CXV.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part V. The Optical Activity of Certain Tartrates in Aqueous Solution.*

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ALTHOUGH the data relative to the rotation values of optically active compounds have greatly accumulated during the past ten or twenty years, it must nevertheless be admitted that the numbers obtained serve chiefly to show how complicated is the problem under investigation. Very few regularities are known, which can claim to be in any sense general, and we have learned merely that external influences such as the temperature, the nature of the solvent, the refrangibility of the light used, and probably also the pressure must all be carefully studied before the connection between rotation value and chemical constitution can be regarded as being more than purely empirical. The chief difficulty seems to lie in the fact that we have little or no means of judging as to when different active substances are in such conditions that their rotation constants are really comparable, and it therefore becomes of very great importance to study, not merely isolated rotation values of different compounds, but rather the variation which rotation is capable of undergoing with alteration of external conditions. Several researches (Trans., 1901, 79, 167 and 477; 1902, 81, 1097 and 1134) have been undertaken with this object, and the present paper is an account of further work in a slightly different direction.

Aqueous solutions of the sodium, potassium, potassium methyl,

potassium ethyl, potassium *n*-propyl, methyl, ethyl, and *n*-propyl salts of tartaric acid have been examined at several concentrations and at a number of different temperatures with the object of discovering: (1) the effect of temperature-change in each case; (2) whether the relationships amongst the data for the alkyl tartrates are simpler in dilute aqueous solution than in the homogeneous condition; (3) whether any connection can be established between the rotation of the tartaryl ion, the three alkyl-tartaryl ions, and the undissociated molecules of the three alkyl tartrates, all in dilute aqueous solution.

The data obtained in the investigation of the foregoing substances will be found collected together at the end of the paper, whilst the general results are shown by the various curves. The strengths (*p*) of the solutions represent grams of anhydrous substance per 100 grams of solution.

Optical Behaviour of the Compounds Examined.

Sodium Tartrate.—The results obtained in the examination of this salt are shown in Fig. 1, which represents the dependence of mole-

FIG. 1.—Molecular rotation of aqueous solutions of sodium tartrate.

cular rotation on concentration and temperature, but is reproduced chiefly on account of the temperature effect, which in all the solutions dealt with in this investigation is of very considerable interest.

Six solutions of sodium tartrate were examined, but in two cases the observations did not extend over any great range of temperature, and therefore only four curves are shown.

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In the most dilute solution ($p=1.5$) it will be noticed that the molecular rotation gradually increases as the temperature rises, but more rapidly at low temperatures than at higher ones, and since in this solution we may assume the substance to be nearly completely dissociated, this curve practically represents the effect of change of temperature on the tartaryl ion in aqueous solution. The next curve ($p=8.56$) shows a generally similar behaviour, but here the rotation reaches a maximum value ($+61.15^\circ$), about 67° , and then diminishes slightly to $+60.6^\circ$ at 100° . The curve for $p=25.06$ is somewhat flatter; a maximum ($+57.8^\circ$) is reached at 55° , and the subsequent diminution in rotation to $+57^\circ$ at 100° is a little greater than before. In the solution having $p=32.9$, the maximum occurs at 50° and the diminution to 100° is 1.2° .

One of the most interesting points about these curves is the occurrence of maximum rotations, but, as will appear subsequently, this is by no means an uncommon phenomenon, and its discussion may be meantime deferred (see p. 1135).

From the curves of Fig. 1 and the data on p. 1143 we find by interpolation the following numbers:

p .	$[M]_D^{20^\circ}$.	$[M]_D^{100^\circ}$.	p .	$[M]_D^{20^\circ}$.	$[M]_D^{100^\circ}$.
1.499	$+60.90^\circ$	$+63.73^\circ$	25.06	$+56.98^\circ$	$+57.00^\circ$
4.154	60.05	—	32.873	54.98	54.10
8.561	59.66	60.60	49.35	—	46.27

From these values, the two curves for sodium tartrate shown in Fig. 3 have been obtained. One of these represents the behaviour of this substance on dilution at 20° , from which it would appear that the tartaryl ion has a greater rotation than undissociated sodium tartrate. By extrapolating to zero concentration, the rotation of the tartaryl ion is found to be very nearly $+61.5^\circ$, and by extrapolating in the opposite direction, which is very much less accurate, the homogeneous salt would appear to have a molecular rotation of about $+15^\circ$.

The second curve for 100° is quite similar in character. Dilute solutions show a higher rotation at 100° than at 20° , but the difference between these values gradually diminishes, until at $p=25$ the rotations at 100° and at 20° are the same. The curve for 100° then falls below that for 20° , from which it may be concluded that whilst the rotation of the ion increases with rise of temperature, the undissociated compound shows the opposite behaviour. By extrapolation, we find for $p=0$, $[M]_D^{100^\circ} = +63.5^\circ$, and for $p=100$, $[M]_D^{100^\circ} = +10^\circ$ (approximately).

Potassium Tartrate.—In Fig. 2 (p. 1119), several of the temperature-rotation curves for potassium tartrate are shown. As regards the influence of temperature-change, the behaviour is, in general, similar to

that of sodium tartrate. The rotation of the most dilute solution ($p=5.43$) increases by some 3° between 0° and 100° . When $p=9.97$, a maximum becomes apparent at about 65° , but is not very pronounced; for $p=39.09$, there is a maximum at 40° , whilst in the next solution ($p=62.61$) the rotation continuously diminishes, so that the behaviour of a concentrated solution, in which we may suppose the influence of the undissociated compound to preponderate, is in striking contrast to that of the most dilute solution, which we may regard as representing the influence of temperature-change on the free ion. From these

FIG. 2.—Molecular rotation of aqueous solutions of potassium tartrate.

curves, and the data on p. 1144, we find by interpolation or extrapolation the following figures:

p .	$[M]_D^{20^\circ}$.	$[M]_D^{100^\circ}$.	p .	$[M]_D^{20^\circ}$.	$[M]_D^{100^\circ}$.
5.429	+63.20°	+64.10°	39.09	+67.40°	+65.25°
9.974	64.15	64.94	56.53	69.01	64.17
25.647	66.56	66.10	62.61	69.19	63.40
30.890	66.90	65.90			

The curves obtained from these data are shown in Fig. 3 (p. 1120). They represent a behaviour different from that of the sodium salt, for it will be noticed that at 20° the rotation increases steadily with increasing concentration, and, therefore, the rotation of undissociated potassium tartrate is greater than that of the tartarylion. By extrapolation

to $p=0$, we find, as might be expected, a value for the rotation of the ion practically identical with that obtained from the curve for the sodium salt; the value $+61.5^\circ$, to which both curves apparently tend, is certainly a close approximation to the truth, and is all the more trustworthy in that the two curves approach it from opposite directions.

On account of the greater solubility of the potassium salt, it is possible to examine strong solutions, and therefore extrapolation to

FIG. 3.—Relationship between concentration and molecular rotation of sodium and potassium tartrates in aqueous solution.

$p=100$ is fairly reliable. The value thus obtained for the homogeneous substance is $[M]_D^{20} + 70^\circ$, which is much greater than the corresponding rotation for the sodium salt.

The curve for 100° reaches a maximum value at about $p=30$. Extrapolation to $p=0$ gives us in this case for the ionic rotation the value $+63^\circ$, which is close to that found from the curve for sodium tartrate ($+63.5^\circ$). Taking the mean of the two values, we find $+63.25^\circ$ as the rotation of the tartaryl ion at 100° in water at infinite

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dilution, an estimate which is probably within 0.5 per cent. of the truth.

Extrapolating in the other direction, we find for the rotation of the

FIG. 4.—Molecular rotation of aqueous solutions of potassium methyl tartrate.

homogeneous salt at 100° the value +58°. The value at 20° was +70°, from which it appears that if homogeneous potassium tartrate

could exist in the liquid condition between 20° and 100° its rotation would rapidly diminish with rise of temperature in the manner shown by the broken line in Fig. 2.

Potassium Methyl Tartrate.—The influence of temperature-change on the rotation of solutions of potassium methyl tartrate is clearly shown by the curves in Fig. 4 (p. 1121).

In the most concentrated solution ($p=47$), a maximum rotation probably occurs at 82° . The curve for $p=25$ is similar, but here there is no doubt about the occurrence of a maximum rotation, which lies at or very near to 64° . For $p=15.2$, a distinct maximum rotation occurs at 57° . The curve for $p=5.3$, the most dilute solution examined, shows the same general characteristics, the maximum rotation being found at 49° .

