

## THE ROTATORY POWER OF TARTARIC ACID.

(TRANSLATED FROM THE FRENCH.)

A Paper by **Mr. G. Bruhat** (École Normale Supérieure, Paris) on "The Rotatory Power of Tartaric Acid" was read by Dr. H. Borns.

It has been known since Biot\* that solutions of tartaric acid show an anomalous rotatory dispersion. The rotatory power for the different lines of the solar spectrum has been measured by Arndtsen† for solutions of different concentrations in water and in mixtures of water and alcohol. These measurements have been resumed for other concentrations and other solvents by Wendell,‡ Lepeschkin,§ Winther,|| and Ascher.¶ The results obtained show that, for every solution, the rotatory power attains a maximum for a certain wave-length, which depends upon the concentration and the nature of the solvent. For diluted aqueous solutions the maximum lies in the violet, for concentrated solutions in the green; for supersaturated aqueous solutions and for certain alcoholic solutions the maximum lies in the yellow, the rotation vanishes in the blue and becomes negative in the violet; when some benzene is added to the solvent, the rotation is negative for all wave-lengths.

The tartaric acid hence shows an altogether anomalous variation of the rotatory power, not only as to wave-length, but also as to the concentration and the nature of the solvent. The temperature variation is, further, much stronger than with most active substances, and the rise of temperature modifies the rotatory dispersion curves in the same way as the dilution.

Researches which I have made as to the anomalies of the rotatory dispersion in the neighbourhood of an absorption band have induced me to inquire, whether it would not be possible to approach the behaviour of the solutions of tartaric acid from this phenomenon and to explain the anomalies by the influence of an ultra-violet absorption band, although it appeared difficult to account, by this same cause, for the anomalous variations with the concentration, since the absorption bands in general are not sufficiently affected by the dilution to produce variations of this importance. Concentrated solutions of the acid appear, indeed, always yellow, when examined in a tube several decimeters in length; they therefore absorb the more refrangible parts of the spectrum to a certain extent; but my spectrometric study has shown that the absorption, which sets in at the extremity of the visible spectrum and increases in the ultra-violet, does not really become strong before we come to wave-lengths of less than  $247\ \mu$ . On the other hand, Cotton has proved that the anomaly in the rotatory dispersion, produced by the existence of absorption bands, is accompanied by circular dichroism; this dichroism is maximum for the wave-length for which the rotation vanishes, and the

\* Biot, *Mém. Acad. Sciences*, **15**, p. 93; 1838.

† Arndtsen, *Ann. de Chim. et Phys.*, iii., **54**, p. 403; 1858.

‡ Wendell, *Wied. Ann.*, **76**, p. 1152; 1898.

§ Lepeschkin, *Ber. Dtsch. Chem. Ges.*, **32**, p. 1180; 1899.

|| Winther, *Zschr. Physik. Chem.*, **41**, p. 161; 1902. **45**, p. 331; 1903.

¶ Ascher, *Inaug. Dissert.*, Berlin; 1912.

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theory, which I shall elsewhere advance, would suggest that it is then measured by an angle which is approximately double that of the maximum rotation. Now a concentrated solution of tartaric acid in alcohol which, in a polarimeter tube of 30 cm., gave a maximum rotation of  $5^{\circ}40'$  near  $550\mu\mu$  and no rotation near  $425\mu\mu$  has not shown any appreciable dichroism (*i.e.*, of more than one minute) for these latter radiations. It is hence impossible to look for the explanation of the anomalies of the rotatory dispersion of tartaric acid in the selective absorption of this acid for the violet or the ultra-violet.

