221. *Physicochemical Studies of Complex Formation involving Weak Acids. Part XI. Complex Formation between Tartaric Acid and (a) Molybdic Acid, (b) Tungstic Acid.*

By H. T. S. BRITTON and PATRICIA JACKSON.

GERNEZ (*Compt. rend.*, 1887, **104**, 785; **105**, 85; 1889, **108**, 942) investigated the changes in rotatory power of solutions of tartaric acid in the presence of alkali molybdates in increasing concentrations. Maximum rotations were obtained when the acid and salts were mixed in equimolecular proportion and this fact was considered to point to the formation of definite complex salts. The same method was adopted by Rosenheim and Itzig (*Ber.*, 1900, **33**, 707) with tartaric acid and alkali molybdates and polymolybdates, and also alkali tungstates and polytungstates; in all cases, the results resembled those of Gernez, equivalence being reckoned with respect to the alkali metal. On stoicheiometric grounds, the complex salts which give these maxima might be considered as containing one molecule of sodium tartrate and varying amounts of either molybdic oxide, *viz.*, 1, 2, 2·33, 2·4, 4; or tungstic oxide, *viz.*, 1, 2·4. Similar conclusions may be drawn from Itzig's observations (*ibid.*, 1901, **34**, 1372) on the maximum rotations set up by the inclusion of varying proportions of either sodium molybdate or ammonium paramolybdate or sodium tungstate or paratungstate in solutions of sodium hydrogen tartrate. The method was employed by Quinet (*Compt. rend.*, 1908, **147**, 203) with tartaric acid and sodium molybdate, but, as Grossmann (*Z. anorg. Chem.*, 1908, **60**, 50; Grossmann and Pötter, *Ber.*, 1905, **38**, 3874) has pointed out, his experimental data are very probably erroneous. Klason and Köhler (*Ber.*, 1901, **34**, 3946) extended Itzig's work and found that the maximum rotations given by sodium hydrogen tartrate depend on other factors besides the amount of alkali metal, such as the ratio of molybdic acid, concentration of the active substance, and the temperature of the solution.

Compounds of the general formula $R_2^I(XO_3)C_4H_4O_6$ (R = alkali metal; X = Mo, W) have been prepared by Rosenheim and Itzig in the crystalline form. In solution, their specific rotations increase with increasing concentration. On the other hand, Henderson and Barr (J., 1896, **69**, 1455) prepared a series of salts, $XO_2(NaC_4H_4O_6)_2$, by dissolving either tungstic or molybdic oxide in boiling alkali hydrogen tartrate solutions. The following work shows that complexes exist in solution corresponding to Rosenheim and Itzig's compounds.

That complex formation occurs when molybdic acid is dissolved in tartaric acid solutions is evident from the increases in optical activity, conductivity, and hydrogen-ion concentration (see Mazzucchelli, *Atti R. Accad. Lincei*, 1910, **19**, ii, 439; Mazzucchelli, Ranucci, and Sabatini, *Gazzetta*, 1913, **43**, ii, 26; Rosenheim and Bertheim, *Z. anorg. Chem.*, 1903, **34**, 442; Grossmann and Krämer, *Ber.*, 1903, **36**, 1606; *Z. anorg. Chem.*, 1904, **41**, 43; Rimbach and Niezert, *ibid.*, 1907, **53**, 397; Wintgen, *ibid.*, 1912, **74**, 281; Rimbach and Ley, *Z. physikal. Chem.*, 1922, **100**, 393).

It was considered that the method devised by Gernez and subsequently used by Rosenheim is open to a fundamental objection, for it involves two variables superimposed upon one another. By inserting sodium molybdate in increasing amounts in tartaric acid solutions of constant concentration, two factors are simultaneously introduced, each of which affects the optical activity of the tartaric acid. First, the increasing alkali-metal ratio will increase the neutralisation of the tartaric acid and, as shown by the present authors (this vol., p. 1001), the rotation will be enhanced; and secondly, the ratio molybdic acid : tartaric acid is made to vary continuously, which, owing to varying amounts of tartaric acid entering into complex formation, will also raise the rotatory power. Moreover, unless free alkali be added to the tartaric acid–alkali molybdate mixtures, any evidence of complex formation occurring during the complete neutralisation of the two acids will not be obtained.

