## **209.** *Physicochemical Studies of Complex Formation involving Weak Acids. Part IX. Complex Formation between Boric and Tartaric Acids.*

By H. T. S. Britton and Patricia Jackson.

Biot observed in 1835 that boric acid increased the rotatory power of tartaric acid solutions. It also increases the electrical conductivity [Magnanini, *Gazzetta*, 1891, **21**, (ii), 215; Amadori, *ibid.*, 1931, **61**, (ii), 215] and the hydrogen-ion concentration (Rimbach and Ley, *Z. physikal. Chem.*, 1922, **100**, 393; Burgess and Hunter, J., 1929, 2838). These properties are usually ascribed to the formation of a complex borotartaric acid, and such a view seems admissible from the fact that boric acid diminishes the conductivity of solutions of sodium tartrate [Magnanini and Bentivoglio, *Gazzetta*, 1893, **23**, (ii), 451] apparently owing to the formation of a borotartrate ion having a lower mobility than that of the tartrate.

Potentiometric titrations of concentrated solutions of mixtures of boric and tartaric acids have been described by Burgess and Hunter and by Lowry (see below), which indicate that boric acid has a pronounced effect in strengthening the tartaric acid in its initial stages of neutralisation and weakening it somewhat in the final. The first authors considered their curve to point to the dibasicity of borotartaric acid, whilst Lowry suggested that the final weakness might be caused by " a little extra work to detach the last carboxyl from the boron."

Many attempts have been made to isolate the complex acid salts in crystalline form from solution, and numerous substances have been described. Burgess and Hunter determined the isotherms at 0°, 25°, and 50° of the ternary system boric acid–tartaric acid–water, but found no evidence of any solid complex acid, the only solid phases being the two simple acids (see also Bancroft and Davis, *J. Physical Chem.*, 1930, **34**, 2479). Recently, Lowry (J., 1929, 2853) and Bancroft and Davis have isolated a potassium borotartrate, $KB(C_4H_4O_6)_2$, in which the boron is believed to exist as the result of a quadricovalent linkage. The ammonium salt and the analogous potassium boromalate have since been described by Jones (J., 1933, 951).

No attempt appears to have been made, however, to bring all the physicochemical evidence together and to formulate a theory regarding the complex acid and salt as they exist in solution. In order to make it possible to interpret conductometric and potentiometric data and to correlate them with polarimetric data it is necessary to confine attention to dilute solutions, and then to extend the conclusions to more concentrated solutions. There is, however, a limit to the dilutions that can be employed, for both Magnanini and Amadori have shown that in very dilute solutions complex formation can hardly be detected by conductivity measurements.

We have confined our attention largely to solutions of the order of decimolar, and have followed the change in $p_H$, conductivity, and optical rotation during the progressive addition of sodium hydroxide to various tartaric–boric acid mixtures. With every amount of boric acid used, a maximum rotation corresponding to the proportions $Na_2T,NaHT,xHBO_2$ was observed, and in alkaline solutions the rotations depended upon the boric acid present ; they were always lower than that of the sodium tartrate and with much boric acid they even became lævorotatory. This is all the more surprising, for both the $p_H$ and the conductivity of the alkaline solutions suggest that sodium *d*-borotartrate, which might have previously been formed, had then become decomposed.

## EXPERIMENTAL.

I. *Rotatory Power.*—Five series of solutions were prepared containing tartaric and boric acids in various degrees of neutralisation. Each solution was $0{\cdot}1M$ with respect to tartaric acid, free and combined, and the different series were respectively 0·025, 0·050, 0·075, 0·3161, and $0{\cdot}500M$ with respect to boric acid. The extent of neutralisation is given in col. 1 of Table I. The rotations were measured in a 4-dm. glass-jacketed tube at 25°, and each measurement is the mean of 20 readings. The rotations were taken with the mercury 5461 Å. line. To facilitate comparison, the data are recorded in cols. 3—7 (Table I) as molecular rotations, in terms of total tartaric acid. The molecular rotation $[M]$ = observed angle/4 × concentration of tartaric acid (free and combined). Col. 8 refers to a similar set of measurements on solutions $1M$ with respect to tartaric acid and $0{\cdot}5M$ with respect to boric acid.