By interpolation from the curves in Fig. 4, the following table is obtained:

p .	$[M]_D^{20^\circ}$.	$[M]_D^{100^\circ}$.	p .	$[M]_D^{20^\circ}$.	$[M]_D^{100^\circ}$.
5.3067	$+45.99^\circ$	$+45.50^\circ$	24.9555	$+42.02^\circ$	$+43.50^\circ$
15.1501	44.00	44.70	47.085	37.54	40.45

These data are plotted in Fig. 7. By extrapolation to $p=0$, the value found for the rotation of the methyl tartaryl ion is $+46.7^\circ$ at 20° , and by extrapolation in the opposite direction the value $[M]_D^{20^\circ} = +24.8^\circ$ is deduced for the superfused homogeneous salt.

A similar examination of the curve for 100° gives $+45.8^\circ$ for the rotation of the ion and $+31.1^\circ$ for that of the homogeneous substance.

These data may be employed in obtaining the theoretical curve showing the influence of temperature-change on the ionic rotation. At 20° , this curve must pass through $+46.7^\circ$, and at 100° through the point $+45.8^\circ$. The other points on the curve may be found with sufficient exactitude by general appearance and from one other important criterion, namely, the occurrence of maximum rotations. These maxima are found at different temperatures according to the concentration of the solution, the maximum rotation being gradually displaced towards lower temperatures as the concentration diminishes, and it is of interest to notice that this displacement is very nearly a linear function of the concentration. This is shown by the fact that a straight line (see Fig. 4) may be drawn through the four maxima. By analogy, therefore, all the other maxima possible for solutions of intermediate concentration should lie along this line, which should thus also pass through the point of maximum rotation of the ion. From these considerations, the broken curve marked methyl tartaryl ion has been drawn. The maximum ionic rotation would occur at or near 46.5° , the corresponding rotation being $+48.1^\circ$.

Potassium Ethyl Tartrate.—The curves for this salt in Fig. 5 (p. 1123)

show the same general characteristics as those for potassium methyl tartrate, but some of the peculiarities noted in the behaviour of the latter are more pronounced, as will be seen by comparing the curves in pairs of corresponding concentrations.

FIG. 5.—Molecular rotation of aqueous solutions of potassium ethyl tartrate.

The rotation of the most dilute solution ($p=5.07$) examined reaches a distinct maximum at 38°, the corresponding rotation being +59.95°. For $p=15.1$, the maximum occurs at a temperature of 46°, the rotation being +57.74°. A solution of $p=34.75$ shows a maximum at 53°, when the rotation is +54.9°, whilst in the last curve

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a distinct maximum is still apparent at 56° , the rotation being $+52.9^\circ$. Since the maximum in the corresponding curve for potassium methyl tartrate has almost vanished, it would appear that the maximum rotation in solutions of potassium ethyl tartrate persists up to greater concentrations than in solutions of the former. In this case also the point of maximum rotation is displaced towards a lower temperature as the concentration diminishes, and this displacement is again linear, as is shown by the straight line passing through the four maxima. The maximum ionic rotation should therefore lie on this line.

The following table has been obtained by interpolation from the experimental data:

p .	$[M]_D^{20^\circ}$.	$[M]_D^{100^\circ}$.	p .	$[M]_D^{20^\circ}$.	$[M]_D^{100^\circ}$.
5.06845	+59.06°	+56.35°	34.747	+53.68°	+53.12°
15.1035	56.95	55.27	46.787	51.02	51.92

Fig. 7 (p. 1126) is obtained partly from these data, and by extrapolation to $p=0$ the values obtained for the ethyl tartaryl ion are $+60^\circ$ at 20° , and $+57^\circ$ at 100° , whilst by extrapolation in the opposite direction we find for the superfused salt, if it could exist in this condition at these temperatures, the values $+41.7^\circ$ at 20° , and $+46.8^\circ$ at 100° . At lower concentrations, the curve for 20° lies above that for 100° , at higher concentrations, the reverse obtains.

The curve showing the behaviour of the ion with variation of temperature (Fig. 5) can be deduced from these data. It must pass through the points $+60^\circ$ at 20° and $+57^\circ$ at 100° , and the maximum rotation must lie on the line passing through the other maxima. The curve marked ethyl tartaryl ion has been obtained in this manner, and hence it may be concluded that the maximum ionic rotation occurs at 37° and has the value $+60.7^\circ$.

Potassium n-Propyl Tartrate.—The curves for this salt, which are shown in Fig. 6 (p. 1125), differ only in detail from those of Figs. 4 and 5. In the three solutions examined, the initial increase of rotation up to the maximum is not so rapid as in corresponding solutions of the other esters, whilst the subsequent diminution is more rapid. The maximum rotation is well marked in all three solutions, and again these points lie approximately along a straight line on which, presumably, the maximum ionic rotation should also fall.*

The data given in the following table are obtained from the three curves:

p .	$[M]_D^{20^\circ}$.	$[M]_D^{100^\circ}$.
4.989	+63.63°	+60.40°
25.01	60.48	58.80
48.46	57.30	57.54

* It was found somewhat difficult to purify this compound so as to obtain perfectly clear solutions for examination (see p. 1148). The results are therefore not quite so accurate as those for the other esters.

The concentration-rotation curves obtained from these data and shown in Fig. 7 may in the first place be compared with the curves given for the other two analogous esters. It will be noticed that variation of concentration produces the greatest effect on the rotation of the methyl ester, both at 20° and at 100° . In this respect the ethyl compound comes next, whilst the rotation of potassium *n*-propyl

FIG. 6.—Molecular rotation of aqueous solutions of potassium *n*-propyl tartrate.

tartrate is least affected. In all three esters the effect of varying concentration is considerably less at 100° than at 20° , so that in the case of the *n*-propyl compound there is not much difference between the rotation of the homogeneous substance at 100° , and that of the ion at the same temperature.

The two concentration curves intersect one another at $p = 45$, and it

may be noticed that this and the corresponding points, $p=27.3$ for the ethyl ester and $p=10$ for the methyl ester, lie very nearly on the straight line shown in the diagram (Fig. 7).

By extrapolation of the two curves, the ionic rotations $+64.7^\circ$ at 20° and $+60.8^\circ$ at 100° are obtained, the rotations of the homogeneous

FIG. 7.—Relationship between concentration and molecular rotation of potassium alkyl tartrates at 20° and 100°

salt being $+51^\circ$ at 20° and $+55.5^\circ$ at 100° . From these data and also from general appearance, the curve in Fig. 6 marked *n*-propyl tartaryl ion has been drawn, and it may be concluded that the maximum ionic rotation occurs at a temperature of 34° , and has the value $+65.1^\circ$.

Methyl Tartrate.—The experiments were carried out in this case in

FIG. 8.—*Molecular rotation of aqueous solutions of methyl tartrate.*

just the same way as with the other substances, although it might perhaps be expected that methyl tartrate, when heated with water at 100°, would undergo hydrolysis to such an extent as to vitiate the

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results. The present experiments show, however, that in these circumstances, methyl tartrate undergoes very little decomposition.

In Fig. 8 (p. 1127), the various concentration-rotation curves obtained are shown. In the case of an ester, which can be examined in the homogeneous liquid condition, a more complete investigation of the rotation phenomena is possible than with the foregoing metallic salts, since the values for the homogeneous ester itself are known, so that there is less necessity for extrapolation.

The molecular rotation of methyl tartrate is small, being only $+3.68^\circ$ at 20° , but it rises considerably on heating, reaching the value $+11.00^\circ$ at 100° —an increase of 7.32° . The addition of a comparatively small quantity of water, so as to give a solution having $p=75$, has a very pronounced effect on the rotation, raising it by more than thirteen degrees to the value $+16.8^\circ$ at 20° . At the same time, however, the influence of temperature-change becomes much less marked, the increase of rotation between 20° and 100° being only 1.9° . Further dilution to $p=49.77$ brings about an increase in rotation to $+26.2^\circ$, and at this concentration an alteration in sign takes place in the influence of temperature-change, the rotation of this solution at 100° being $+23.71^\circ$. Further dilution increases the rotation at a somewhat diminishing rate, and, as the rotation increases, the temperature-coefficient becomes more distinctly negative. The behaviour of a dilute aqueous solution of methyl tartrate therefore presents a striking contrast to that of the homogeneous ester.

Interpolation from these curves gives the following table:

p .	$[M]_D^{20^\circ}$.	$[M]_D^{100^\circ}$.	p .	$[M]_D^{20^\circ}$.	$[M]_D^{100^\circ}$.
5.169	$+37.40^\circ$	$+31.72^\circ$	49.77	$+26.15^\circ$	$+23.71^\circ$
10.23	36.40	30.44	74.87	16.92	18.72
24.88	33.30	28.25	100.00	3.68	11.00

From these data, the concentration-rotation curves in Fig. 11 have been drawn. By extrapolation, the molecular rotations at infinite dilution are found to be $+38.5^\circ$ at 20° and $+32.2^\circ$ at 100° .

Ethyl Tartrate.—The data given in a former paper (Trans., 1901, 79, 171) regarding the optical behaviour of aqueous solutions of ethyl tartrate are unfortunately insufficient to allow of a satisfactory estimate of the rotations of the various solutions at 100° . The behaviour of ethyl tartrate has accordingly been re-examined.

