220. *Physicochemical Studies of Complex Formation involving Weak Acids. Part X. Complex Formation between Tartaric Acid and* (a) *Arsenic Acid,* (b) *Arsenious Acid,* (c) *Antimonous Hydroxide, in Acid and Alkaline Solutions. The Dissociation Constants of Arsenious and Arsenic Acids.*

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

ALTHOUGH it has long been known that complex tartrates of the tartar emetic type, $R(XO)C_4H_4O_6$ ($R = NH_4$, Na, K; $X = As^{III}$, Sb^{III}), exist, and that in solution they have much higher rotatory powers than their corresponding alkali hydrogen tartrates, their nature is still in doubt. Hädrich (*Z. physikal. Chem.*, 1893, **12**, 494; see also Svanberg, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 26, 1) attempted to establish the mode of ionisation of tartar emetic in solution by determination of the equivalent conductivity at different dilutions, but found that $\Lambda_{1024} - \Lambda_{32} = 42$. Svanberg states that the antimonyl tartrate complex is not appreciably hydrolysed. Kahlenberg (*Z. physikal. Chem.*, 1898, **17**, 603) concludes from the conductivities of potassium arsenyl tartrate solutions that dilution causes considerable hydrolysis. Landolt (*Ber.*, 1873, **6**, 1077) finds that in alkaline solutions the rotatory powers of potassium and sodium arsenyl tartrates are very similar to those of the corresponding normal alkali tartrates, and concludes that the complex tartrates must be decomposed into the alkali arsenite and tartrate. Grossmann (*Z. physikal. Chem.*, 1906, **57**, 533) found that tartar emetic solutions became lævorotatory on being made alkaline, and attributed this to displacement of the hydrogen atoms of the alcoholic groups. With either sodium hydrogen carbonate or carbonate the rotation is smaller, but it never becomes lævorotatory.

Lowry and Austin (*Phil. Trans.*, 1922, *A*, **222**, 249) state that, regarded from the standpoint of Drude's equation, the rotatory dispersion of tartar emetic is definitely "simple," whereas "complexity" is strongly developed in tartaric acid and its esters.

Although Pelouze (*Ann. Chim. Phys.*, 1842, **6**, 63) prepared a complex tartrate involving quinquevalent arsenic, *viz.*, $K(AsO_2)C_4H_4O_6,2\frac{1}{2}H_2O$, no enquiry into its possible complex nature has been made. The structure of complex salts of the emetic type has been the subject of much conjecture (see, *e.g.*, Reihlen and Hezel, *Annalen*, 1931, **487**, 213).

Dissociation Constants of Arsenic and Arsenious Acids.—Before commencing our investigation, we determined the dissociation constants of these two acids by glass electrode titration. The existing knowledge of their mode of ionisation is scanty, probably owing to the difficulty of determining hydrogen-ion concentrations of arsenical solutions. The difficulty is now removed by the introduction of the glass electrode, and Hughes (J., 1928, 491) has used it to measure the p_H values at 25° at half-neutralisation of the second stage of arsenic acid, *viz.*, 6·70, and of the first stage of arsenious acid, *viz.*, 9·07. As the solutions were 0·025*M*, it follows that p_{K_2} of $H_3AsO_4 = 6{\cdot}70$, and p_{K_1} of $H_3AsO_3 = 9{\cdot}07$. Using indicators, Goldfinger and Schweinitz (*Z. physikal. Chem.*, 1932, *B*, **19**, 219) find the latter value to be $9{\cdot}4 \pm 0{\cdot}3$, whereas, by making spectroscopic determinations of the ion concentrations of solutions of arsenious oxide in alkali of various concentrations, they find $p_{K_2} = 3 \times 10^{-14}$ (1—6×10^{-14}). Conductivity has led to widely differing results for arsenious acid; *e.g.*, Wood (J., 1908, **93**, 415) and von Zawidzky (*Ber.*, 1903, **36**, 1429) found $2{\cdot}65 \times 10^{-9}$ and $2{\cdot}1 \times 10^{-8}$ respectively at 25°. For arsenic acid, Luther (*Z. Elektrochem.*, 1907, **13**, 294), by means of electrical conductivity at 25°, obtained the value 5×10^{-3} for K_1, whereas Washburn (*J. Amer. Chem. Soc.*, 1908, **30**, 31; 1913, **35**, 681) found $4{\cdot}8 \times 10^{-3}$. The latter stated that K_2 and K_3 for arsenic acid were probably lower than the respective values for phosphoric acid, whereas Blanc (*J. Chim. physique*, 1920, **18**, 28) calculated $K_2 = 4 \times 10^{-5}$ and $K_3 = 6 \times 10^{-10}$ from conductometric titration curves.