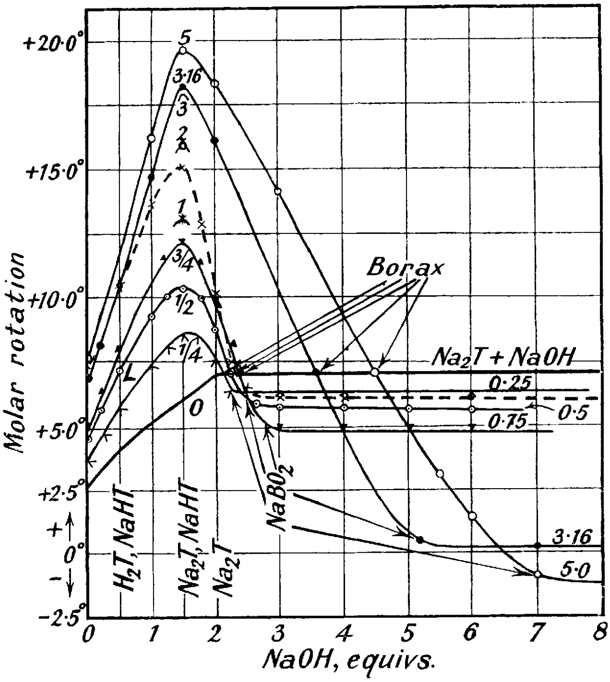
These rotations are plotted in Fig. 1 against the equivalents of alkali present in the solutions. The heavy line is that of the neutralisation of $0{\cdot}1M$-tartaric acid, and the broken line corresponds to the data in col. 8. The different curves are marked by the molecular ratio of boric acid : tartaric acid. The most remarkable observation brought out by these curves is that the maximum rotations occur in each case when the tartaric acid has undergone three-quarters neutralisation, *i.e.*, corresponding to $Na_2T,NaHT$. It is also seen that the smaller proportions of boric acid exert a relatively larger influence in determining the magnitude of these maxima than do the greater amounts. Thus the increase produced by 0·5 mol. of boric acid to 1 mol. of tartaric acid is 10·35°—5·88° = 4·47°, compared with the rotation of tartaric

TABLE I.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $[H_2T]$ = | 0·1 | 0·1 | 0·1 | 0·1 | 0·1 | 0·1 | 1·0 |
| $[HBO_2]$ = | 0·0 | 0·025 | 0·05 | 0·075 | 0·3161 | 0·50 | 0·5 |
| $\frac{[HBO_2]}{[H_2T]}$ = | 0 | 0·25 | 0·5 | 0·75 | 3·161 | 5·0 | 0·5 |
| $\frac{[NaOH]}{[H_2T]}$. | Molecular rotations. | | | | | | |
| 0 | 2·60° | 3·63° | 4·45° | 4·78° | 6·98° | 7·70° | 7·38° |
| 0·2 | 3·25 | | 5·63 | | | | 8·09 |
| 0·25 | | 4·68 | | 6·33 | | | |
| 0·50 | | 5·68 | 7·18 | 7·98 | | | 10·54 |
| 1·00 | 5·10 | 7·30 | 9·30 | | 14·73 | 16·23 | 13·63 |
| 1·25 | | 8·10 | 10·03 | 11·50 | | | |
| 1·50 | 5·88 | 8·58 | 10·35 | 12·13 | 18·23 | 19·65 | 15·06 |
| 1·75 | | 8·45 | | 11·30 | | | |
| 1·80 | 6·55 | | 9·95 | | | | 12·85 |
| 2·00 | 7·00 * | 7·58 | 8·68 | 9·58 | 16·10 | 18·30 | 10·19 |
| 2·125 | | 7·00 * | | | | | |
| 2·25 | 7·00 | 6·38 | 7·03 * | 8·10 | | | |
| 2·375 | | | | 7·05 * | | | |
| 2·25 | | | | | | | 7·50 * |
| 2·50 | 7·00 | | | | | | 6·52 |
| 2·65 | | | 5·80 | | | | |
| 3·00 | | 6·30 | 5·68 | 4·83 | | 14·08 | 6·14 |
| 3·581 | | | | | 7·10 * | | |
| 4·0 | | 6·32 | 5·65 | 4·83 | | | 6·00 |
| 4·5 | | | | | | 7·03 * | |
| 5·0 | | | 5·58 | 4·78 | | | 5·98 |
| 5·161 | | | | | 0·50 | | |
| 5·5 | | | | | | 3·07 | |
| 6·0 | | 6·25 | 5·53 | | 0·38 | 1·45 | |
| 7·0 | | | | | | −0·85 | |
| 12·0 | | | | | | −1·38 | |

* See p. 1005.