It has also been attempted to account for the variations of the rotatory power with the concentration by the influence of the molecules of the solvent interposed between the active molecules, for instance, by some influence which they might exert on the arrangement and the movements of the atoms in the interior of the active molecule; but we could not, on these grounds, account for the occurrence of an anomaly of the rotatory dispersion in a transparent solution. Further, the theory of Lorentz, developed by Livens\* for solutions, leads to a relation between the rotatory power  $[\rho]$  and the index of refraction  $\nu$  of this form:

$$[\rho] = A \cdot (\nu^2 - 1)(\nu^2 + 2)/(\lambda^2 - \lambda_0^2).$$

This formula would not cause us to foresee any anomalous rotatory dispersion since the index  $\nu$ —which, even for concentrated aqueous solutions of tartaric acid, does not differ by  $1/20$  from the index of water—does not undergo any very pronouncedly anomalous variations. Nor does it explain the variation of the rotatory power with the concentration, since the variation of the rotatory power for the D line decreases with the concentration, whilst the index for this same line increases.† The assumption of a purely physical effect of the solvent will not explain the anomalies of the variations of the rotatory power of the tartaric acid therefore.

We are thus induced to assume that there exist in solutions of tartaric acid two active compounds endowed with rotations in the opposite sense and of different rotatory dispersions, whose relative proportions depend upon the nature of the solvent, on the concentration, and the temperature. The hypothesis permits of explaining at the same time the anomalies of the variations of the rotatory power with those three factors and the anomalies of the dispersion. By an analogous phenomenon Darmois‡ has explained the variability of the rotatory power of essences of turpentine and the anomalous rotatory dispersion shown by certain of these essences; the dispersion curves which he gives for mixtures of the two pinenes are entirely analogous to those found for solutions of tartaric acid. He points out that in the case of such mixtures containing two active substances, the rotatory powers  $\alpha_1, \alpha_2, \alpha_3, \beta_1, \beta_2, \beta_3$ , given by three different solutions for two monochromatic radiations should satisfy the equation

$$\frac{\alpha_3 - \alpha_1}{\alpha_2 - \alpha_1} = \frac{\beta_3 - \beta_1}{\beta_2 - \beta_1}.$$

In the case of aqueous solutions of tartaric acid this relation is well supported by the experiments of Arndtsen, who was led to suggest that for each radiation the rotatory power was connected with the quantity of water  $e$  by a linear function:

$$\begin{aligned}\alpha &= A + Be \\ \beta &= A' + B'e.\end{aligned}$$

\* Livens, *Phil. Mag.*, vi., **25**, p. 817; 1913.

† Cheneveau, *Recueil de Constantes Soc. Franc. de Phys.*, p. 474.

‡ Darmois, *Ann. de Chim. et Phys.*, viii., **22**, p. 247; 1911.

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The formula is likewise confirmed by the experiments of Wendell, which also suggest a linear relation, and by the measurements made by Winther, who found that the ratios  $(\beta_2 - \beta_1)/(a_2 - a_1)$  (Lösungs-dispersions koeffizient) were independent of the concentrations and had further the same value for alcoholic solutions. He observed, moreover, that the analogous ratios for the same solution at two different temperatures  $(\beta'_2 - \beta'_1)/(a'_2 - a'_1)$  (Dispersions koeffizient) are constant and essentially equal to the preceding ratios—which proves that one may explain the strong variation of the rotatory power with temperature by the variation of the proportions of the two active compounds.

The hypothesis of two active compounds in equilibrium with one another in variable proportions hence well accounts for the anomaly of the rotatory dispersion and its variation with concentration and temperature. It likewise accounts for the variation with the nature of the solvent; it is, however, difficult to obtain numerical values for solvents except alcohol, the solubility of the tartaric acid being in general too small to admit of precise measurements of the rotation. We can at any rate say that the general trend of the curves is the same as that of the curves given by alcoholic or aqueous solutions, or solutions extrapolated from the former according to the rule of Daremois.

Which is the nature of these two compounds? It is impossible to suggest any intervention of electrolytic dissociation. The cryometric measurements and the conductivity determinations are in accord and show that this dissociation only becomes appreciable for solutions which are too diluted to admit of taking rotatory power measurements. We should then have to suppose that the very small number of ions which exist possess a very high rotatory power, which is not confirmed by the results observed with neutral tartrates, in the case of which dissociation really does intervene.