Table I gives data obtained by titrating a solution of arsenic acid with sodium hydroxide at 18° by means of the glass electrode and the ballistic galvanometer circuit. The p_H and p_K values calculated therefrom (see Britton, "Hydrogen Ions," 1932) are recorded for each successive addition of 0·125 equiv. of alkali. The titration curve is very similar to that of

TABLE I.

Titration of 100 *c.c. of* 0·01214M-H_3AsO_4 *with* 0·0995N-NaOH.

NaOH, equivs.	0·125.	0·250.	0·375.	0·500.	0·625.	0·750.	0·875.
First stage of neutralisation.							
p_H	2·35	2·42	2·52	2·62	2·78	2·98	3·30
p_{K_1}	2·24	2·29	2·28	2·23	2·25	2·25	2·23
Mean $p_{K_1} = 2{\cdot}25$; $K_1 = 5{\cdot}62 \times 10^{-3}$.							
Second stage of neutralisation.							
p_H	5·96	6·31	6·56	6·75	6·98	7·23	7·58
p_{K_2}	6·81	6·78	6·78	6·75	6·76	6·75	6·75
Mean $p_{K_2} = 6{\cdot}77$; $K_2 = 1{\cdot}70 \times 10^{-7}$.							
Third stage of neutralisation.							
p_H	10·51	10·83	11·04	11·22	11·36	11·45	11·55
p_{K_3}	11·51	11·49	11·49	11·54	11·58	11·55	11·58
Mean $p_{K_3} = 11{\cdot}53$; $K_3 = 2{\cdot}95 \times 10^{-12}$.							

phosphoric acid and contains two well-defined inflexions corresponding with the formation of the mono- and the di-sodium salt. The value of K_1 is slightly higher than those obtained by Luther and Washburn. That of K_2 is in agreement with the single measurement of Hughes, and also shows that, evidently owing to weakness of the ionisation, Blanc's value is in error.

Arsenious acid on titration with alkali behaves as a very weak monobasic acid, the salt NaH_2AsO_3 being formed. This is marked by an inflexion. The titration curve is almost identical with that of boric acid. Further addition of alkali gives strongly alkaline solutions, the p_H values of which cannot be determined by means of the glass electrode with sufficient accuracy to permit of the calculation of K_2 and K_3. In any case these constants are extremely small, much smaller than 10^{-12} (cf. Goldfinger and Schweinitz), and consequently the secondary and tertiary arsenites are considerably hydrolysed in solution. Table II gives p_{K_1} values based on the p_H values obtained during glass-electrode titrations at 18° using (i) the ballistic galvanometer circuit, and (ii) the thermionic electrometer valve circuit (Harrison, J., 1930, 1530). The two methods gave almost identical values, although the use of the condenser-ballistic galvanometer involves the extraction of a little current from the cell during the charging of the condenser, whereas the use of the valve enables measurements to be made on open circuit. Polarisation errors inherent in the condenser method are apparently compensated for by the fact that the calibration of the electrode is carried out under exactly parallel conditions.

TABLE II.

Glass electrode titrations of
(i) 100 c.c. of 0·01704*M*-H_3AsO_3 with 0·0995*N*-NaOH (ballistic galvanometer);
(ii) 50 c.c. of 0·09135*M*-H_3AsO_3 with 0·2005*N*-NaOH (electrometer triode).

	NaOH, equivs.	0·125.	0·25.	0·375.	0·5.	0·625.	0·75.	0·875.
(i)	p_H	8·42	8·77	9·04	9·28	9·50	9·74	10·06
	p_{K_1}	9·28	9·25	9·26	9·28	9·28	9·26	9·21
	Mean $p_{K_1} = 9{\cdot}26$; $K_1 = 5{\cdot}50 \times 10^{-10}$.							
(ii)	p_H	8·34	8·74	9·02	9·26	9·49	9·71	10·06
	p_{K_1}	9·19	9·22	9·24	9·26	9·27	9·23	9·21
	Mean $p_{K_1} = 9{\cdot}23$; $K_1 = 5{\cdot}89 \times 10^{-10}$.							