FIG. 1.



acid at the same stage of neutralisation, whereas the change produced by increasing the boric acid from 3·161 to 5·0 mols. is 19·65°—18·25° = 1·40° (Table I). A similar effect is seen in the case of the initial free acid solutions. A rapid diminution in the rotation occurs after passing the maximum, but at 2 mols. of alkali, the rotations are still much higher than that of the sodium tartrate alone. Each of the curves intersects the sodium tartrate–alkali line at points, marked by arrows and " Borax," which correspond exactly with the neutralisation of one-half of the boric acid in the respective solutions. The rotations corresponding with these points are indicated by asterisks (*) in Table I. This agrees with the fact that in dilute solutions of sodium tartrate, the inclusion of borax does not alter the rotation of the active salt. With more alkali the rotations fall still lower, but the curves become inflected when the neutralisation of the boric acid is complete in the form of sodium metaborate. The location of these points is marked by arrows indicating $NaBO_2$. Thereafter the rotatory power assumes an approximately constant value, which is lævorotatory in the case of those solutions containing sodium borate in amounts equal to, or more than, $5NaBO_2 : 1Na_2T$. The broken line in Fig. 4 D shows the effect of increasing amounts of sodium metaborate on the rotation of sodium tartrate in alkaline solutions. The ordinate (to the left) gives the ratio of the observed rotation to the rotation of the sodium tartrate.

The broken line in Fig. 1 is that of the neutralisation of 1*M*-tartaric acid and 0·5*M*-boric acid solutions. Although the curve is of the same form as those of the more dilute solutions, it will be seen that the maximum value is much higher than that given by the same ratio of the two acids in a solution ten times more dilute (denoted by " ½ ").

Table II (*a*) gives the observed and molecular rotations produced by 0·1*M*-tartaric acid and *xM*-boric acid solutions, in which the tartaric acid is 75% neutralised, *i.e.*, by 0·15*M*-sodium hydroxide. The last line gives the values of the rotations compared with that of the same tartaric solution, without boric acid, similarly neutralised. The values are plotted in Fig. 4 D against the mols. of boric acid. In a similar way, Table II (*b*) and Fig. 4 C refer to 1·0*M*-tartaric acid, *xM*-boric acid, and 1·5*M*-sodium hydroxide solutions. It happens, however, that during neutralisation of *M*-tartaric acid solutions with sodium hydroxide, crystallisation of sodium hydrogen tartrate occurs and the rotation of such a solution at three-quarters neutralisation cannot be experimentally determined. The values given in parentheses in Table II (*b*) were extrapolated from the values of *M*-tartaric acid and *M*-sodium tartrate, $\alpha_{25^\circ}$ being 9·01° and 26·84° respectively. The solutions 0·1*M*-tartaric acid + 0·5*M*-boric acid and 1*M*-tartaric acid + 1*M*-boric acid are very nearly saturated with respect to boric acid, and it is therefore interesting to note that the ratios of $[M]_{\text{max.}}/[M]_{\text{Na}_2\text{T,NaHT}}$ in both cases are almost identical.

TABLE II.

(*a*) 0·1*M*-Tartaric acid, *xM*-boric acid, 0·15*M*-sodium hydroxide.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| *xM*-$HBO_2$ ............ | 0 | 0·025 | 0·05 | 0·075 | 0·10 | 0·15 | 0·20 | 0·3161 | 0·50 |
| $\alpha_{25^\circ}$ ...................... | 2·35° | 3·43° | 4·14° | 4·85° | 5·24° | 5·86° | 6·37° | 7·29° | 7·86° |
| $[M_{\text{max.}}]^{25^\circ}_{5461}$ ............ | 5·88° | 8·58° | 10·35° | 12·13° | 13·10° | 14·65° | 15·93° | 18·23° | 19·65° |
| $\frac{[M_{\text{max.}}]}{[M_{\text{Na}_2\text{T,NaHT}}]}$ ......... | — | 1·46 | 1·76 | 2·06 | 2·23 | 2·49 | 2·71 | 3·10 | 3·34 |