The present rotation experiments are confined to 0·1*M*-tartaric acid solutions, so as to eliminate any effects that alkali-metal ions may have (cf. Part VIII, this vol., p. 998). The optical activity of tartaric acid in the presence of constant amounts of either molybdic or tungstic acid has been studied throughout, and beyond, the neutralisation of the two acids. In the case of both molybdic and tungstic acids, maximal rotations were given by proportions corresponding to the formation of complexes of the general formula $Na_2(XO_3)_xC_4H_4O_6$, whilst quinhydrone-electrode titrations provide conclusive proof that x may be unity and may also assume higher values.

EXPERIMENTAL.

Optical Rotatory Power.—Table I gives the rotations (λ5461 Å.) at 25° of three series of solutions of tartaric and molybdic acid, in which the molecular ratios of the two acids were severally 1 : 0·25, 1 : 0·5, and 1 : 0·75, in various degrees of neutralisation with sodium hydroxide. The molecular rotations are plotted in Fig. 1, against the number of equivs. of alkali added, being denoted by the heavy lines marked 0·75 Mo, 0·5 Mo and 0·25 Mo. The solutions were prepared from sodium molybdate, tartaric acid, sodium hydroxide, and, in the case of the initial solutions of the three series, hydrochloric acid in appropriate quantity. The concentrations of sodium chloride thereby introduced, shown in the tables in parentheses, are too small to have any appreciable effect on the rotation.

The curve given at the bottom of Fig. 1 (see Part VIII) is that of the neutralisation of 0·1*M*-tartaric acid. Each of the molybdic–tartaric acid curves shows that maximum rotations are given by solutions containing 2 equivs. of alkali. It will be seen later that this alkali has united with the tartaric acid to form normal sodium tartrate, which in turn has combined with the molybdic acid, thus

$$Na_2(MoO_3)_xC_4H_4O_6.$$

Another interesting observation is that further alkali results in rapid diminution of rotatory power until the alkali is sufficient to neutralise the molybdic acid as sodium molybdate, Na_2MoO_4, the rotations then becoming exactly equal to that of the parent sodium tartrate. The addition of further alkali gives no change in rotation. Hence it is inferred that the complex molybdotartrate, formed whilst the solution is still incompletely neutralised, is entirely broken down in alkaline solution into normal sodium tartrate and sodium molybdate.

Fig. 1.

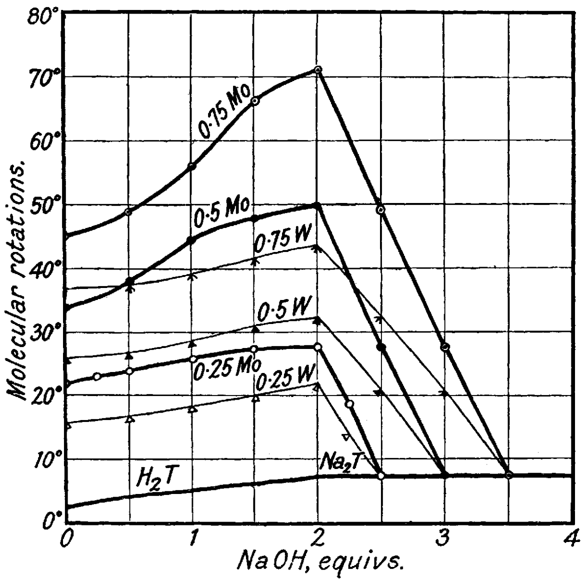


TABLE I.

Solutions of 0·1*M*-tartaric acid + 0·025*M*-MoO_3 + *xM*-NaOH.