The rotation-temperature curves are shown in Fig. 9 (p. 1129). They are, on the whole, similar to those for methyl tartrate, but there is one point of interest at least in which they differ, which could not have been observed from the previous results. It will be noticed that the curves for $p=5$, $p=10.08$, and $p=25.03$ at low temperatures, that is, between 0° and 40° , are concave to the horizontal axis. As the tempera-

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FIG. 9.—Molecular rotation of aqueous solutions of ethyl tartrate.

ture rises, the rate of diminution of rotation increases. But at a certain temperature, which is higher the more dilute the solution, a change takes place, the curves become convex, the rate of diminution

of rotation becomes less, and the curves therefore show a point of inflection. As the concentration of the solutions increases, the initial concave part of the curve gradually disappears towards the left in such a way that the curve for $p = 50.2$ has, between 0° and 100° , only a convex appearance. The departure in these instances from the somewhat simpler shape of curve characteristic of methyl tartrate is but slight, and, had only one curve been examined, might well have been regarded as being due to experimental error, but since all four curves show an analogous behaviour, the more complex character of the ethyl tartrate curve must be admitted. This peculiar form is, however, only slightly marked in a solution with $p = 50.2$, and it is therefore not surprising that for the more concentrated solution ($p = 75$) the curve bears a much closer resemblance to that for the homogeneous ester.

By interpolation from these curves, the following table is obtained :

p .	$[M]_D^{20^\circ}$.	$[M]_D^{100^\circ}$.	p .	$[M]_D^{20^\circ}$.	$[M]_D^{100^\circ}$.
5	+54.6°	+45.30°	50.225	+36.10°	+33.82°
10.08	53.5	43.80	75	24.40	30.15
25.03	48.73	39.30	100	15.78	27.75

It might naturally be expected that ethyl tartrate would be affected by solution in water in just the same manner as methyl tartrate, and that any difference observed would be of degree only. It has, however, just been pointed out that with regard to temperature-change in dilute solution the two esters do not behave quite similarly, and the curves in Fig. 11, drawn from the above data, show that both at 20° and at 100° there are also well-marked differences in the influence of varying concentration.

Similarly, it should be noticed that the two concentration curves for ethyl tartrate are not of the same shape, that for 100° resembling only one-half (from $p = 50$ to $p = 100$) of that for 20° .

By extrapolation of these curves, the molecular rotation of ethyl tartrate at 20° appears to be very nearly +55.3° at infinite dilution, whilst at 100° it has the value +46.8°.

n-Propyl Tartrate.—On account of the fact that *n*-propyl tartrate is not miscible in all proportions with water, the observations made with it could not be so complete as with the other two esters. A preliminary trial showed that a solution of $p = 10$ (approximately) could be made in the cold, and the first solution examined was nearly of that strength. When the solution was heated to about 30° , however, it became milky and drops of *n*-propyl tartrate separated.*

* *n*-Propyl tartrate, therefore, becomes less soluble in water with rise of temperature, and may, in this connection, be employed in a lecture experiment. By shaking up water and the ester at the ordinary temperature for a few seconds and allowing to

It was impossible to determine the rotation of this solution above 24° , whilst the next, for which $p = 6.99$, just began to turn milky at 77° . A

FIG. 10.—*Molecular rotation of n-propyl tartrate.*

third solution, $p = 7.006$, was also examined, but, like the other two, only through a somewhat limited range of temperature. The most settle, an upper aqueous layer is obtained, which almost immediately becomes turbid if the tube be held in the hand or immersed in warm water.

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important of the solutions of *n*-propyl tartrate investigated was that of $p=4.017$, since its rotation and density could be determined up to 100° .

The curves for this solution and the homogeneous ester are shown in Fig. 10 (p. 1131), the contrast between them being very striking. Whilst the rotation of the pure ester increases by some 16° between 0° and 100° , that of the dilute solution diminishes by an almost exactly equal amount; the line for the solution is straight, whilst that for the ester is curved; the rotation of the dilute solution at 0° is more than 2.5 times as great as that of the pure ester at the same temperature, whereas they would probably be almost equal at a temperature of 130° . It may also be noticed that in respect to temperature-change the dilute solution behaves somewhat differently from both methyl and ethyl tartrates, the curve being apparently a straight line.

Owing to the insolubility of the ester, it is in this case not possible to draw a complete concentration-rotation curve, which is unfortunate because, since dilution has different effects on methyl and ethyl tartrates, it would be most interesting to know how the rotation of *n*-propyl tartrate would be modified by the same cause.

The following data, obtained by interpolation from the experimental data, show the influence of concentration change so far as it could be determined in this case.

p .	$[M]_D^{20^{\circ}}$.	$[M]_D^{100^{\circ}}$.	p .	$[M]_D^{20^{\circ}}$.	$[M]_D^{100^{\circ}}$.
4.017	+62.01°	+49.3°	7.006	+60.79°	—
6.995	61.18	—	10.02	58.85	—

From the results obtained it would appear that the initial part of the curve for 20° resembles the initial part of the ethyl tartrate curve, and this in turn between $p=0$ and $p=50$ resembles the whole of the methyl tartrate curve, as will be seen from Fig. 11 (p. 1133). It is not possible to state exactly what the remainder of the *n*-propyl tartrate curve would be like, but it would probably resemble that for ethyl tartrate as shown by the broken line in Fig. 11.

By extrapolation, the molecular rotation at infinite dilution is found to be $+63^{\circ}$ at 20° and $+49.6^{\circ}$ at 100° .

General Consideration of Results.

That each of the three classes of compounds examined shows a characteristic behaviour, especially as regards the influence of temperature-change, is quite in agreement with the dissociation theory. It is to be expected that solutions of the three alkyl tartrates, containing undissociated molecules, would differ markedly from solutions of the potassium alkyl tartrates, but only in detail from each other, and that

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FIG. 11.—Relationship between concentration and molecular rotation of alkyl tartrates at 20° and 100°.

both these series should in turn differ from sodium or potassium tartrate.

On the other hand, several facts may be noted which do not at first sight accord so well with the ionic theory. A reference to Figs. 3, 7, and 11 will show that, with one exception, all the compounds examined behave in the same manner with regard to variation in concentration. This exception is potassium tartrate, the rotation of which (at 20°) diminishes with dilution, whilst the rotations of all the other substances increase. It is not surprising that the concentration-rotation curves shown in Fig. 7 for the potassium alkyl tartrates should resemble each other, but it could scarcely have been expected that the curves in Fig. 11 for methyl tartrate should also be of very nearly the same type. This nevertheless is the case. The methyl tartrate curves bear, indeed, a greater likeness to the potassium alkyl tartrate curves than they do to those for ethyl tartrate.

Now the influence of dilution on methyl tartrate solutions must be ascribed to solvent action. It is almost certain that there is at least no ionic dissociation. But in potassium methyl tartrate, for instance, both ionic dissociation and solvent action are effective. It might therefore be imagined that, as dilution increases, the solvent action of the water, together with the gradual production of methyl tartaryl ions, which are much less symmetrical than the methyl tartrate molecule, would have a very pronounced effect on the shape of the concentration-rotation curve. Since, however, the curves are very similar, it must be assumed that the greater part of the alteration of rotation with variation of concentration is due to solvent action, and that the effect of the dissociation of the molecules into ions (as distinct from solvent action) is of much less importance, as will be seen from the following table.

Molecular Rotation at 20°.

	Potassium methyl tartrate.	Δ.	Methyl tartrate.	Δ.	Ethyl tartrate.	Δ.
At infinite dilution...	+ 46·7°		+ 38·50°		+ 55·30°	
Homogeneous salt ...	24 8	21·9°	3·68	34·82°	15·78	39·52°

Thus the total change in the rotation of methyl tartrate due to solution in water is 34·8°, whilst the total change in the rotation of potassium methyl tartrate is considerably less, namely, 21·9°. Now since the total change in the rotation of ethyl tartrate due to solution is only slightly greater than the corresponding change in the rotation of methyl tartrate, it may be assumed that if no dissociation were to take place in potassium methyl tartrate with increasing dilution its rotation also would undergo a change of more than 30° due to solvent action alone. The actual change is, however, less, and this must be

ascribed to the influence of dissociation, which thus exercises a depressing effect on the rotation of potassium methyl tartrate, the opposite to what might, at first sight, be expected. An undissociated molecule in dilute solution has a greater rotation than an ion in the same circumstances.

Again, in spite of the fact that the formula of the molecule of potassium methyl tartrate (or the methyl tartaryl ion) appears more asymmetric than that of the methyl tartrate molecule, there is comparatively little difference in the behaviour of the two substances as regards change of concentration.