(*b*) 1*M*-Tartaric acid, *xM*-boric acid, 1·5*M*-sodium hydroxide.

| | | | |
|---|---|---|---|
| *xM*-$HBO_2$ .......................... | 0·0 | 0·5 | 1·0 |
| $\alpha_{25^\circ}$ .................................. | (22·38°) | 60·24° | 75·45° |
| $[M_{\text{max.}}]^{25^\circ}_{5461}$ .......................... | (5·60°) | 15·06° | 18·86° |
| $\frac{[M_{\text{max.}}]}{[M_{\text{Na}_2\text{T,NaHT}}]}$ ...................... | — | 2·69 | 3·37 |

The molecular rotations, referred to the tartaric acid contents only, of a series of borotartaric acid solutions 0·1*M* with respect to tartaric acid are given in Table III, col. 4, and the last column records the ratios of these rotations to that of the tartaric acid alone. These are plotted in Fig. 4 C and so are the ratios corresponding to 1*M*- and 2*M*-tartaric acid solutions and the same solutions containing 0·5 g.-mol. of boric acid per litre. For *M*-tartaric acid, $[M]^{25^\circ}_{5461} =$ 2·25°, and it becomes 7·38° in *M*-tartaric acid + 0·5*M*-boric acid, whence 7·38°/2·25° = 3·28. Similarly 2*M*-tartaric acid gives $[M]^{25^\circ}_{5461} =$ 1·85°, and 5·72° in 2*M*-tartaric acid + 0·5*M*-boric acid solution, the ratio being 3·10.

II. $p_H$ *Titration Curves.*—The heavy curve at the bottom of Fig. 2 is that of the titration of 50 c.c. of 0·1*M*-tartaric acid with 0·2771*M*-sodium hydroxide at 18° and was obtained by means of the hydrogen electrode. The thinner lines, taken in order downwards refer to the titration of mixtures of 0·1*M*-tartaric acid with 0·05*M*, 0·075*M*, 0·3161*M*, and 0·5*M*-boric

TABLE III.

| $\frac{[HBO_2]}{[H_2T]}$. | $\kappa_{25°}$. | $p_H$. | $[M]^{25°}_{5461}$. | $\frac{\kappa_{BT}}{\kappa_{H_2T}}$. | $\frac{[H^{\cdot}]_{BT}}{[H^{\cdot}]_{H_2T}}$. | $\frac{[M]_{BT}}{[M]_{H_2T}}$. |
|---|---|---|---|---|---|---|
| 0 | 3·70 | 1·92 | 2·67° | — | — | — |
| 0·25 | 4·85 | 1·81 | 3·63 | 1·31 | 1·29 | 1·36 |
| 0·50 | 5·65 | 1·77 | 4·45 | 1·53 | 1·41 | 1·66 |
| 0·75 | 6·28 | 1·73 | 4·85 | 1·70 | 1·55 | 1·81 |
| 1·00 | 6·83 | 1·71 | 5·10 | 1·85 | 1·62 | 1·91 |
| 1·50 | 7·65 | 1·63 | 5·65 | 2·07 | 1·95 | 2·11 |
| 2·00 | 8·27 | 1·60 | 6·15 | 2·24 | 2·09 | 2·30 |
| 3·00 | 9·33 |  | 6·88 | 2·52 |  | 2·58 |
| 3·161 | 9·44 | 1·51 | 6·93 | 2·55 | 2·57 | 2·59 |
| 4·00 | 9·85 | 1·47 | 7·38 | 2·66 | 2·82 | 2·76 |
| 5·00 | 10·42 | 1·43 | 7·70 | 2·82 | 3·09 | 2·88 |

acid respectively. Even in such dilute solutions, the boric acid is thus seen to have a marked effect in increasing the strength of the acid, the precise amount depending upon the proportion of boric acid to tartaric acid in the solution. The borotartaric acid curves either cross, or tend to cross, the tartaric acid curve at a point corresponding approximately to three-quarters neutralisation of the tartaric acid. Immediately after the addition of 2 equivs. of alkali, the curves exactly follow the course of neutralisation of boric acid, and in every case the $p_H$ value at the mid-point of these sections is equal to $p_{K_{HBO_2}}$. The intersection of the borotartaric acid curves with those of tartaric acid at about three-fourths neutralisation is more apparent in the middle and upper pairs of curves (set out separately). They correspond respectively to the titrations of 50 c.c. of 1*M*-tartaric acid, and of 1*M*-tartaric acid + 0·5*M*-boric acid, with 2*M*-sodium hydroxide; and 50 c.c. of 0·5*M*-tartaric acid, and 0·5*M*-tartaric acid + 0·5*M*-boric acid, with 1·231*M*-sodium hydroxide. These two pairs of curves are very similar to those described by Lowry for a 2*M*-tartaric acid + 1*M*-boric acid mixture.