Whereas the mean value, $5{\cdot}7 \times 10^{-10}$, for K_1 for arsenious acid is a little smaller than that indicated by Hughes's p_H value and a little larger than that recorded by Goldfinger and Schweinitz, it is very different from the values found by means of conductivity by Wood and von Zawidzky.

The Alleged Complex Formation between Quinquevalent Arsenic and Tartaric Acid.—In view of the fact that a complex salt has been reported by Pelouze (*loc. cit.*), it was thought possible that arsenic pentoxide would affect the rotatory power of tartaric acid in the course of its neutralisation with sodium hydroxide. A series of solutions corresponding with different stages in the neutralisation of 0·1*M*-tartaric acid + 0·1*M*-arsenic acid was investigated at 25°. In every case the observed rotation was equal to that caused by the tartaric acid at the particular stage of neutralisation. It is therefore unlikely that complex formation occurs (cf. Henderson and Ewing, J., 1895, **67**, 102), although no electrometric work has been carried out. As Pelouze's salt was prepared by the dissolution of arsenic oxide in potassium hydrogen tartrate, it seems probable that arsenic acid is sufficiently strong to displace tartaric acid thus: $KHT + H_3AsO_4 \longrightarrow KH_2AsO_4 + H_2T$, so that, unless care was taken, crystallisation would yield an equimolecular mixture of the primary arsenate and tartaric acid. Such a mixture would have the composition $K(AsO_2)C_4H_4O_6,2H_2O$, *i.e.*, very nearly that of Pelouze's salt.

Solutions of Tartaric Acid and Arsenious Acid.—Rotatory power. For the purpose of studying the effect of arsenious oxide on the rotatory power of solutions of tartaric acid during its neutralisation at 25° with sodium hydroxide, five series of solutions, neutralised to different extents, were prepared; each was 0·1*M* with respect to the initial tartaric acid and either 0·025, 0·05, 0·075, 0·1, or 0·1775*M* with respect to arsenic. The molecular rotations $[M]^{25°}_{5461}$ (l = 4 dm.) shown in Table III are calculated on the basis of the original tartaric acid concentration. As shown in Part VIII (this vol., p. 1000), $[M] = \alpha_{obs.}/lc = \alpha_{obs.}/4 \times 0{\cdot}1$.

TABLE III.

Effect of Arsenious Acid on the Rotation of Tartaric Acid during Neutralisation.

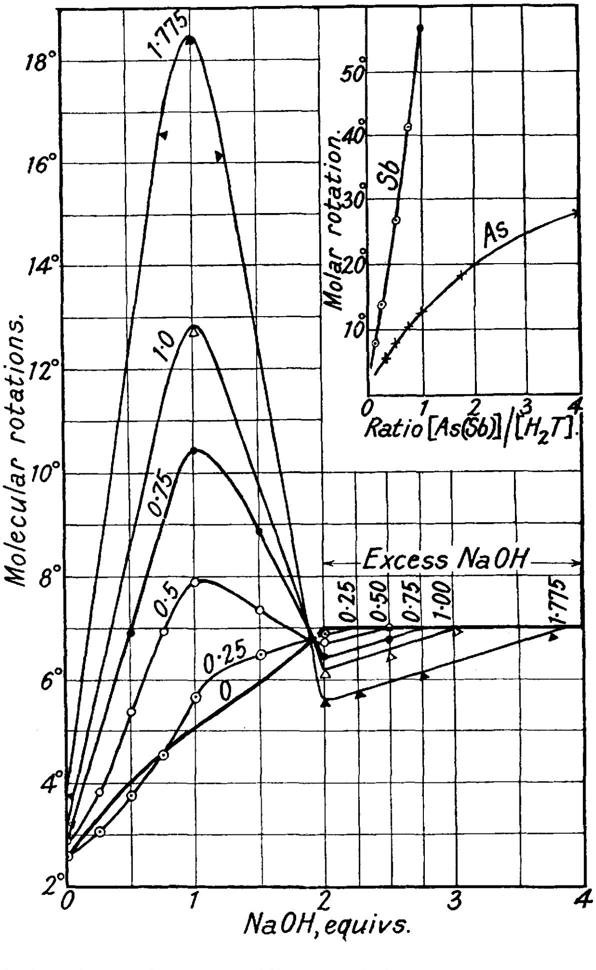
$[H_2T]$ =	0·1	0·1	0·1	0·1	0·1	0·1
$[H_3AsO_3]$ =	0	0·025	0·05	0·075	0·10	0·1775
$\frac{[NaOH]}{[H_2T]}$.						
0	2·60°	2·56°	2·87°	2·92°	3·21°	3·72°
0·25		3·07	3·82	4·40		
0·5		3·75	5·37	6·92		
0·75		4·52	6·90	9·15		16·57
1·00	5·10	5·67	7·87	10·42	12·82	18·49
1·25						16·17
1·50	5·88	6·47	7·35	8·87		
1·75						
2·00	7·00	6·87	6·72	6·42	6·20	8·60
2·258						5·62
2·50	7·00	6·97	7·02	6·75	6·51	5·80
2·75						
3·00		7·00	7·02	6·96	7·00	6·15
3·775						
4·00		7·00	7·00	7·00		6·90
4·50				7·02		
5·00				7·00		