$\frac{[NaOH]}{[H_2T]}$	0	0·25	0·50	1·0	1·5	2·0	2·25	2·5	3·0	4·0	5·0
xM-NaOH	0 (0·05*M*-NaCl)	0·025	0·05	0·10	0·15	0·20	0·225	0·25	0·30	0·40	0·50
$\alpha_{obs.}$	8·74°	9·07°	9·47°	10·19°	10·85°	10·94°	7·42°	2·79°	2·79°	2·78°	2·79°
$[M]^{25°}_{5461}$	21·85°	22·67°	23·67°	25·47°	27·12°	27·35°	18·55°	6·97°	6·97°	6·95°	6·97°

Solutions of 0·1*M*-tartaric acid + 0·05*M*-MoO_3 + *xM*-NaOH.

$\frac{[NaOH]}{[H_2T]}$	0	0·5	1·0	1·5	2·0	2·5	3·0	4·0	5·0
xM-NaOH	0 (0·1*M*-NaCl)	0·05	0·1	0·15	0·20	0·25	0·30	0·40	0·50
$\alpha_{obs.}$	13·48°	15·13°	17·74°	19·07°	19·82°	10·95°	2·98°	2·81°	2·80°
$[M]^{25°}_{5461}$	33·7°	37·82°	44·35°	47·67°	49·55°	27·37°	7·45°	7·02°	7·00°

Solutions of 0·1*M*-tartaric acid + 0·075*M*-MoO_3 + *xM*-NaOH.

$\frac{[NaOH]}{[H_2T]}$	0	0·5	1·0	1·5	2·0	2·5	3·0	4·0	5·0
xM-NaOH	0 (0·15*M*-NaCl)	0·05	0·10	0·15	0·20	0·25	0·30	0·40	0·50
$\alpha_{obs.}$	17·95°	19·49°	22·31°	26·44°	28·19°	19·57°	10·95°	2·80°	2·80°
$[M]^{25°}_{5461}$	44·87°	48·72°	55·77°	66·10°	70·47°	48·92°	27·37°	7·00°	7·00°

Table II gives similar data corresponding to the neutralisation of 0·1*M*-tartaric acid in the presence of 0·25, 0·5, and 0·75 mol. of tungstic acid. The molecular rotations, which are plotted as thin lines in Fig. 1, and marked by 0·75 W, 0·5 W, and 0·25 W respectively, again reveal maxima with 2 equivs. of alkali and rotations which are identical with those of sodium tartrate alone when 2·5, 3, and 3·5 equivs. respectively of alkali are added—such amounts being those necessary to convert the tungstic acid quantitatively into sodium tungstate. As the solutions are rendered increasingly alkaline the rotations remain constant, as for the other series.

TABLE II.

Solutions of 0·1M-tartaric acid + 0·025M-WO_3 + xM-NaOH.

$\frac{[NaOH]}{[H_2T]}$	0	0·5	1·0	1·5	2·0	2·5	3·0	3·5
xM-NaOH	0 (0·25M-NaCl)	0·05	0·1	0·15	0·20	0·25	0·30	0·35
$\alpha_{obs.}$	6·32°	6·74°	7·30°	8·04°	8·67°	2·91°	2·81°	2·78°
$[M]^{25°}_{5461}$	15·80°	16·85°	18·25°	20·10°	21·67°	7·27°	7·02°	6·95°

Solutions of 0·1M-tartaric acid + 0·05M-WO_3 + xM-NaOH.