Biot\* had thought that the phenomena he observed were due to a combination between the tartaric acid and water. This assumption does not render clear why the same phenomena are observed with solvents other than water. We can show that this assumption must be rejected by studying the rotatory dispersion of pure tartaric acid in the absence of any solvent. Biot had been able to obtain transparent masses of superfused tartaric acid, and had observed positive rotations for the red rays and negative rotations for blue rays; at a temperature of  $35^\circ\text{C}$ . he even succeeded in obtaining negative rotations for red rays. I have taken these experiments up again, and I have made my measurements with some precision.

The crystallised tartaric acid is placed in a tube, 5 cm. long and 2 cm. in diameter, which can be heated up to  $180^\circ\text{C}$ . in an electric furnace. The tube is placed in a beam of an electric arc between two Glazebrook prisms; the tube is directed with the aid of a finder lens which also converges the luminous rays on the ring (eyepiece). The acid melts when heated to  $180^\circ$  and begins to boil; the light then reappears in the field which is crossed by bubbles. When the analyser is turned, beautiful colours of normal dispersions are seen; the light which passes is green for an azimuth of  $+8^\circ$ , red for an azimuth of  $+15^\circ$ , and shows the transition tint at  $+11^\circ$ . When we stop heating and watch the rotatory dispersion during the cooling period, we observe analogous colours down to temperatures of about  $90^\circ\text{C}$ ., yet with that difference that all the azimuths are becoming smaller: at  $90^\circ\text{C}$ . the azimuth of the transition tint is  $+9^\circ$ . When the temperature continues to fall, the colours, while remaining in the same sequence, become less and less intense, and the azimuths decrease further, that of the transition tint being  $+6.5^\circ$  at  $50^\circ\text{C}$ . At about  $45^\circ\text{C}$ . we no longer see any blue nor red. We notice a lilac

\* Biot, *Ann. de Chim. et Phys.*, iii., 28, p. 351; 1850.

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tint, intense particularly near  $45^\circ$ , and brilliant yellow for the lower azimuths. Afterwards, the temperature still falling, the yellow turns into orange and then into red, whilst the azimuth becomes negative; the azimuth of the lilac tint also diminishes, being 0 or  $1^\circ$  for ordinary temperature, whilst for all the higher azimuths the colouring appears blue. We thus recognise that tartaric acid possesses, when liquid at  $180^\circ\text{C.}$ , a normal rotatory dispersion, and that the dispersion diminishes at lower temperatures, particularly below  $100^\circ\text{C.}$ ; about  $45^\circ\text{C.}$  the rotation is maximum for the yellow, and at ordinary temperature it decreases in algebraical value from the red to the violet, vanishing in the middle of the visible spectrum.

It is rather difficult to obtain exact measurements of the rotation for the different colours of the spectrum. When the acid is fused and maintained liquid about  $180^\circ\text{C.}$ , bubbles are being liberated which agitate the liquid by convection currents, and give rise to a partial depolarisation of the light; this bubbling is moreover accompanied by a chemical change of the fused material, and we have to operate quickly. On cooling almost all the bubbles congregate near the surface while the acid is still viscous; crystalline particles may, however, remain in suspension, and the acid may undergo a more or less irregular temper when we pass from the solidification temperature to the ordinary temperature. It may even occur, when we try to cool below ordinary temperature, that fissures form in the mass of acid owing to the unequal dilatation of the acid and of the tube in which it is contained. The fissures render polarimetric observation impossible. Attempts made to anneal the mass have never succeeded; for a mass of superfused tartaric acid which has been cooled to ordinary temperature crystallises rapidly and throughout the mass as soon as we heat up to  $100^\circ\text{C.}$  again. The depolarisation produced by the superfused material and the irregularities of the light rays through this substance make the use of a penumbra-polarimeter impossible. It remains possible, however, to determine the extinction-position in monochromatic light between two Glazebrook prisms; by focussing the finder on the bubbles or the solid particles, which may be in suspension, the polarised light which they diffuse may be rendered little troublesome.