Owing to complex formation, boric acid is much more soluble in solutions of tartaric acid than in water. The solubility of arsenious and antimonous oxides is similarly increased, but not to such an extent. Arsenious oxide, like boric acid, increases the rotations of tartaric acid, as shown by the data in the first line of Table III. The curves given in Fig. 1, marked with the ratios of $[H_3AsO_3]/[H_2T]$, show, with the exception of the 0·25 graph, that maximum rotations are produced when 1 equiv. of alkali is present. The heavy line, marked 0, represents the neutralisation of tartaric acid, and it will be observed that in the 0·25 graph somewhat higher rotations were given with 1—2 equivs. of alkali. The maximum rotations shown in Table III reveal that the rotation of 0·1*M*-sodium hydrogen tartrate is increased 2·51 times (from 5·10° to 12·82°) by the inclusion of 1 mol. of arsenious acid in the solution. By using larger proportions of the acid greater rotations are realised, but the relative increases per mol. of acid are smaller, being 1·98 for 2 mols. (20·25°) and 1·36 for 4 mols. (27·85°). This is seen more clearly by means of the curve marked As in the inset in Fig. 1. The shape of the curve suggests that the reaction might be expressed by equilibria governed by the equation $2NaHT + As_2O_3 \rightleftharpoons Na_2(As_2O_3)(HT)_2$, or perhaps $2NaHT + As_2O_3 \rightleftharpoons 2Na(AsO)T + H_2O$.

Another interesting point is that the solutions containing 2 equivs. of sodium hydroxide are less dextrorotatory than those of sodium tartrate alone. With larger amounts of arsenious oxide than are recorded in Table I, the rotations become still lower, *e.g.*, with 3·705 mols. it is 4·67°. (At this stage the complex solutions are of minimum stability; in fact, with more concentrated tartrate solutions, arsenious oxide is precipitated when this proportion of alkali has been added.)

Addition of alkali beyond 2 equivs. causes a linear increase in rotation until, at the stage corresponding to NaH_2AsO_3, it is equal to that of the alkaline solution of sodium tartrate alone. This is clearly due to the extreme weakness of the second and third stages of ionisation of arsenious acid. Incidentally, the fact that arsenious is a weaker acid than tartaric acid in either of its two stages shows that the increased solubility of arsenious oxide in sodium hydrogen tartrate solutions cannot be attributed to a normal acid–base reaction as had been previously suggested in the case of arsenic oxide.

FIG. 1.



Electrometric measurements. These are illustrated in Fig. 2. The upper curves represent conductometric titrations of 75 c.c. of $0{\cdot}1M$-tartaric acid + xM-arsenious acid solutions with $0{\cdot}2771N$-sodium hydroxide at 25°. The lowest curve during the first half of the neutralisation, and ending with a "break" with 2 equivs. of alkali, is that of tartaric acid alone. In order of increasing conductivity are the curves for which $x = 0{\cdot}025, 0{\cdot}05, 0{\cdot}075$, and $0{\cdot}1775$.