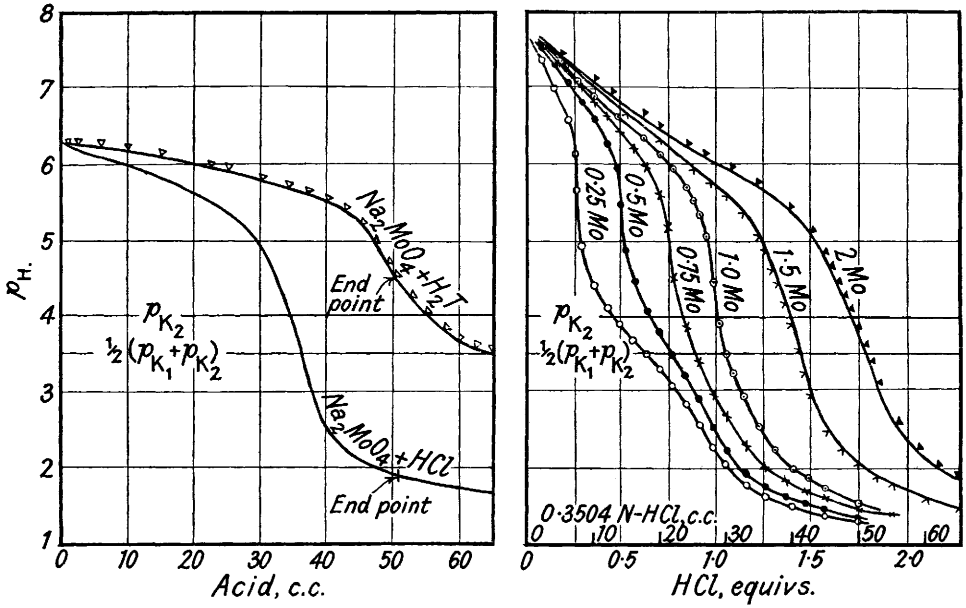
$\frac{[NaOH]}{[H_2T]}$	0	0·5	1·0	1·5	2·0	3·0	3·5	4·0	5·0
xM-NaOH	0 (0·1M-NaCl)	0·05 (0·05M-NaCl)	0·1	0·15	0·20	0·30	0·35	0·4	0·5
$\alpha_{obs.}$	10·32°	10·72°	11·54°	12·38°	12·84°	2·80°	2·78°	2·79°	2·80°
$[M]^{25°}_{5461}$	25·80°	26·80°	28·85°	30·95°	32·10°	7·00°	6·95°	6·97°	7·00°

Solutions of 0·1M-tartaric acid + 0·075M-WO_3 + xM-NaOH.

$\frac{[NaOH]}{[H_2T]}$	0	0·5	1·0	1·5	2·0	2·5	3·0	3·5	4·0
xM-NaOH	0 (0·15M-NaCl)	0·05 (0·1M-NaCl)	0·1 (0·05M-NaCl)	0·15	0·2	0·25	0·3	0·35	0·4
$\alpha_{obs.}$	14·59°	15·09°	15·65°	16·62°	17·45°	12·99°	8·21°	2·83°	2·81°
$[M]^{25°}_{5461}$	36·47°	37·72°	39·12°	41·55°	43·62°	32·47°	20·52°	7·07°	7·02°

The first two solutions in the neutralisation of 0·1M-tartaric acid and 0·075M-tungstic acid were unstable, for on standing for a day they became cloudy and subsequently underwent partial precipitation. Mutarotation was observed only in the case of these two solutions.

FIG. 2.



Electrometric Measurements.—The possibility of complex formation occurring between molybdic acid (and tungstic acid) and tartaric acid was investigated in the first place by following the change in p_H, as indicated by the quinhydrone electrode at 18° during the titration of sodium molybdate (and sodium tungstate) with tartaric acid. The upper curve to the left of Fig. 2 shows the p_H change during the successive addition of 0·1M-tartaric acid to 50 c.c. of 0·1M-sodium molybdate solution, whereas the lower curve represents the titration of 50 c.c. of sodium molybdate with 0·1967N-hydrochloric acid. Similarly, the corresponding curves in Fig. 3 relate to sodium tungstate under identical conditions.

The titration curves of the sodium salts with hydrochloric acid are similar to those described by Britton and German (J., 1930, 1249, 2154), and show that the solutions become distinctly acid some time before the end-point (at 50·8 c.c.) is reached. In the tartaric acid curves, however, the mid-points of the inflexions correspond with the addition of 2 equivs. (50·0 c.c.) of alkali. Moreover, there is a tendency for higher p_H values to be set up during the reaction with tartaric acid. Thereafter the p_H values are such as would be caused by buffer action between the added tartaric acid and some sodium tartrate.