The tartaric acid was directly fused in the polarimeter tube of 5 cm. length; the light employed was that of an electric arc purified spectroscopically by the arrangement of Brace\*; the width of the spectrum bands used ranged from 20 to  $10\mu$ . Under these conditions, and taking ten readings of the analyser position at extinction, I found that for the red, yellow, or green radiations these ten readings were distributed over an interval of 45 or 60 minutes; their mean may therefore be considered as exact within about 10 minutes. I have always verified, when recommencing the measurements after having turned the tube through  $90^\circ$  about its axis, that the temper of the superfused acid did not exert any influence. Yet the different experiments have not yielded entirely identical rotatory dispersion curves; this is due to the chemical modifications which the tartaric acid undergoes while fusing; I shall study their effect on the rotatory power.

The results of a few series of observations are given in the following table. Series I concerns a tube containing tartaric acid which was kept fused in an electric furnace, regulated to maintain as constant a temperature as possible; the temperature would fluctuate between  $180$  and  $185^\circ\text{C.}$  The measurements were taken very quickly so as to avoid chemical decomposition, and each result is the mean of four observations. Series II to V refer to a tube which was observed at different temperatures; it was placed in an electric thermostat whose temperature was kept steady within  $\frac{1}{4}^\circ\text{C.}$ ; the

\* Brace, *Phil. Mag.*, vi., 5, p. 161; 1903.

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temperatures in these cases were below  $100^{\circ}\text{C}$ ., so that alteration of the tartaric acid was not to be feared, and it was possible to wait a sufficiently long time and to allow proper time for careful readings. I have calculated the rotatory power by the ordinary formula, taking the density of the super-fused acid at 1.70, which was found by a determination made at ordinary temperature. For the last four series of measurements this density may certainly be accepted; for the solidified acid is glued to the walls of the polarimeter tube and withdrawn from the influence of dilatation. This may not quite hold for Series I, in which the acid was liquid.

I. Temperature  $180^{\circ}$  to  $185^{\circ}\text{C}$ .

|                        |     |                  |                  |                  |              |              |                  |
|------------------------|-----|------------------|------------------|------------------|--------------|--------------|------------------|
| Wave-length ...        | ... | 636              | 588              | 547              | 513          | 490          | 447              |
| Rotations observed ... | ... | $11^{\circ} 15'$ | $13^{\circ} 30'$ | $15^{\circ} 15'$ | $17^{\circ}$ | $18^{\circ}$ | $19^{\circ} 30'$ |
| Rotatory power ...     | ... | $13.25$          | $15.9$           | $18$             | $20$         | $21.15$      | $22.95$          |

II. Temperature  $100^{\circ}\text{C}$ .

|                    |                  |                  |                  |                  |                  |                 |                 |                  |
|--------------------|------------------|------------------|------------------|------------------|------------------|-----------------|-----------------|------------------|
| Wave-length ...    | 665              | 630              | 610              | 603              | 584              | 565             | 545             | 534              |
| Rotations observed | $7^{\circ} 48'$  | $8^{\circ} 10'$  | $8^{\circ} 32'$  | $8^{\circ} 57'$  | $9^{\circ} 16'$  | $9^{\circ} 37'$ | $10^{\circ} 8'$ | $10^{\circ} 27'$ |
| Rotatory power ... | $9.15$           | $9.60$           | $10.05$          | $10.5$           | $10.9$           | $11.3$          | $11.9$          | $12.25$          |
| Wave-length ...    | 516              | 512              | 510              | 499              | 490              | 486             | 465             | 447              |
| Rotations observed | $10^{\circ} 58'$ | $10^{\circ} 58'$ | $10^{\circ} 59'$ | $11^{\circ} 19'$ | $11^{\circ} 17'$ | $11^{\circ} 9'$ | $11^{\circ} 4'$ | $10^{\circ} 54'$ |
| Rotatory power ... | $12.9$           | $12.9$           | $12.9$           | $13.3$           | $13.25$          | $13.1$          | $13.0$          | $12.8$           |