FIG. 2.

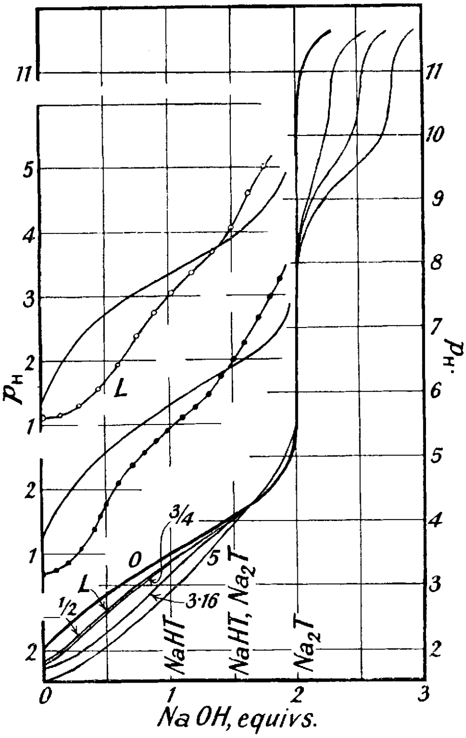
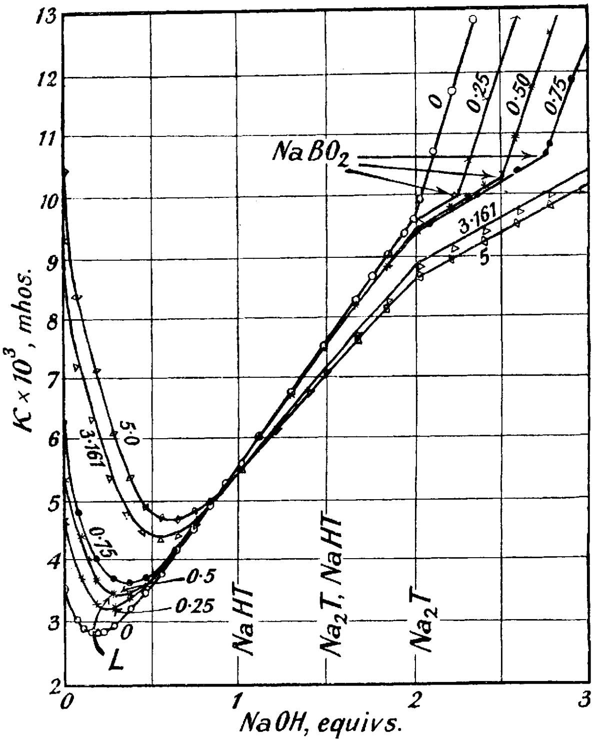


FIG. 3.



Some data are recorded in cols. 3 and 6, Table III, showing the effect of increasing the amount of boric acid in 0·1*M*-tartaric acid solution on (1) the hydrogen-ion concentration (or activity) and (2) the relative ionisations (or activities) as obtained from a comparison of hydrogen-ion concentration of the borotartaric mixture with that of 0·1*M*-tartaric acid. The falling $p_H$ values correspond to increases in ionisation which become nearly treble that of the acid alone when the solution contains 5 mols. of boric acid to 1 mol. of tartaric acid. The values given in the sixth column are represented graphically in Fig. 4 A. This diagram also gives the ratios of hydrogen-ion concentrations in the borotartaric acid mixture to those in tartaric acid for a series of solutions in which the latter acid was maintained at the concentrations indicated on the graphs. These curves, which were constructed from some observations of Rimbach and Ley, reveal very clearly the increasing effect of smaller proportions of boric acid on the ionisation of tartaric acid in more concentrated solutions.