It might be considered that the incidence of these inflexions at 2 equivs. of alkali points to the formation of complex salts, $Na_2XO_3C_4H_4O_6$ (X = Mo or W), but this is not quite the case, for the p_H values subsequently set up suggest the existence of a little sodium tartrate in the solution. Hence the reactions cannot be completely expressed in the form $Na_2MoO_4 + H_2\bar{T} \longrightarrow Na_2\bar{T},MoO_3 + H_2O$ and $Na_2WO_4 + H_2\bar{T} \longrightarrow Na_2\bar{T},WO_3 + H_2O$. An estimate of the amount of the sodium tartrate which had not thus reacted with the molybdic and tungstic acids can be made from a consideration of the amounts of tartaric acid that had to be added in excess of 2 equivs. to bring the solutions to (1) $p_H = p_{K_2}$ of tartaric acid (*i.e.*, to a stage corresponding to three-fourths neutralisation of tartaric acid), (2) $p_H = \frac{1}{2}(p_{K_1} + p_{K_2})$ of tartaric acid (*viz.*, to the stage of its half-neutralisation) (see Britton, " Hydrogen Ions," 1932). Thus, in the molybdate titration, p_H 4·0 (*i.e.*, p_{K_2}) was reached when 55·0 c.c. of tartaric acid had been added, and consequently the 5 c.c. in excess must have been buffered by an amount of sodium tartrate produced by the reaction of 15 c.c. of tartaric acid with the sodium molybdate.

Hence it follows that, of the 50 c.c. of tartaric acid required to react with sodium molybdate, 50 — 15 = 35 c.c. reacted to produce sodium tartrate which apparently, by combining with the molybdenum trioxide, was unable to exert any buffer action. Up to this stage the reaction might be expressed thus: $Na_2MoO_4 + 0{\cdot}7H_2\bar{T} \longrightarrow 0{\cdot}7Na_2\bar{T},MoO_3 + 0{\cdot}3Na_2MoO_4$. Incidentally, it happens that the mid-point of the hydrochloric acid curve corresponds to an equivalent amount of hydrochloric acid having failed to react. During the subsequent addition of tartaric acid, sodium tartrate appears to have been formed, and the molybdic acid probably was involved in complex formation. The same amount of free sodium tartrate is indicated by the amount of excess tartaric acid required to reach p_H 3·5, *i.e.*, $\frac{1}{2}(4{\cdot}0 + 3{\cdot}0)$, 65 c.c. of acid being added.