It is seen that arsenious acid, although its conductivity in aqueous solution is negligible compared with that of a $0{\cdot}1M$-tartaric acid solution, increases the conductivity of the latter; with 0·25 and 0·5 mol. of arsenious acid the increases are too small to be measured; with 0·75 mol. the increase is $0{\cdot}1 \times 10^{-3}$ mho, and with 1·775 mols. it is $0{\cdot}66 \times 10^{-3}$ mho. Nevertheless, the increased strength of the complex acid makes itself apparent in the first halves of the titration curves. When 1 equiv. of alkali has been added, *i.e.*, corresponding with

$$NaHT,xH_3AsO_3,$$

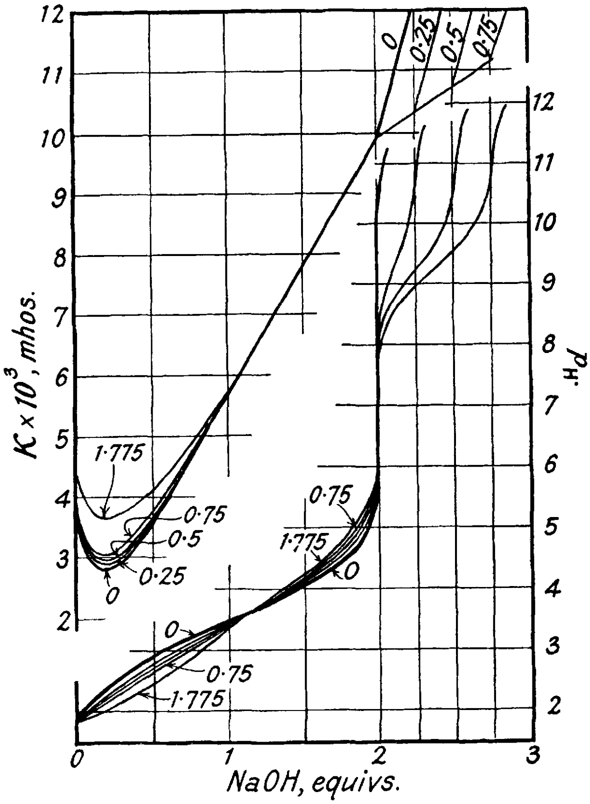
the specific conductivities all become equal and continue so until 2 equivs. of alkali have been added. With further alkali the first stage of ionisation of arsenious acid undergoes neutralisation which is terminated by "breaks," followed by lines having the slopes due to excess of alkali. These curves therefore indicate that complex formation occurs during the reaction with 0—1 equiv. of alkali, but not in alkaline solutions.

Similar conclusions are forthcoming from the p_H curves, obtained by means of the glass electrode and the electrometer triode circuit for a similar set of titrations, the only difference being that the initial volumes were 50 c.c. instead of 75 c.c. Of the p_H curves in Fig. 2 (lower set) the heavy line relates to tartaric acid alone. The effect of arsenious oxide is slightly to increase the hydrogen-ion concentration at first, the p_H curves lying below that of the tartaric acid. Soon after 1 equiv. of alkali has reacted, the curves reverse their order with respect to that of tartaric acid, and immediately after 2 equivs. of alkali are added the titration curves become those of the arsenious acid, the p_H values then set up not being influenced by the sodium tartrate previously formed.

It appears from both the rotation and the electrometric curves that complex formation occurs in acid solutions until the alkali suffices to form the hydrogen tartrate; it is then at a maximum, the extent depending on the proportion of arsenious oxide present. With greater amounts of alkali, the complex undergoes decomposition, but this does not become complete until the alkali suffices to form both the normal sodium tartrate and sodium dihydrogen arsenite.

Solutions of Tartaric Acid and Antimonous Oxide.—Antimonous oxide has extremely feeble amphoteric properties : it dissolves in solutions of strong acids and strong bases provided that excess of either acid or base be present; yet it will dissolve to an appreciable extent in tartaric acid, and the presence of tartrates increases the solubility of the oxide in alkaline solutions. The solubility in acid solutions is greatly increased when sufficient alkali is added to convert the tartaric acid into the hydrogen tartrate, and it is from such solutions that the class of salts known as the " emetics " may be crystallised. When added to emetic solutions, acids (*e.g.*, nitric and hydrochloric), alkalis, and alkali carbonates cause precipitation. Alkalis in larger quantities, however, bring about redissolution of the hydrated antimonous oxide, but the quantities of alkali required for this purpose are much smaller than those necessary when tartrates are absent.