III. *Conductometric Titrations.*—Fig. 3 gives a series of conductometric titrations at 25° with 0·2771*M*-sodium hydroxide of 75 c.c. of solutions 0·1*M* with respect to tartaric acid, and 0·025, 0·05, 0·075, 0·3161, or 0·5*M* to boric acid. The graphs are marked by the molecular ratios of boric to tartaric acid. The ordinates at the beginning of the titrations illustrate the power possessed by the boric acid, which itself has negligible conductivity, of increasing the conductivity of the mixed acids in solution. The extent of the increase depends both on the concentration of the tartaric acid and on the proportion of boric acid added. Col. 2 of Table III gives the specific conductivities of 0·1*M*-tartaric acid alone and of solutions containing increasing amounts of boric acid; col. 5 gives the ratios of these conductivities to that of 0·1*M*-tartaric acid, and these ratios are plotted in Fig. 4 B. Amadori (*loc. cit.*) has also determined the conductivities at 25° of tartaric–boric acid solutions in which the concentrations of both acids were varied. His data were used to construct the other curves in Fig. 4 B, which show the effect of adding increasing quantities of boric acid to tartaric acid solutions of the concentrations marked on the curves. They show that, as the concentration of the tartaric acid is increased, boric acid, even in relatively small amounts, produces a much more rapid increase in conductivity. As shown by the $p_H$ curves, this increased conductivity is caused by increased ionisation, and this fact is reflected in the conductometric graphs in Fig. 3. The moderate strength of the first stage of ionisation of tartaric acid is responsible for the small diminution in conductivity, through the substitution of hydrogen ions by sodium ions during the early part of the titration until a minimum is reached, after which the ionisation of the acid is sufficiently repressed that the conductivity again increases owing mainly to the formation of sodium bitartrate and, subsequently, of the normal tartrate. The addition of more and more boric acid to the tartaric acid not only raises the conductivity of the acid solutions, but, as the curves show, imparts to the mixture the function of a strong acid. For instance, with 5 mols. of boric acid, there is a rapid decrease in conductivity during the addition of the first 0·5 equiv. of alkali. The positions at which the minima occur are determined by the quantity of boric acid. Another important observation is that after the minima have been passed the conductivities gradually become lower than those indicated by the tartaric acid graph, the divergence being greater the greater the amount of boric acid. Nevertheless, definite " breaks " are produced with 2 equivs. of alkali, and the remaining sections of the curves correspond exactly with the neutralisation of the whole amounts of boric acid, followed by the straight lines indicating that unattacked alkali is passing into the solutions.

In connexion with the differences in conductivity occurring when the tartaric acid had been completely neutralised, Magnanini and Bentivoglio (*loc. cit.*) found, for example, by adding 5 mols. of boric acid to 1 mol. of sodium tartrate at 25° that in 0·1*M*-tartrate solution the molecular conductivity was diminished by 16 mhos and, in the case of 0·05*M*-sodium tartrate solution, by 13 mhos. In the present titrations, the concentration of sodium tartrate formed when 2 equivs. of alkali were added was 0·0581*M*. In the simple tartaric acid titration, the specific conductivity then was $9{\cdot}75 \times 10^{-3}$ mho, and $8{\cdot}70 \times 10^{-3}$ mho in the 5 : 1 titration, thus showing a decrease in $\mu$ of 18. With 0·75 mol. of boric acid, $\kappa = 9{\cdot}46 \times 10^{-3}$ mho and therefore the difference was 5, whilst in the 3·161 : 1 titration, $\kappa$ was $8{\cdot}91 \times 10^{-3}$, decrease = 14.

## DISCUSSION.

Comparison of the curves in A, B, and C of Fig. 4 reveals the important effect of the concentration of tartaric acid on the magnitude of the increases in hydrogen-ion concentration, specific conductivity, and optical activity produced by adding boric acid. In the highest concentrations represented, *viz.*, 1—2*M*-tartaric acid, rapid linear increases occur with 0·5 mol. of boric per mol. of tartaric acid, whereas in the more dilute solutions boric acid yields smaller and gradually diminishing increases as the proportion is made larger. If it be assumed that these changes are the result of some chemical combination between the two acids in forming a complex borotartaric acid,