A close similarity might have been expected between the normal alkali tartrates and the three alkyl esters, but, on the contrary, the two series are markedly dissimilar. As regards the influence of temperature-change, the two metallic salts behave alike; the rotations of the homogeneous substances diminish with rise of temperature, whereas in dilute solution they increase. With rise of temperature, all three homogeneous esters, however, show a rapidly increasing rotation, whilst in dilute solution the rotation as rapidly, or almost as rapidly, diminishes. Thus, although in the homogeneous state all the molecules are of the same type, $T \angle_R^R$, the behaviour of the two series is quite

different, whilst in dilute solutions, where the active groups $T \angle$ and $T \angle_R^R$ are, it might be imagined, at least of the same degree of asymmetry, the behaviour is again opposite.

The Occurrence of Maximum Rotations.—It has been shown in the foregoing part of this paper that in several cases maximum rotations occur in certain solutions at definite temperatures, and that in one instance a maximum is apparent in a concentration-rotation curve. The latter, which represents the behaviour of potassium tartrate at 100°, is shown in Fig. 3, and may possibly be explained in the following manner.

The rotation of the homogeneous salt at 100° is +58.2°. The addition of water gradually increases the rotation of the dissolved substance in much the same way that the rotation of the alkyl tartrates is increased by dilution. On account of this analogy, and also because down to a concentration of about $p=50$ there is not likely to be much dissociation, this increase in rotation must be ascribed almost entirely to solvent action. If no dissociation at all occurred, then probably the rotation would constantly increase with further dilution. At medium concentrations, however, dissociation becomes appreciable, and potassium tartaryl ions, TK^- , are first formed. Since this brings about a diminution of rotation, these must have a smaller rotation

than the dissolved, undissociated molecule. The curve tends to become, and at $p = 30$ does become, horizontal. With further dilution, tartaryl ions form, and, as these have a still lower rotation, their gradual increase in solution is attended with a constant diminution of rotation. The maximum, therefore, occurs at the concentration at which the potassium tartaryl ions preponderate.

A similar explanation will account for the form of the concentration curve at 20° , but at this temperature it should be noticed that the solvent action of water at high concentrations is not so marked as at 100° . The rotation of an undissociated molecule of potassium tartrate in dilute solution at 20° would presumably be almost the same as the molecular rotation of the homogeneous compound. The concentration-rotation curve, therefore, if no dissociation took place, would be nearly a horizontal straight line. Dissociation into potassium tartaryl ions causes the downward tendency of the curve, which becomes more rapid as dilution increases and tartaryl ions are formed.

It would appear, therefore, that in addition to other points already mentioned, the metallic salts of tartaric acid show an opposite behaviour in respect to the solvent action of water, since, as has just been shown, dilution in concentrated solutions of sodium and potassium tartrates causes a greater increase of rotation at 100° than at 20° , whereas dilution of solutions of the alkyl tartrates produces a much more marked effect at 20° than it does at 100° .

The occurrence of maxima in rotation-temperature curves is rare, the first instance of this having been discovered by P. F. Frankland and Wharton (*Trans.*, 1896, 69, 1587), who showed that ethyl dibenzoyltartrate in the homogeneous condition has a pronounced maximum rotation at 60° . The next examples were discovered by Grossmann and Pötter (*Ber.*, 1904, 37, 84), who found that ammonium and sodium molybdanylbimalates in solutions of several concentrations show maximum rotations at 35° and 50° respectively. In the present paper, five other instances at least are described.

In solutions of potassium and sodium tartrates, the maxima are not very pronounced. They can also be readily explained. Since in very dilute solutions of these salts (Figs. 1 and 2) the rotation increases with rise of temperature, at first fairly rapidly, afterwards more slowly, whilst concentrated solutions show an opposite behaviour, the rotation constantly diminishing and rather less rapidly at low temperatures than at higher ones, it seems clear that in solutions of intermediate concentration the influence of the dissociated molecules will preponderate at low temperatures, causing, on the whole, a slight increase of rotation, whilst at higher and increasing temperatures, on the other hand, when the rotation of the dissociated molecules is almost constant, the form of the curve will be chiefly determined by the behaviour of

the undissociated substance present, in consequence of which the rotation diminishes.

The maxima in the rotations of the potassium alkyl tartrates are more interesting and much more pronounced. They are not due to the different behaviour of coexistent but dissimilar active groups, since even the ionic rotations show distinct maxima. Nevertheless, the following explanation—if it is correct—somewhat resembles that given above. From Figs. 8, 9 and 10, it will be seen that, in dilute solution, the rotations of the alkyl tartrates rapidly increase with fall of temperature. On the other hand, the rotations of sodium and potassium tartrates, in dilute solution, increase as the temperature rises.

Now the methyl tartaryl ion, for example, is composed of two parts, one of which, $\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\cdot\text{CH}_3$, is the same as either half of the methyl tartrate molecule, whilst the other part, $\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\cdot$, is the same as one half of the tartaryl ion. It is therefore possible that in dilute solution each of these parts produces the same effect that it exerts when united to another group like itself. On heating from low temperatures up to about 30° , the influence of the former group is to depress the rotation, whilst that of the latter is to increase it. Thus there are two opposing influences at work, and at first the ionised group exercises the preponderating effect, an increase of rotation being the net result. At a certain temperature, that at which the maximum occurs, these influences become equal. When this temperature has been passed, the group

obtains the ascendancy, and in consequence the rotation diminishes on further heating.

That this supposition is correct seems to be borne out by the following considerations. It will be noticed from Figs. 8, 9, and 10 that the rotation of a methyl tartrate solution ($p=5.17$) between 0° and 100° diminishes by 6° . For ethyl tartrate, the diminution ($p=4.9989$) is 10.2° , whilst for propyl tartrate ($p=4.02$) the rotation falls by 15.7° . We should therefore expect from these figures that the influence of the group $\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{R}$ would be more marked in potassium propyl tartrate than in potassium ethyl tartrate, and in the latter more than in potassium methyl tartrate. The influence of the group $\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\cdot$ should therefore, on the other hand, be most apparent in potassium methyl tartrate, so that the initial rise in the curve for this substance should be more rapid and continue further than in the curves for the other two compounds, and the diminution after the maximum is passed should be less. This is in reality what happens. The temperature of maximum rotation is higher for the methyl than for the ethyl compound, and for the latter higher than for potassium propyl tartrate,

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whilst the initial rise and subsequent fall in rotation show just the gradation that might be expected.

Now, although maximum rotations are most apparent in the five instances mentioned, it may be noticed that perhaps there is also a maximum in the methyl tartrate solution ($p=49.77$), and it is practically certain that temperature-rotation curves for solutions of concentrations between $p=50$ and $p=70$ would exhibit this phenomenon more definitely. As can easily be deduced from the curves in Fig. 4, a solution of $p=66$, for instance, would show a maximum at a temperature near 50° .

Maximum rotations of this kind can scarcely be explained in either of the two ways mentioned above. The phenomenon must be due solely to solvent action. There is no dissociation to account for it. The form of the curve represents a compromise between the behaviour of the homogeneous ester and its very dilute solutions. The rotation of the pure ester at low temperatures increases on heating, much more rapidly than that of the dilute solution diminishes, whilst at higher temperatures the rotation of the dilute solution diminishes more rapidly than that of the homogeneous ester increases. The net result therefore in a solution of intermediate concentration is a slight initial increase to a somewhat indistinct maximum, with a subsequent slight diminution.

Comparison of Rotation Values.

The rotations of the alkyl tartrates in the homogeneous condition and in solution are contrasted in the following table:

	$[M]_D^{20^{\circ}}$		$[M]_D^{100^{\circ}}$	
	Homogeneous ester.	Infinitely dilute solution.	Homogeneous ester.	Infinitely dilute solution
Methyl tartrate.....	+3.68°	+38.5°	+11.00°	+32.2°
Ethyl „	15.78	55.3	27.75	46.8
n-Propyl „	29.66	63.0	40.60	49.6

The total modification of rotation due to solution in each case is most conveniently shown as follows:

Total Change of Molecular Rotation due to Solution.

	20°.	100°.	Δ .
Methyl tartrate.....	34.82°	21.20°	13.62
Ethyl „	39.52	19.05	20.30
n-Propyl „	33.34	9.00	24.34

It is apparent from these numbers that the increase of rotation due to solution is by no means a constant function of the original rotation, the values for methyl, ethyl and n-propyl tartrates in infinitely dilute solution at 20° being respectively 10.46, 3.467, and 2.124 times

as great as the values in the homogeneous condition. On the contrary, the actual increase in rotation at 20° —on the average about 36° —is approximately the same in all three cases, but at 100° , although the alterations in rotation for methyl and ethyl tartrates are again nearly equal, their order of magnitude is reversed, whilst the change for *n*-propyl tartrate is less than half as great as that for either of the other two esters.