III. Temperature  $67.6^{\circ}\text{C}$ .

|                    |     |                 |                 |                 |                |                 |                 |                 |
|--------------------|-----|-----------------|-----------------|-----------------|----------------|-----------------|-----------------|-----------------|
| Wave-length ...    | ... | 681             | 646             | 609             | 583            | 547             | 523             | 507             |
| Rotations observed | ... | $6^{\circ} 11'$ | $6^{\circ} 12'$ | $6^{\circ} 51'$ | $7^{\circ}$    | $7^{\circ} 12'$ | $7^{\circ} 20'$ | $7^{\circ} 25'$ |
| Rotatory power ... | ... | $7.28$          | $7.29$          | $8.06$          | $8.23$         | $8.47$          | $8.61$          | $8.72$          |
| Wave-length ...    | ... | 494             | 494             | 487             | 482            | 468             | 453             | 442             |
| Rotations observed | ... | $7^{\circ} 18'$ | $7^{\circ} 28'$ | $7^{\circ} 6'$  | $7^{\circ} 9'$ | $6^{\circ} 52'$ | $6^{\circ} 2'$  | $4^{\circ} 57'$ |
| Rotatory power ... | ... | $8.58$          | $8.78$          | $8.36$          | $8.41$         | $8.07$          | $7.10$          | $5.82$          |

IV. Temperature  $44.6^{\circ}\text{C}$ .

|                    |                 |                 |                 |                 |                 |                 |                 |                 |                 |
|--------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Wave-length ...    | 667             | 664             | 636             | 618             | 602             | 596             | 589             | 576             | 569             |
| Rotations observed | $4^{\circ} 10'$ | $4^{\circ} 20'$ | $4^{\circ} 24'$ | $4^{\circ} 20'$ | $4^{\circ} 38'$ | $4^{\circ} 39'$ | $4^{\circ} 26'$ | $4^{\circ} 20'$ | $4^{\circ} 25'$ |
| Rotatory power ... | $4.90$          | $5.10$          | $5.18$          | $5.10$          | $5.45$          | $5.47$          | $5.21$          | $5.27$          | $5.17$          |
| Wave-length ...    | 546             | 535             | 524             | 510             | 510             | 498             | 490             | 462             | 430             |
| Rotations observed | $4^{\circ} 18'$ | $4^{\circ} 23'$ | $4^{\circ} 3'$  | $4^{\circ} 8'$  | $4^{\circ}$     | $3^{\circ} 35'$ | $3^{\circ} 28'$ | $2^{\circ} 12'$ | $1^{\circ} 4'$  |
| Rotatory power ... | $5.06$          | $5.15$          | $4.76$          | $4.84$          | $4.71$          | $4.21$          | $4.07$          | $2.59$          | $1.26$          |

V. Temperature  $15^{\circ}\text{C}$ .

|                     |                 |                  |                 |                  |                 |                  |                  |                  |         |
|---------------------|-----------------|------------------|-----------------|------------------|-----------------|------------------|------------------|------------------|---------|
| Wave-length ...     | 679             | 664              | 629             | 613              | 592             | 581              | 571              | 550              | 538     |
| Rotations observed  | $1^{\circ} 15'$ | $1^{\circ} 23'$  | $1^{\circ} 5'$  | $1^{\circ}$      | $39'$           | $39'$            | $+20'$           | $-14'$           | $-18'$  |
| Rotatory power ...  | $1.47$          | $1.63$           | $1.27$          | $1.17$           | $0.76$          | $0.76$           | $0.39$           | $-0.27$          | $-0.35$ |
| Wave-length—        | 532             | 515              | 503             | 489              | 488             | 417              | 455              | 448              |         |
| Rotations observed— | $-43'$          | $-1^{\circ} 17'$ | $-2^{\circ} 1'$ | $-2^{\circ} 55'$ | $-3^{\circ} 1'$ | $-4^{\circ} 55'$ | $-6^{\circ} 12'$ | $-8^{\circ} 32'$ |         |
| Rotatory power—     | $-0.85$         | $-1.51$          | $-2.36$         | $-3.33$          | $-3.55$         | $-5.79$          | $-7.30$          | $-10.05$         |         |