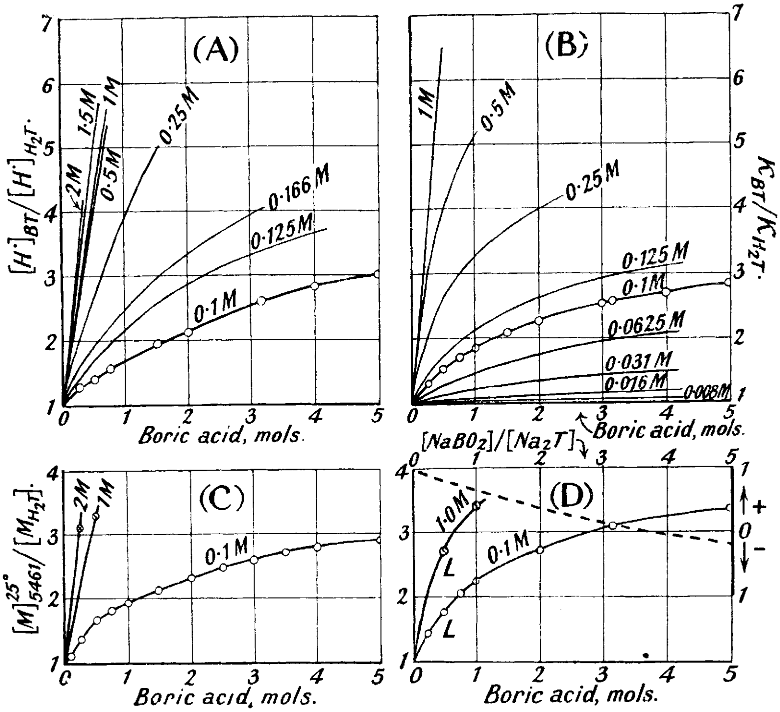
$$x\text{Tartaric acid} + \text{boric acid} \rightleftharpoons \text{borotartaric acid},$$

then, according to the law of mass action,

$$\bar{K} = [\text{Tartaric acid}]^x[\text{Boric acid}]/[\text{Borotartaric acid}].$$

If $x$ be greater than unity, then the stability of the complex acid will be more dependent on the concentration of the tartaric acid than on that of the boric acid. Hence, it follows that in the more concentrated tartaric acid solutions, boric acid would form a relatively greater amount of borotartaric acid than when the two simple acids are mixed in the same proportion in more dilute solutions. The greater increases in the physical properties, which in the circumstances would be ascribed to the concentration of the complex borotartaric acid, in the concentrated solutions appear to justify the view that a complex acid, which is stronger and more optically active than tartaric acid, is actually formed.

FIG. 4.



On the grounds of the mass-law expression, it would appear that the initial and the final slope of the curves might correspond chiefly with the formation of the complex acid, for, at the beginning, the tartaric acid is in large excess, whereas at the end, the boric acid is in excess. By drawing tangents to each curve at the beginning and at the end, it is found that they intersect at points, the abscissæ of which are 0·5 mol. boric acid : 1 mol. of tartaric acid. This might be considered as evidence of the formation of ditartaric–monoboric acid; this proportion happens to be that in Lowry's salt, $H_2T,KHT,HBO_2$.

The behaviour in solution of the sodium analogue of Lowry's salt should therefore be indicated by the points, L, in Fig. 1, 2, and 3. The positions of these points do not warrant any conclusions being made regarding the individuality of the salt. It might be held that the 5 boric : 1 tartaric conductometric curve in Fig. 3 offers some evidence of the monobasic nature of ditartaric–boric acid, as the strong-acid section of the graph terminates when approximately 0·5 equiv. of alkali has been added, and the salt formed is $NaHT,H_2T,xHBO_2$. In such a dilute solution, however, it is by no means certain that all the tartaric acid is converted into the borotartaric acid, and it is therefore probable that, had the solubility of the boric acid permitted greater amounts to be included in the tartaric acid solution, the strong-acid section might have extended over a wider range of neutralisation.

On the contrary, the maximum rotations in Fig. 1, and the convergence or intersection of the $p_H$ curves in Fig. 2, seem to provide definite and convincing evidence that a complex salt is formed when 1·5 equivs. of alkali have been added per mol. of tartaric acid. In the light of the previous argument, the salt then formed is $Na_2T,NaHT,HBO_2$. The nature of the curve in Fig. 4 D affords evidence of the same proportion of boric acid in the salt as is present in the original acid. Incidentally, such a salt would appear to be the normal salt of a tribasic complex acid. Lowry's salt would thus appear to be an acid salt (see also Jones, J., 1933, 951).

