolation by means of a characteristic diagram.

4. Presence and movement of negative minima is assumed to be a temperature relationship for enantiomorphs, and is of rarer occurrence than maxima of negative rotation. Utilisation for configuration purposes depends upon a consideration of the following points: (*a*) Movement of minima; (*b*) the sign of $d\alpha/dT$ on crossing the axis; (*c*) no intersection of temperature–rotation curves in the negative region; (*d*) effect of solvents.

5. The possibility of eight types of maxima and minima having temperature–rotation curves convex towards the axis is considered.

6. Intersection of temperature–rotation curves takes place in a definite order and gives rise to an enveloping curve of maximum temperature rotation.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[*Received, July 26th,* 1927.]