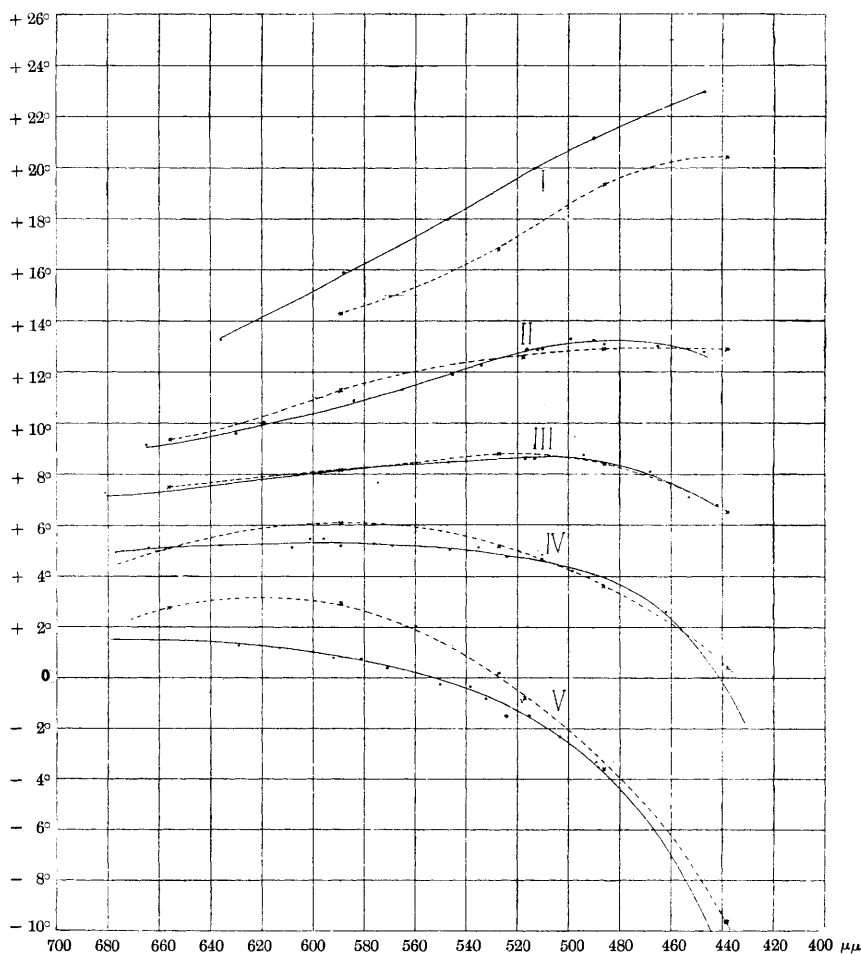
The drawn-out curves present these results. Their general character has been stated: the dispersion, normal for the liquid acid at  $180^{\circ}\text{C}$ ., becomes anomalous below  $100^{\circ}\text{C}$ .; the rotation diminishes for all radiations as

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the temperature is lowered, and the maximum rotation is at the same time displaced towards the red. The dotted curves represent the rotatory powers of aqueous and alcoholic solutions as studied by Arndtsen, and further, the rotatory powers of the pure acid extrapolated according to the formulæ of Arndtsen. The analogy of the two systems of curves is striking: *The cause*

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- I. Acid fused at  $180^{\circ}$ . 5 per cent. aqueous solution.  
 II. Acid superfused at  $100^{\circ}$ . 30 per cent. aqueous solution.  
 III. Acid superfused at  $67.6^{\circ}$ . 50 per cent. aqueous solution.  
 IV. Acid superfused at  $44.6^{\circ}$ . Solution in a mixture of water and alcohol.  
 V. Acid superfused at  $15^{\circ}$ . Pure acid by extrapolation from aqueous solution.



which produces the anomalous dispersion and its variation, both with the concentration and with the temperature, is the same for the solutions as for the pure acid.