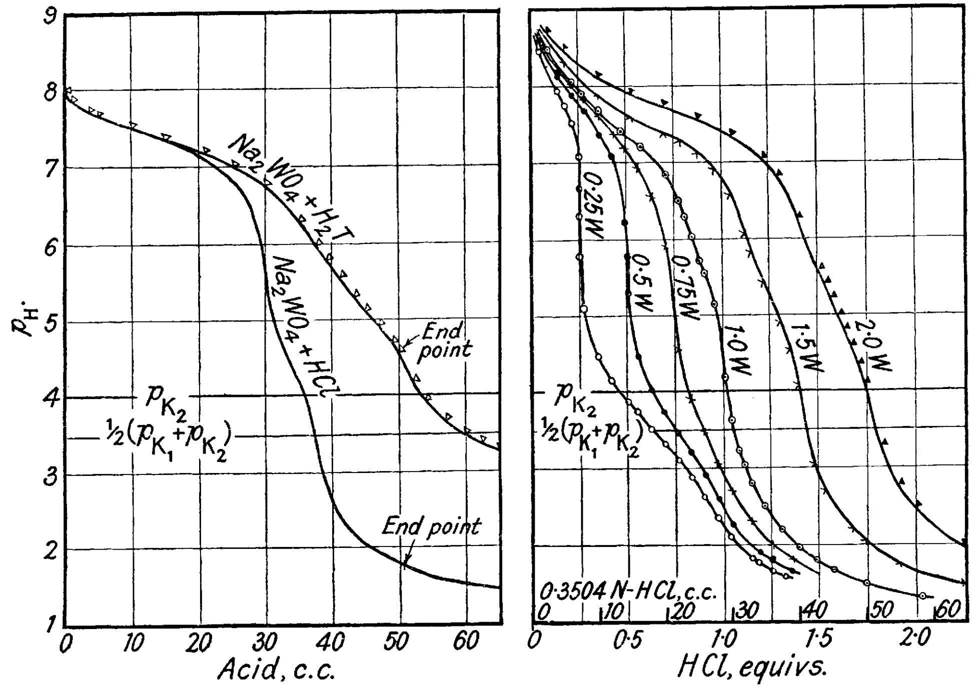
In the tungstate titration, p_H 4·0 and 3·5 are given with 54·0 and 61 c.c. respectively of tartaric acid. Hence, the former result points to 50 — (3 × 4) = 38 c.c., and the latter to 50 — 11 = 39 c.c. of tartaric acid having reacted to form sodium tartrate which immediately combined with the liberated tungstic acid. The mean, 38·5 c.c., shows that 1·54 equivs. of tartaric acid by reaction led to complex formation, and again, such an amount of a mineral acid, *e.g.*, hydrochloric acid, would have formed a fairly stable sodium polytungstate indicated by the point of the lower inflexion of the tungstate–hydrochloric acid curve. That complex formation does not occur during the last stages of the reaction with either sodium molybdate or tungstate seems to be associated with the fact that then the solutions are just becoming appreciably acid. The two sets of curves given at the right of Figs. 2 and 3 respectively refer to titrations with 0·3504*N*-hydrochloric acid of 50 c.c. of solutions that were each 0·1*M* with respect to sodium tartrate and 0·025, 0·05, 0·075, 0·1, 0·15, and 0·2*M* with respect to (1) sodium molybdate and (2) sodium tungstate. The individual curves are marked by the molecular ratios of sodium molybdate or sodium tungstate to sodium tartrate.

The curves in Fig. 2 show that well-defined inflexions were produced in the 0·25, 0·5, 0·75, and 1 titrations when the hydrochloric acid was exactly that required to react with the sodium molybdate. In the 1·5 and 2 titrations the inflexions appeared some time before the stoicheiometrical amounts of hydrochloric acid had been added. Moreover, the p_H values during the initial stages were appreciably higher than those that are characteristic of the straightforward decomposition of sodium molybdate with hydrochloric acid, as is seen from the left diagram of Fig. 2. That these observations are also true of the tungstate–tartrate titrations is shown by Fig. 3.

It is particularly instructive that the inflexions should occur with 2 equivs. of hydrochloric acid per mol. of either sodium molybdate or tungstate when the molecular ratio of the molybdate or tungstate to sodium tartrate does not exceed unity. As shown by the left-hand diagrams of Figs. 2 and 3, these inflexions (*i.e.*, when complex formation does not occur) are produced approximately at 1·5 equivs. of acid. It seems highly probable that these inflexions coupled with the initial p_H's are to be accounted for by the molybdic or tungstic oxide uniting with the sodium tartrate: *e.g.*, $Na_2\bar{T} + MoO_3 \longrightarrow Na_2MoO_3\bar{T}$. That these complex salts are formed in the 1 : 1 ratio (*i.e.*, $Na_2\bar{T} : XO_3$) seems to be proved by the fact that, when less sodium tartrate is present than is necessary to give this ratio, the inflexions appear before the 2 equivs. of hydrochloric acid are added.