The only regularity observable is found in the differences between these numbers, which increase as the series is ascended. That is to say, the change in the rotation of methyl tartrate due to solution is 13.62° less at 100° than at 20° , the figures for ethyl and *n*-propyl tartrates being 20.30° and 24.34° respectively. Temperature-change therefore makes itself most distinctly felt in the case of the *n*-propyl ester and least in that of the methyl ester.

For the potassium alkyl tartrates, we have the following data :

	$[M]_D^{20^\circ}$		$[M]_D^{100^\circ}$	
	Homogeneous substance.	Infinitely dilute solution.	Homogeneous substance.	Infinitely dilute solution.
Potassium methyl tartrate...	+24.8°	+46.7°	+31.1°	+45.8°
„ ethyl „ ...	41.7	60.0	46.8	57.0
„ <i>n</i> -propyl „ ...	51.0	64.7	55.5	60.8

The changes in rotation due to solution are shown below :

Total Change of Molecular Rotation due to Solution.

	20°	100°	Δ
Potassium methyl tartrate	21.9°	14.7°	7.2
„ ethyl „	18.3	10.2	8.1
„ <i>n</i> -propyl „	13.7	5.3	8.4

It will be noticed that the change in rotation due to solution is slightly less for the ethyl than for the methyl compound and least for the *n*-propyl ester. At 100° , the order of magnitude of the changes is the same as at 20° , but the changes are considerably smaller, and by nearly equal amounts, as shown in the column marked Δ . Thus the change due to solution for potassium methyl tartrate is 7.2° , for potassium ethyl tartrate, 8.1° , and for potassium propyl tartrate, 8.4° less at 100° than at 20° , numbers which show at least the same gradation as those for the corresponding alkyl tartrates. Indeed, the whole general behaviour of the potassium alkyl tartrates is not unlike that of the alkyl tartrates, another indication that the influence of dissociation is comparatively slight.

It is obvious from the data given above and from the various diagrams that solution in water greatly modifies the rotations of the tartrates under consideration. It was suggested on p. 1117 that the

relationships amongst the data for dilute solutions might show greater regularity than those for the pure compounds, since the former may all be regarded as being determined under the same external conditions. The following tables show to what extent this is the case:

	[M] _D ^{20°}			[M] _D ^{100°}		
	Homogeneous substance.	Δ.	Infinite dilution.	Homogeneous substance.	Δ.	Infinite dilution.
Methyl tartrate	+3.68°	12.27°	+38.5°	+11.40°	16.75°	+32.2°
Ethyl "	15.95	13.71	55.3	27.75	46.8	14.6°
n-Propyl "	29.66		63.0	40.60	12.85	2.8
Potassium methyl tartrate	+24.8°	16.9°	+46.7°	+31.1°	15.7°	+45.8°
" ethyl "	41.7	9.3	60.0	46.8	57.0	11.2°
" n-propyl "	51.0		64.7	55.5	8.7	60.8

It will be noticed, as has been previously pointed out (this vol., p. 770), that the increase of rotation in passing from methyl tartrate to the ethyl ester is less at 20°, but greater at 100°, than the increase in passing from ethyl to n-propyl tartrate. This is very possibly due to an incorrect choice of temperatures at which to institute comparisons, for it might certainly be expected that the first increment of 2CH₂ should produce a greater effect on rotation than the second. It is, therefore, interesting to observe that both at 20° and 100° in dilute solution the change of rotation in passing from ethyl to n-propyl tartrate is less than that in passing from methyl to ethyl tartrate. To a certain degree, therefore, the relationships between the rotations of these esters are simpler when the data for dilute solutions, rather than for the esters themselves, are compared, since the effect of temperature change becomes slightly less anomalous. At the same time, however, the simplification is by no means great. At 20°, the increase of rotation due to the second increment of 2CH₂ is nearly half that due to the first, whilst at 100° it is only one-fifth as great.

The relationships amongst the data for the potassium alkyl esters are comparatively little altered by solution. The second increment of CH₂ in all cases produces a less effect than the first. This change of rotation is less in solution than in the homogeneous condition, and the relationships amongst the data for 20° are much the same as the relationships amongst those for 100°.

Having thus examined the data for the alkyl tartrates and the potassium alkyl tartrates as regards total solvent action, the rotations of all these substances in dilute solution may now be compared with the rotation of the tartaryl ion.

The data for the purpose are tabulated below. The column Δ₁ gives the differences between the rotation of each compound and that of the tartaryl ion; the column Δ₂ contains the differences between the rotations of the mono-alkyl tartaryl ion and those of the alkyl esters.

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	$[M]_D^{20}$	Δ_1	Δ_2	$[M]_D^{100}$	Δ_1	Δ_2
Tartaryl ion	+61.5°	—	—	+63.25°	—	—
Methyl tartaryl ion	46.7	-14.8°	8.2°	45.80	-17.45°	23.60°
Methyl tartrate	38.5	-23.0		32.20	-31.05	
Ethyl tartaryl ion	60.0	-1.5	4.7	57.00	-6.25	10.20
Ethyl tartrate	55.3	-6.2		46.80	-16.45	
<i>n</i> -Propyl tartaryl ion	64.7	+3.2	1.7	60.80	-2.45	11.20
<i>n</i> -Propyl tartrate	63.0	+1.5		49.60	-13.65	

In these figures, some regularity is apparent. At 20°, the addition of a methyl group to the tartaryl ion brings about a considerable diminution of rotation; a second methyl group produces a further depression, but less than the first. The addition of one ethyl group slightly depresses the rotation of the tartaryl ion, a second effects a greater decrease. The addition of one propyl group increases the rotation above that of the ion, whilst the introduction of a second causes, as in the other two cases, a diminution,* but the rotation still remains greater than that of the free ion.

At 100°, the changes produced are more pronounced, although of much the same kind, but the rotation is always diminished below that of the tartaryl ion by the addition of one or two alkyl groups.

From what has been said, it must be admitted that the subjection of the substances investigated to conditions as closely similar as possible, namely, solution in water and examination at identical temperatures, is insufficient to reveal any constant connection between chemical composition and rotation. New relationships are found, differing considerably from those obtained with the homogeneous substances, but they are scarcely less complex. It is especially obvious that in every case the influence of temperature changes is of paramount importance in modifying these relationships.

In an earlier paper (this vol., p. 771), a suggestion was made for the comparison of the rotation data of methyl, ethyl, and *n*-propyl tartrates, and based on the temperatures of inactivity of the compounds, these temperatures being regarded as "corresponding."

Now the three potassium alkyl tartrates all show distinct maximum rotations in very dilute solution. The rotation of potassium methyl tartrate, or rather, of the methyl tartaryl ion, reaches a maximum value of +48.1° at a temperature of 46.5°. This is, at least in aqueous

* This resembles the effect of substituting, successively, the two hydroxylic hydrogen atoms of methyl and ethyl tartrate by acyl groups like $\text{CH}_3\cdot\text{CO}-$, $\text{C}_6\text{H}_5\cdot\text{CO}-$, $-\text{NO}_2$, &c. The first substitution is usually accompanied by an increase of molecular rotation, whilst the second brings about a diminution (McCrae and Patterson, *Trans.*, 1900, **77**, 1108; and Frankland, Heathcote, and Miss Hartle, *Trans.*, 1903, **83**, 159).

solution, the greatest rotation which the molecule can possibly have ; in the given circumstances, it reaches its configuration of maximum asymmetry. In like manner, the ethyl tartaryl ion has its greatest rotation of $+60.7^{\circ}$ at a temperature of 37° , whilst the maximum rotation of the *n*-propyl tartaryl ion, namely, $+65.1^{\circ}$, occurs at a temperature of 34° . Is it possible, then, that temperatures of maximum rotation ought also to be regarded as "corresponding," so that the rotations of the three potassium alkyl esters should be compared either at the temperatures at which the maximum rotations are reached or at temperatures defined in some way by them ?

Again, an examination of Figs. 8 and 9 will show that, judging by the general form of the curves, methyl and ethyl tartrates may possibly, in very dilute solution, have maximum rotations at temperatures below 0° , that for ethyl tartrate being the lower, whilst if a maximum occurs in dilute solutions of *n*-propyl tartrate it would be found at a still lower temperature, so that these temperatures would be graded in the same manner for the alkyl tartrates as is actually the case for the potassium alkyl esters, the temperature of maximum rotation being highest in both cases for the methyl and least for the *n*-propyl esters.

Moreover, from Figs. 1 and 2, it seems by no means unlikely that even the ionic rotation for potassium and sodium tartrates would show a maximum above 100° ; * if so, this value ought perhaps to be compared, irrespective of temperature, with the other maxima. The rotation of methyl tartrate in infinitely dilute solution at a temperature below 0° would then be comparable with the rotation of the methyl tartaryl ion at 46.5° , and both with that of the tartaryl ion at a temperature above 100° .