The pure tartaric acid, liquid or superfused, must then contain, like the solutions, the two compounds in equilibrium to which we have ascribed the

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explanation of the anomalies. The hypothesis of the formation of hydrates must necessarily be rejected therefore. We might, on the contrary, suppose that the tartaric acid became dehydrated, and that the two compounds in equilibrium were the acid itself and an anhydride; but we could not then explain why the displacement of this equilibrium takes place in the same sense—corresponding to an increase in rotatory power—when we dilute the tartaric acid solution in water or in some other solvent (ethyl or methylalcohol, acetone, acetic acid) and when we raise the temperature of the fused acid. It will hence be advisable to reject this hypothesis as well.

The second compound which exists in the solutions or in the superfused mass can hence only be a complex compound, which is formed by the grouping of several molecules of tartaric acid. This compound will be destroyed by the dilution, in any solvent whatever, or by the elevation of the temperature; these two factors will thus act in the same sense and produce simple tartaric acid, whose rotatory power would be to the right, whilst that of the complex would be to the left and would increase the rotations. The rotations would, on the other hand, be diminished and might be made negative, as experiments indicate, by the addition to the solution of substances like benzene and its homologues which possess the well-known property of favouring polymerisation.

We may attempt to demonstrate the existence of such complex compounds by methods which enable us to determine the molecular mass of the bodies in solution. Aignan\* believed to have proved, by determining the osmotic pressure of a solution of 5 per cent., the existence of a compound  $(C_4H_6O_6)_2$ ; but his measurements do not inspire much confidence, and it appears safer to have recourse to freezing-point determinations. We know from Raoult that the diluted aqueous solutions of tartaric acid show normal depressions at the congelation points. I have taken up these experiments again, and I have followed them up to concentration of 70 g. of acid in 100 g. of water. Deviations from Raoult's law did not appear before the concentration exceeded 25 per cent., and these deviations were not in the expected sense, and must be ascribed merely to the insufficiency of Raoult's law for concentrated solutions. Solutions of tartaric acid in acetic acid also follow Raoult's law up to 2 per cent., and they do not deviate from it at higher concentrations more than solutions of other substances do.

We must then assume that, in aqueous solutions of 25 per cent., as well as in solutions in acetic acid of 2 per cent., all of which present a very marked anomaly in the rotatory dispersion with a maximum rotation in the blue or violet of the spectrum, the proportion of polymerised tartaric acid is very small and does not exceed 2 or 3 per cent. If we accepted this value, we might—the rotatory power of the non-polymerised tartaric acid being known, which is that observed in solutions at infinite dilution—calculate the rotatory power of the complex; we should then find values which vary from the line C to the line F, between about  $-80^\circ$  and  $-200^\circ$ . The high order of these figures has nothing extraordinary, when we suppose that we have to deal with molecular complexes which owe their rotatory power to the arrangement of the molecules, like the crystals. The values thus calculated for the rotatory power of the pure tartaric acid and of the molecular complex, the existence of which would give rise to the various anomalies, are altogether comparable to the values shown by the rubidium tartrate, whose rotatory power in solution is  $+25.63^\circ$ , and in the crystallised state  $-388^\circ$  (for the D line, along the optical axis). We might also compare these values with the still larger figures for the rotatory power of certain liquid crystals.

\* *Ann. de Chim. et Phys.*, vii., I, p. 433; 1894.