Further additions of alkali, according to Fig. 2, merely cause the quantitative decomposition of the salt into normal sodium tartrate and sodium metaborate. The conductometric curves, Fig. 3, reveal that when 2 equivs. of alkali are added and sodium tartrate should be formed, the conductivity is too low, from which it is inferred that boric acid is still in a state of combination with the tartrate ion, thereby imparting to it a reduced ionic mobility. Thereafter, an excess of alkali appears to bring about complete decomposition.

Difficulties, however, occur in the interpretation of the optical-rotation curves, for they show that the alkaline solutions do not give rise to rotations peculiar to the sodium tartrate alone, but to smaller rotations, and, indeed, if the proportion of sodium borate be sufficiently large, to lævorotation. It is curious that on half-neutralisation of the boric acid, *i.e.*, on production of boric acid and sodium borate in the proportion existing in borax, the optical rotations become equal to that of the sodium tartrate alone. Points corresponding with these conditions, however, lie on curves indicating rapid decreases in optical activity, which end in inflexions when the two parent acids have been completely neutralised. Further additions do not cause appreciable variations in optical activity.

It is just possible that a sodium borotartrate may still exist in alkaline solution, despite the fact that the potentiometric curves provide no clues. This would be true if the complex acid were extremely weak, say $\bar{K} = 10^{-14}$, and such a likelihood might possibly explain the lower conductivities during the neutralisation of the boric acid. As far as can be ascertained by physicochemical methods, neither of the two alcoholic groups of tartaric acid possesses an acid character, although some of the alcoholic groups in glycerol, hexoses, and phenols often are acidic, so much so that their dissociation constants can be measured. It is a well-known fact that glycerol and mannitol enhance the strength of boric acid, evidently owing to complex formation, and it may be that similar complex formation involving the alcoholic groups of sodium tartrate and boric acid is present in alkaline solution, although the sodium tartrate present in the titrated solutions had no measurable effect on the $p_H$ values during neutralisation of the boric acid. Such a complex salt would be formed to any great extent only in a solution containing a large excess of alkali, or in alkaline solution containing an excess of either sodium borate or sodium tartrate. In the solutions referred to in Fig. 3, the sodium tartrate concentration is maintained at $0{\cdot}1M$, whereas the borate concentration is varied. As those solutions containing the highest quantities of sodium borate were lævorotatory, it would appear that the ionised complex salt is lævorotatory, and hence the variations produced by the use of smaller proportions of borate would be the resultant of the activity of the sodium *d*-tartrate and whatever amount of the lævo-complex tartrate that might have been formed, the relative amounts being determined by the proportion of boric to tartaric acid originally taken.

It was thought possible that the complex originally present might decompose with the formation of some *l*-tartaric acid. This idea was abandoned for two reasons. First, it failed to account for the rotation of $0{\cdot}1M$-sodium tartrate being unaltered by the presence of varying amounts of borax, and secondly, it might conceivably be possible to prepare *l*-tartaric acid by acidifying alkaline borotartrate solutions in which such inversion had taken place. Rotations of such solutions during acidification might be expected to lie below those of the direct titration. The forward titration rotations are, however, reproduced with very slight divergences, due no doubt to the neutral-salt effect.

If different complexes are stable in acid and in alkaline solution, it is probable that there exists a $p_H$ of maximum instability for both types. If so, this may be that of solutions of sodium tartrate containing borax, where the tartrate is present as simple tartrate. This would explain the rotations observed for such solutions.

In the previous paper of this series an attempt was made to calculate the observed rotations of certain tartaric acid solutions from the molecular rotation of their several components. In the borotartaric acid solutions here dealt with, conditions prevailing during neutralisation are such that the optical nature of the solutions is too complicated to admit, as yet, of theoretical calculation of the curves. Further, even if the actual type of constituents were known, the curves are still composite, representing superimposed curves, *i.e.*, those of the complexes and that of unattacked tartaric acid, the relative proportions of which are governed by mass-law requirements.

Fuller discussion of the theoretical significance of the optical maxima is postponed until work on certain other oxides has been completed.

One of us (P. J.) gratefully acknowledges a grant from H. M. Department of Scientific and Industrial Research.

WASHINGTON SINGER LABORATORIES,
UNIVERSITY COLLEGE, EXETER.

[*Received, March* 19*th*, 1934.]