Further proof of the composition of the two complex tartrates is forthcoming from the p_{H} values set up after the inflexions. Thus, as before, the tartaric acid will be three-quarters neutralised when the solution has acquired a p_{H} of 4 and half-neutralised at p_{H} 3·5. In these titrations, however, hydrochloric acid is used, and consequently these stages of neutralisation will result from replacement of the sodium tartrate present in the solutions. Table III, which was compiled directly from the titration graphs, gives the amounts of hydrochloric acid that were added to bring the solutions to p_{H} 4·0 and p_{H} 3·5 (cols. 3 and 6 respectively). Cols. 4 and 7 give the quantities of hydrochloric acid that were necessary in excess of the amounts, given in col. 2, to react with the alkali molybdate or tungstate. By assuming that the molybdic and tungstic acids, liberated by addition of 2 equivs. of hydrochloric acid, immediately reacted with 2 equivs. of sodium tartrate present in the solution to form $\mathrm{Na_2MoO_3\overline{T}}$ or $\mathrm{Na_2WO_3\overline{T}}$, then the amount of sodium tartrate existing in the solution is known. To bring the solution to p_{H} 4 one-quarter of this sodium tartrate must have been converted into tartaric acid and sodium chloride. Actually, the solution will consist of an equimolar mixture of sodium tartrate and sodium hydrogen tartrate; *e.g.*, in a $0{\cdot}25\mathrm{Na_2XO_4,Na_2\overline{T}}$ titration, 0·25 mol. of $\mathrm{XO_3}$ will be set free on adding 0·5 mol. of hydrochloric acid. The 0·25 mol. of $\mathrm{XO_3}$ combines with 0·25 mol. of sodium tartrate to form $\mathrm{Na_2XO_3\overline{T}}$, leaving 0·75 mol. of sodium tartrate in solution to give rise to buffer action on adding more hydrochloric acid. As 50 c.c. of 0·1*M*-sodium tartrate require 28·54 c.c. of 0·3504*N*-hydrochloric acid for the complete replacement of the tartaric acid, it follows that in the 0·25 titrations the 0·75 mol. of sodium tartrate would require $\frac{3}{4}$ of 28·54 = 21·41 c.c. To bring the solution to p_{H} 4·0, back-titration must be carried one-quarter of the way, *i.e.*, by adding $\frac{1}{4} \times 21{\cdot}41$ c.c. = 5·4 c.c. of hydrochoric acid. Similarly, to bring the solution to p_{H} 3·5 (half-neutralisation) $\frac{1}{2} \times 21{\cdot}41 = 10{\cdot}7$ c.c. must be added. The theoretical excesses, recorded in cols. 5 and 8 of Table III, are calculated in this way, and when they are compared with the amounts, obtained directly from the curves, show that the underlying assumptions are fully justified.

FIG. 3.



The final portions of the titrations of sodium molybdate and sodium tungstate with tartaric acid seem to indicate that some molybdic and tungstic acid might enter into the complex salt

TABLE III.

Titration $\frac{Na_2XO_4}{H_2T}$.	HCl, c.c., to decompose Na_2XO_4.	HCl, c.c., to set up p_H 4·0.	Excess HCl, c.c. Obs.	Excess HCl, c.c. Calc.	HCl, c.c., to set up p_H 3·5.	Excess HCl, c.c. Obs.	Excess HCl, c.c. Calc.
Sodium molybdate–sodium tartrate titrations with hydrochloric acid.							
0·25	7·14	12·7	5·6	5·4	17·8	10·7	10·7
0·50	14·27	18·3	4·0	3·6	21·6	7·3	7·1
0·75	21·41	23·4	2·0	1·8	25·2	3·8	3·6
1·00	28·54	28·7	0·2	0			
Sodium tungstate–sodium tartrate titrations with hydrochloric acid.							
0·25	17·14	12·5	5·4	5·4	18·0	10·9	10·7
0·50	14·27	17·6	3·3	3·6	21·6	7·3	7·1
0·75	21·41	23·2	1·8	1·8	25·6	4·2	3·6
1·00	28·54	29·0	0·5	0			