If, in solutions of all the substances examined, maximum rotations actually exist, it is probable that the curves for very dilute solutions in the rotation-temperature diagrams (Figs. 1, 2, 4, 5, 6, 8, 9, and 10) represent, in the case of the alkyl tartrates, only one limb, the descending one ; for the potassium alkyl tartrates, both limbs, and for potassium and sodium tartrates again only one limb, the ascending one, of curves which are in all three cases of a similar kind.

* The explanation of the maxima given on p. 1138 would then probably require modification. The maximum ionic rotation could not be accounted for by the different behaviour of dissimilar, but coexistent, groups.

EXPERIMENTAL DATA.

Sodium Tartrate.

The sodium tartrate used was twice recrystallised from water and then corresponded with the formula $C_4H_4O_6Na_2 \cdot 2H_2O$.

I. $p = 1.77713$ hydrated or 1.499 anhydrous salt.

t , †	α_D^{20} (400 mm.).	d .	$[\alpha]_D^{20}$ *	$[M]_D^{20}$.
16.7°	+1.890°	1.0096	+26.33°	+60.62°
32.5	1.923	1.0054	26.91	61.94
51.2	1.940	0.9978	27.35	62.96
98.5	1.911	0.9713	27.68	63.71

* The specific rotations are those of the hydrated salt.

† These and the following observations are recorded in the order in which they were made.

II. $p = 4.92493$ hydrated or 4.154 anhydrous salt.

t .	α_D^{20} (400 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
18.5°	+5.277°	1.0282	+26.05°	+59.98°

III. $p = 10.1507$ hydrated or 8.5614 anhydrous salt.

t .	α_D^{20} (249.6 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
9.1°	+6.868°	1.0630	+25.50°	+58.69°
23.4	6.977	1.0584	26.01	59.89
37.8	7.038	1.0535	26.36	60.68
98.5	6.820	1.0212	26.35	60.66
62.5	7.000	1.0413	26.53	61.07
13.6	6.918	1.0616	25.72	59.20

IV. $p = 29.7125$ hydrated or 25.06 anhydrous salt.

t .	α_D^{20} (100 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
8.6°	+8.698°	1.1936	+24.53°	+56.41°
27	8.757	1.1844	24.89	57.23
45.4	8.752	1.1741	25.09	57.70
98.4	8.400	1.1406	24.79	57.01
81.3	8.540	1.1518	24.96	57.40
70.75	8.615	1.1585	25.03	57.56
51.85	8.750	1.1704	25.16	57.87

V. $p = 39.08$ hydrated or 32.873 anhydrous salt.

t .	α_D^{20} (40 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
29.8°	+4.685°	1.2504	+23.97°	+55.18°
9.1	4.692	1.2620	23.79	54.75
98.5	4.429	1.2053	23.51	54.12
68.1	4.595	1.2262	23.98	55.19
50.5	4.651	1.2377	24.04	55.36

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VI. $p = 58.515$ hydrated or 49.35 anhydrous salt.

$t.$	$\alpha_D^{25} (40 \text{ mm.}).$	$d.$	$[\alpha]_D^{25}$	$[M]_D^{25}$
99°	$+6.405^\circ$	1.3586	$+20.14^\circ$	$+46.32^\circ$
89.5	6.482	1.3648	20.29	46.47

Densities determined.

I.		II.		III.		IV.		V.		VI.	
$t.$	$d.$	$t.$	$d.$	$t.$	$d.$	$t.$	$d.$	$t.$	$d.$	$t.$	$d.$
17.02°	1.0095	14.91°	1.02921	13.23	1.0617	11.4°	1.1924	12.3°	1.2603	100°	1.3580
23.30	1.0075	27.35	1.02553	27.02	1.0572	26.38	1.1840	35.7	1.2468	—	—
31.25	1.0057	—	—	48.2	1.0481	51.6	1.1706	55.3	1.2347	—	—
45.2	1.0005	—	—	95	1.0203	77.6	1.1542	99.3	1.2049	—	—
46.7	0.9998	—	—	—	—	—	—	—	—	—	—
59.8	0.9935	—	—	—	—	—	—	—	—	—	—

Potassium Tartrate.

The potassium tartrate, $K_2C_4H_4O_6 \cdot \frac{1}{2}H_2O$, was twice crystallised and dried on porous plate in the air.

I. $p = 5.64501$ hydrated or 5.429 anhydrous salt.

$t.$	$\alpha_D^{25} (400 \text{ mm.}).$	$d.$	$[\alpha]_D^{25} *$	$[M]_D^{25}$
16.1°	$+6.253^\circ$	1.0353	$+26.75^\circ$	$+62.96$
29.9	6.320	1.0310	27.07	63.72
99	6.112	0.9937	27.24	64.11
78.7	6.217	1.0074	27.33	64.32
50.35	6.297	1.0227	27.27	64.18

* The values for specific rotation refer to the hydrated salt.

II. $p = 10.3707$ hydrated or 9.974 anhydrous salt.

$t.$	$\alpha_D^{25} (400 \text{ mm.}).$	$d.$	$[\alpha]_D^{25}$	$[M]_D^{25}$
12.7°	$+11.987^\circ$	1.0677	$+27.06^\circ$	$+63.70$
21.8	12.017	1.0648	27.21	64.03
71.3	11.948	1.0418	27.65	65.06
98.5	11.732	1.0245	27.60	64.97

III. $p = 26.6665$ hydrated or 25.647 anhydrous salt.

$t.$	$\alpha_D^{25} (100 \text{ mm.}).$	$d.$	$[\alpha]_D^{25}$	$[M]_D^{25}$
17.4°	$+8.917^\circ$	1.1833	$+28.26^\circ$	$+66.50$
34.2	8.898	1.1753	28.39	66.82
47.4	8.867	1.1681	28.47	66.99
65.5	8.763	1.1578	28.38	66.80
99	8.520	1.1369	28.10	66.14

IV. $p = 32.12$ hydrated or 30.89 anhydrous salt.

$t.$	$\alpha_D^{25} (100 \text{ mm.}).$	$d.$	$[\alpha]_D^{25}$	$[M]_D^{25}$
18°	$+11.186^\circ$	1.2266	$+28.39^\circ$	$+66.82^\circ$
37.2	11.172	1.2170	28.58	67.23
55.7	11.082	1.2064	28.60	67.31
98	10.624	1.1794	28.04	66.00

V. $p = 40.645$ hydrated or 39.09 anhydrous salt.

$t.$	α_D^{20} (40 mm.).	$d.$	$[\alpha]_D^{20}$	$[M]_D^{20}$
17°	+6.036°	1.2975	+28.62°	+67.35°
29.7	6.021	1.2908	28.69	67.56
68	5.877	1.2683	28.50	67.08
99	5.640	1.2496	27.76	65.32

VI. $p = 58.777$ hydrated or 56.53 anhydrous salt.

$t.$	α_D^{20} (40 mm.).	$d.$	$[\alpha]_D^{20}$	$[M]_D^{20}$
28.2°	+9.993°	1.4607	+29.1°	+68.48°
16.3	10.148	1.4678	29.41	69.20
63.8	9.588	1.4390	28.34	66.70
55.3	9.690	1.4444	28.54	67.16
99	9.090	1.4159	27.31	64.27

VII. $p = 65.1$ hydrated or 62.61 anhydrous salt.

$t.$	α_D^{20} (40 mm.).	$d.$	$[\alpha]_D^{20}$	$[M]_D^{20}$
16.1°	+11.778°	1.5347	+29.47°	+69.36°
36.4	11.507	1.5223	29.03	68.33
99	10.425	1.4829	27.00	63.54

Densities determined.

I.		II.		III.		IV.		V.		VI.		VII.	
$t.$	$d.$	$t.$	$d.$	$t.$	$d.$	$t.$	$d.$	$t.$	$d.$	$t.$	$d.$	$t.$	$d.$
18.16°	1.03484	12.44°	1.06763	18.97°	1.18262	10°	1.2304	17.7°	1.2970	20.5°	1.4654	27.7°	1.5276
29.89	1.03133	24.65	1.06384	27.8	1.1786	28.66	1.2214	29.93	1.2906	42	1.4525	47.8	1.5153
49.05	1.0235	50.6	1.0528	48.7	1.1680	49	1.2193	48.45	1.2798	79.3	1.4290	81	1.4946
78.5	1.0074	81.4	1.0354	76.8	1.1513	78	1.1926	81	1.2605	—	—	—	—

Potassium Methyl Tartrate.—The rotation of solutions of potassium, sodium, lithium, calcium, and barium tartrates have already been determined by Fayollat (*Compt. rend.*, 1893, 117, 630), but only at one concentration and at atmospheric temperature. The preparation of potassium methyl tartrate was originally described by Guérin (*Annalen*, 1837, 22, 250), who obtained a salt containing half a molecule of water of crystallisation.