in amounts greater than 1 mol. per mol. of sodium tartrate. In the 1·5 and 2·0 $Na_2XO_4 : Na\overline{T}$ titrations, it would be expected that if the complex salts, $Na_2XO_3\overline{T}$, alone were formed, the back-titrations of the 0·5 and 1 mol. of Na_2XO_4, that were not involved in the formation of the complex salts, would follow the normal courses of molybdate and tungstate p_H titration curves. The inflexions are, however, somewhat delayed; *e.g.*, in the 1·5 and 2·0 molybdate–tartrate titrations the inflexion is produced with 1·7 and 1·5 equivs. of acid respectively, whilst in the titration without tartrate, the same stage of the inflexion occurs with 1·4 equivs. of hydrochloric acid. It is probable that these delays, though small, are the result of the formation of complex molybdotartrates containing more than 1 mol. of molybdic acid as governed by some such equilibria as $x\text{MoO}_3 + \text{Na}_2\text{MoO}_3\overline{\text{T}} \rightleftharpoons \text{Na}_2(\text{MoO}_3)_{x+1}\,\overline{\text{T}}$. This reaction would account for the fact that the rotatory power of 0·1*M*-sodium tartrate solutions to which various amounts of molybdic acid have been added continues to increase regularly up to the saturation of the solution. It does not remain constant when more than 1 mol. of molybdic acid has been added to 1 mol. of sodium tartrate, such as would be expected if $Na_2MoO_3\overline{T}$ alone existed. Similar observations hold in the case of the tungsten complex.

CONCLUSION.

The polarimetric results show that both molybdic and tungstic acids behave similarly in forming complexes with sodium tartrate. The gradual formation of complex salts during the neutralisation of the tartaric acid is shown by the increase in rotation. When sufficient alkali is added to convert the complex salts into sodium tartrate and sodium molybdate, or tungstate, the optical activity becomes equal to that of sodium tartrate alone, and remains so when the solution contains excess alkali. Complex formation is then undoubtedly non-existent. The p_H values (Figs. 2 and 3) of solutions of sodium molybdate or tungstate and sodium tartrate are, however, higher than those that could be attributed to either of the solutes alone. Regarding the complexes formed in acid and neutral solutions, the p_H curves confirm the optical data and also indicate that the salts $Na_2(MoO_3)C_4H_4O_6$ and $Na_2(WO_3)C_4H_4O_6$ are stable in neutral and acid solutions. In presence of excess of either alkali molybdate or tungstate they appear to combine with further amounts of the respective abnormal acid. This agrees with the regular increase in rotatory power of solutions of sodium tartrate caused by increasing proportions of either molybdic or tungstic acid.

On referring to the sets of rotation–neutralisation curves in Fig. 1, it is seen that the curves, obtained by Gernez, Rosenheim, and others, represent, apart from changes in optical activity, two variables. These curves, then, are constructed from a number of points each lying on parallel neutralisation curves of tartaric acid containing various proportions of molybdic acid. Sodium molybdate generally reduces the rotation of $Na_2(MoO_3)C_4H_4O_6$, and therefore the maximum rotation will occur when the sodium molybdate and tartaric acid are present in equimolar proportion. In a similar manner, and as found by Rosenheim and Itzig, the maximum rotations, though much greater, will be given with equimolecular quantities of tartaric acid and sodium quadrimolybdate, $Na_2Mo_4O_{13}$. Presumably this maximum value should indicate the formation of $Na_2(MoO_3)_4C_4H_4O_6$. In view of the stability of the salts, $Na_2(MoO_3)C_4H_4O_6$ and

$Na_2(WO_3)C_4H_4O_6$, and also of the fact that molybdic and tungstic acids respectively are able to enhance their rotatory powers, it seems probable that in the presence of these acids there occurs further combination, which is determined by the equilibria

$$Na_2(XO_3)C_4H_4O_6 + xXO_3 \rightleftharpoons Na_2(XO_3)_{x+1}C_4H_4O_6.$$

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