The specimen employed corresponded with the formula $C_4H_4O_6(CH_3)K$, and was obtained in moderately large asymmetric crystals having a very distinct cleavage parallel to the longest axis; it decomposed with frothing at 216 — 217° , but showed indefinite signs of melting several degrees lower.

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I. $p = 5.3067$.

t .	α_D^t (400 mm.).	d .	$[\alpha]_D^t$.	$[M]_D^t$.
10.6°	+4.869°	1.0272	+22.33°	+45.11°
21.5	4.970	1.0243	22.86	46.17
17.2	4.920	1.0253	22.61	45.66
30	5.032	1.0220	23.19	46.85
41.2	5.071	1.0177	23.48	47.42
52.6	5.045	1.0124	23.47	47.42
65.7	4.987	1.0054	23.37	47.20
99	4.707	0.9834	22.55	45.55
14.7	4.900	1.0259	22.50	45.45

II. $p = 15.1501$.

t .	α_D^t (400 mm.).	d .	$[\alpha]_D^t$.	$[M]_D^t$.
7.7°	+13.763°	1.0801	+21.02°	+42.47°
20.7	14.235	1.0759	21.83	44.10
15	14.054	1.0779	21.52	43.46
27.8	14.360	1.0732	22.08	44.60
39.9	14.557	1.0680	22.49	45.44
52.9	14.573	1.0613	22.66	45.77
75.7	14.300	1.0479	22.52	45.49
98	15.880	1.0321	22.19	44.83

III. $p = 24.9555$.

t .	α_D^t (100 mm.).	d .	$[\alpha]_D^t$.	$[M]_D^t$.
10.6°	+5.744°	1.1349	+20.28°	+40.98°
35.6	6.036	1.1237	21.52	43.48
52.2	6.086	1.1145	21.88	44.20
63.2	6.066	1.1078	22.03	44.51
99	5.823	1.0819	21.57	43.57
15.1	5.807	1.1330	20.54	41.49

IV. $p = 47.085$.

t .	α_D^t (40 mm.).	d .	$[\alpha]_D^t$.	$[M]_D^t$.
10.1°	+4.267°	1.2758	+17.76°	+35.87°
24.3	4.510	1.2672	18.90	38.17
17.7	4.387	1.2712	18.32	37.02
33	4.583	1.2617	19.29	38.96
70.4	4.667	1.2360	20.05	40.50
99	4.583	1.2150	20.03	40.46

Densities determined.

I.		II.		III.		IV.	
t .	d .	t .	d .	t .	d .	t .	d .
16.7°	1.0255	16.6°	1.0774	13.6°	1.1336	15.1°	1.2727
30.0	1.0220	26.3	1.0739	26.7	1.1279	31	1.2631
47.6	1.0146	40.2	1.0679	49.3	1.1162	48	1.2519
63.9	1.0062	59.1	1.0580	56.1	1.1120	63.1	1.2411
78	0.9981	64.5	1.0548	82.3	1.0949	79.2	1.2297
—	—	77.5	1.0463	—	—	—	—

ROTATION OF OPTICALLY ACTIVE COMPOUNDS. PART V. 1147

Potassium Ethyl Tartrate.—This compound, which was also described by Guérin (*Annalen*, 1837, 22, 250), has been partially examined as regards rotation by Fayollat (*Compt. rend.*, 1893, 117, 630).

The specimen employed showed a slight appearance of melting at 205° and decomposed suddenly at 212°. When heated at 120°, it lost no weight, and analysis indicated the formula $C_4H_4O_6(C_2H_5)K$.

I. $p = 5.06845$.

t .	α_D^{20} (400 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
8.1°	+5.577°	1.0236	+26.87°	+58.05°
14.9	5.627	1.0223	27.14	58.63
23.2	5.676	1.0203	27.44	59.27
40.4	5.704	1.0144	27.73	59.90
61.1	5.570	1.0049	27.34	59.05
75.4	5.437	0.9962	26.92	58.14
98	5.194	0.9793	26.16	56.51

II. $p = 15.1035$.

t .	α_D^{20} (400 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
15°	+16.930°	1.0700	+26.19°	+56.57°
7.6	16.717	1.0723	25.81	55.74
23.6	17.083	1.0670	26.50	57.24
39.4	17.106	1.0603	26.70	57.68
56.3	16.943	1.0512	26.68	57.63
78.3	16.407	1.0329	26.29	56.80
98	15.863	1.0235	25.65	55.41

III. $p = 34.747$.

t .	α_D^{20} (100 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
7°	+9.895°	1.1750	+24.23°	+52.35°
19.7	10.096	1.1687	24.86	53.70
37	10.190	1.1589	25.31	54.66
54.6	10.140	1.1480	25.42	54.91
74.2	9.910	1.1348	25.13	54.29
99	9.560	1.1170	24.63	53.20

IV. $p = 46.787$

t .	α_D^{20} (100 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
14.6°	+13.566°	1.2380	+23.42°	+50.59°
25.1	13.684	1.2314	23.75	51.30
40.2	13.907	1.2215	24.33	52.56
56.8	13.846	1.2099	24.49	52.90
72.2	13.677	1.1988	24.39	52.67
98.6	13.267	1.1787	24.06	51.97

Densities determined.

I.		II.		III.		IV.	
t .	d .	t .	d .	t .	d .	t .	d .
13.3°	1.0226	13.1°	1.0706	13.3°	1.1720	31.7°	1.2271
22.05	1.0206	30.51	1.0643	32.42	1.1616	52.0	1.2130
31.37	1.0177	55.3	1.0518	47.9	1.1524	63.5	1.2050
47.9	1.0114	80	1.0369	64.7	1.1413	79.3	1.1933
79.2	0.9937	—	—	79	1.1314	—	—

Potassium n-Propyl Tartrate.

In preparing potassium *n*-propyl tartrate, 94 grams of *n*-propyl tartrate were dissolved in about 200 c.c. of *n*-propyl alcohol and a hot solution of 22.5 grams of pure potassium hydroxide in the same alcohol added slowly, with constant stirring. A turbidity ensued, and on cooling the whole mass became solid. Owing to this tendency of the substance to set with water like a soap, its purification was difficult. A small quantity of water was added and the mixture heated on the water-bath. An amount of acetone, insufficient to bring about precipitation, was then added, and the solution repeatedly passed through a double filter-paper surrounded with a steam-jacket, but this did not give a perfectly clear filtrate. The product, on cooling, became almost solid, and the adhering liquid was removed as completely as possible at the pump, and the solid washed with acetone. The cake thus obtained was triturated with acetone in order to remove the *n*-propyl alcohol completely, filtered at the pump, spread on a porous plate, and allowed to dry in the air, 38 grams of the salt being thus obtained. The melting point was not sharp, the substance softening and showing signs of melting at 161°, and decomposing with frothing at 192°.

0.8000 yielded 0.3042 K_2SO_4 . $K = 17.05$.

$C_4H_4O_6(C_3H_7)K$ requires $K = 16.96$ per cent.

The whole of the product was again dissolved in a small quantity of hot water and hot *n*-propyl alcohol added until turbidity ensued. The solution was filtered when hot, allowed to cool, and the precipitate, freed from liquid as far as possible at the pump, was then triturated in a beaker with acetone, filtered again, and washed with acetone. The precipitate was then dried on a porous plate in air and finally over sulphuric acid under diminished pressure.

0.6817 yielded 0.2573 K_2SO_4 . $K = 16.92$.

A solution of this substance was made up, but it was so turbid, owing to the presence of filter-paper fibre and light powder from the porous plates used in drying the material, that observations could only be made with great difficulty. The potassium *n*-propyl tartrate was therefore dissolved in a small quantity of hot water and the solution filtered through a double layer of paper surrounded with a steam-jacket, but, as the filtrate was still turbid, some pure animal charcoal was added, after which it was heated on the water-bath for about 15 minutes and then filtered. This gave a clear filtrate, which was evaporated to dryness in a glass basin on the water-bath and

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then dried thoroughly over sulphuric acid under diminished pressure. The following observations were made with this substance :

I. $p = 4.98903$.

t .	α_D^{20} (400 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
8.9°	+5.497°	1.0219	+26.96°	+63.08°
24.1	5.534	1.0179	27.25	63.75
50.6	5.476	1.0077	27.23	63.72
36.8	5.551	1.0135	27.44	64.22
71.4	5.330	0.9967	26.80	62.71
98.4	5.052	0.9788	25.87	60.53

II. $p = 25.01$.

t .	α_D^{20} (100 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
12.4°	+7.108°	1.1105	+25.59°	+59.88°
21.9	7.173	1.1060	25.93	60.68
51.9	7.133	1.0896	26.18	61.25
69.9	6.963	1.0779	25.83	60.45

III. $p = 48.4602$.

t .	α_D^{20} (100 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
8.2°	+14.253°	1.2255	+24.00°	+56.16°
23.7	14.523	1.2157	24.65	57.68
38.1	14.527	1.2058	24.86	58.18
70.2	14.530	1.1826	25.04	58.60
99	13.853	1.1610	24.62	57.61
63.1	14.420	1.1878	25.05	58.63
53.2	14.496	1.1950	25.03	58.58
7.8	14.191	1.2258	23.89	55.90

Densities determined.

I.		II.		III.	
t .	d .	t .	d .	t .	d .
18.3°	1.01954	13.3°	1.1101	13.4°	1.2224
22.05	1.01856	33.2	1.1003	29.8	1.2116
29.65	1.01623	47.1	1.0926	50.3	1.1967
49.4	1.0082	61.7	1.0836	80.3	1.1751
79.2	0.9919	81.8	1.0697	—	—

Methyl Tartrate.—For rotation values of the homogeneous ester, compare this vol., p. 766.

I. $p = 5.16915$.

t .	α_D^{20} (400 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
17.2°	+4.425°	1.0146	+21.10°	+37.57
30.7	4.348	1.0105	20.81	37.06
49.9	4.205	1.0028	20.28	36.12
64.2	4.055	0.9953	19.71	35.10
99	3.597	0.9731	17.88	31.84
17.4	4.400	1.0145	20.97	37.36

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II. $p = 10.2298$.

t .	α_D^{20} (400 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
17.2°	+ 8.631°	1.0302	+ 20.47°	+ 36.47°
30.3	8.535	1.0254	20.34	36.23
47.5	8.278	1.0183	19.87	35.39
66.4	7.845	1.0077	19.03	33.89
99	6.907	0.9849	17.14	30.53
17.5	8.610	1.0300	20.43	36.39

III. $p = 24.8854$.

t .	α_D^{20} (249.6 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
18°	+ 12.542°	1.0776	+ 18.74°	+ 33.37°
35.7	12.255	1.0687	18.46	32.88
54.5	11.690	1.0569	17.81	31.71
17.2	12.537	1.0779	18.73	33.33
99	10.260	1.0356	15.95	28.41
17.4	12.496	1.0778	18.67	33.23

IV. $p = 49.7715$.

t .	α_D^{20} (100 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
16.7°	+ 8.529°	1.1646	+ 14.71°	+ 26.21°
38.3	8.340	1.1487	14.59	25.98
17.4	8.517	1.1642	14.70	26.18
62.7	7.940	1.1287	14.13	25.17
99.5	7.276	1.0968	13.33	23.74
17.1	8.470	1.1645	14.61	26.03
27.8	8.410	1.1566	14.61	26.02

V. $p = 74.8685$.

t .	α_D^{20} (100 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
17.4°	+ 8.839°	1.2538	+ 9.42°	+ 16.77°
28.3	9.065	1.2439	9.74	17.34
44.8	9.255	1.2283	10.06	17.92
65.4	9.322	1.2082	10.31	18.35
98.5	9.229	1.1740	10.50	18.70

Densities determined.

I.		II.		III.		IV.		V.	
t .	d .	t .	d .	t .	d .	t .	d .	t .	d .
19.55°	1.01386	17.86°	1.03003	17.65°	1.0778	18.5°	1.1633	16.9°	1.2543
26.37	1.01198	26.73	1.02719	31.77	1.0709	32	1.1536	39.8	1.2333
31.83	1.01016	33.13	1.02474	51.6	1.0593	55.5	1.1349	58	1.2156
48	1.0035	47.7	1.0181	73	1.0450	77.7	1.1161	77	1.1967
78.9	0.9863	77.5	1.0007	—	—	—	—	—	—

Ethyl Tartrate.—The ester, prepared by the hydrogen chloride saturation method, had an observed rotation of 9.39° at 20° in a 100 mm. tube. Values for the molecular rotation of undiluted ethyl tartrate at a number of different temperatures will be found in a former paper (this vol., p. 767).

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I. $p = 4.99894$.

t .	$\alpha_D^{25} (400 \text{ mm.})$	d .	$[\alpha]_D^{25}$	$[M]_D^{25}$
11.1°	+5.380°	1.0118	+26.53°	+54.76°
28.7	5.306	1.0071	26.35	54.28
43.6	5.117	1.0014	25.56	52.64
65	4.784	0.9905	24.15	49.76
98.3	4.280	0.9690	22.09	45.50
10.7	5.377	1.0120	26.57	54.74

II. $p = 4.99917$.

t .	$\alpha_D^{25} (400 \text{ mm.})$	d .	$[\alpha]_D^{25}$	$[M]_D^{25}$
18.3°	+5.382°	1.0100	+26.65°	+54.89°
12.6	5.402	1.0116	26.70	55.00

III. $p = 10.0756$.

t .	$\alpha_D^{25} (400 \text{ mm.})$	d .	$[\alpha]_D^{25}$	$[M]_D^{25}$
10.3°	+10.840°	1.0235	+26.28°	+54.14°
25.8	10.577	1.0199	25.74	53.01
41.4	10.183	1.0131	24.94	51.38
68.9	9.300	0.9988	23.11	47.62
98	8.417	0.9785	21.34	43.97

IV. $p = 25.0338$.

t .	$\alpha_D^{25} (100 \text{ mm.})$	d .	$[\alpha]_D^{25}$	$[M]_D^{25}$
12°	+6.380°	1.0605	+24.03°	+49.50°
23.3	6.210	1.0559	23.49	48.89
98	4.820	1.0052	19.15	39.46
54.1	5.647	1.0380	21.73	44.77

V. $p = 50.225$.

t .	$\alpha_D^{25} (100 \text{ mm.})$	d .	$[\alpha]_D^{25}$	$[M]_D^{25}$
16.4°	+9.880°	1.1179	+17.60°	+36.25°
31.2	9.630	1.1070	17.32	35.68
50.1	9.334	1.0915	17.03	35.07
98	8.660	1.0490	16.44	33.86

VI. $p = 75.05$.

t .	$\alpha_D^{25} (100 \text{ mm.})$	d .	$[\alpha]_D^{25}$	$[M]_D^{25}$
17.1°	+10.264°	1.1697	+11.69°	+24.08°
29.5	10.718	1.1585	12.33	25.40
50.2	11.447	1.1391	13.39	27.58
68.4	11.653	1.1216	13.84	28.52
98	11.970	1.0915	14.61	30.10

Densities determined.

I.		II.		III.		IV.		V.		VI.	
t .	d .	t .	d .	t .	d .	t .	d .	t .	d .	t .	d .
18.6°	1.00999	19.4°	1.00985	19°	1.02193	18.8°	1.0580	13.5°	1.1200	14.8°	1.1718
21.65	1.00920	21.6	1.00926	21.4	1.02122	23	1.0560	27.2	1.1100	40	1.1487
30.20	1.00662	—	—	33.8	1.01663	49.9	1.0407	49.8	1.0918	62.2	1.1275
47.2	0.9997	—	—	61.4	1.0029	81.6	1.0185	93.4	1.0479	99.4	1.0903
64.4	0.9909	—	—	80.7	0.9908	—	—	—	—	—	—
83.6	0.9793	—	—	—	—	—	—	—	—	—	—

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n-Propyl Tartrate.—For rotation values of the homogeneous ester, compare this vol., p. 767.

I. $p = 4.01741$.

t .	α_D^{20} (400 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
17°	+4.314°	1.0064	+26.67°	+62.47°
30.2	4.163	1.0027	25.84	60.51
21.1	4.250	1.0053	26.31	61.61
41.4	4.025	0.9986	25.07	58.71
66.8	3.680	0.9852	23.24	54.44
98	3.283	0.9653	21.16	49.57

II. $p = 6.99482$.

t .	α_D^{20} (249.6 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
17.6°	+4.637°	1.0118	+26.25°	+61.47°
45.6	4.317	1.0017	24.68	57.81

III. $p = 7.00601$.

t .	α_D^{20} (400 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
17.1°	+7.411°	1.0120	+26.13°	+61.20°
29	7.178	1.0084	25.40	59.48
47	6.766	1.0010	24.12	56.49

IV. $p = 10.0198$.

t .	α_D^{20} (400 mm.).	d .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
16.7°	+10.310°	1.0179	+25.27°	+59.19°
18.8	10.193	1.0172	25.00	58.56
17	10.313	1.0177	25.28	59.21

Densities determined.

I.		II.		III.		IV.	
t .	d .	t .	d .	t .	d .	t .	d .
19.3°	1.00584	17.97°	1.01182	17.8°	1.01185	16.9°	1.01779
23.97	1.00463	23.3	1.01032	24.35	1.00998	23.3	1.0158
35.9	1.0007	38.24	1.0048	47.1	1.0008	—	—
55.6	0.9917	56.6	0.9957	—	—	—	—
77.3	0.9794	—	—	—	—	—	—

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