FIG. 2.



Rotatory power. Owing to the limited solubility of antimonous oxide in tartaric acid, it was more convenient to prepare solutions corresponding to various stages of neutralisation of tartaric acid from the free acid, sodium emetic, sodium hydrogen tartrate, and sodium tartrate, and in some cases to add suitable quantities of either hydrochloric acid or sodium hydroxide. The concentrations of sodium chloride thereby introduced (noted in Table IV) were too small to have any appreciable effect on the rotations.

Table IV gives the rotations observed for those sections of the neutralisation of $0{\cdot}1M$-tartaric acid and xM-antimonous hydroxide in which precipitation did not occur. In all cases, precipitation took place in the region of the complete neutralisation of the tartaric acid, and redissolution did not begin until several equivalents of alkali in excess had been added. Solutions containing low ratios of antimonous hydroxide underwent precipitation only on standing. It was possible therefore to take polarimetric readings before precipitation occurred. In Fig. 3 the molecular rotations are plotted against the number of equivalents of alkali present, and the periods during which precipitation occurred are indicated by broken lines. The curves are marked by the molecular ratios of antimony hydroxide to total tartaric acid.

Unlike the arsenious–tartaric acid rotation curves, the maximum in the antimony curves coincides with 1 equiv. of alkali in one case only, *viz.*, for the equimolecular mixture of tartaric acid and antimonous hydroxide, which corresponds to the sodium emetic $NaHT,Sb(OH)_3$. Incidentally, it happens that an $M/10$-solution of sodium hydrogen tartrate is then nearly saturated with respect to antimonous hydroxide. Table IV gives the rotations for the 5461 line for the equimolecular mixture, and these also show a maximum with 1 equiv. of alkali.

The rotations when smaller amounts of antimonous hydroxide are dissolved in $0{\cdot}1M$-sodium hydrogen tartrate solutions are lower, as seen in Fig. 3, or more clearly from the two higher curves of the inset, which were constructed from the following data for both the 5461 Å. and the D line :

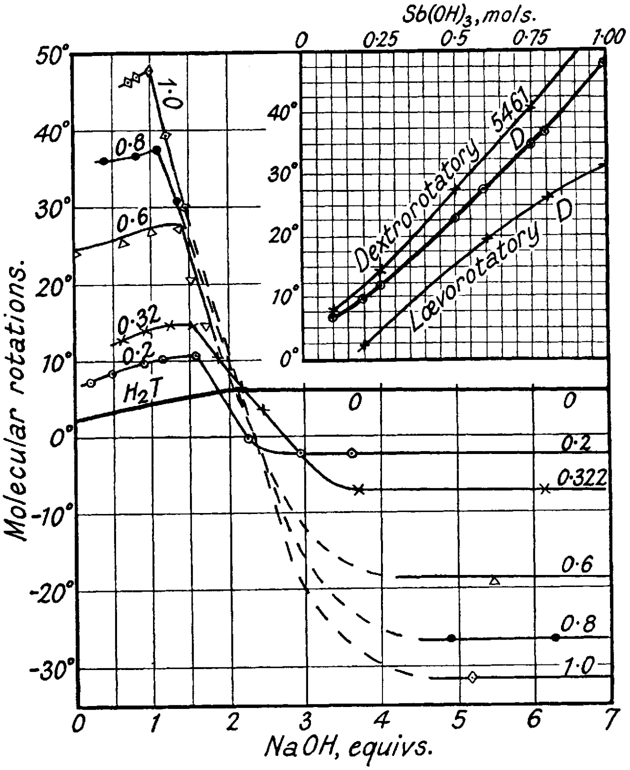
Effect of adding antimonous hydroxide to 0·1M-*sodium hydrogen tartrate at* 25°.

$Sb(OH)_3$, mols./l. ...	0·01	0·02	0·025	0·05	0·06	0·075	0·08	0·10
$[M]_{D}^{25°}$	6·95°	9·83°	11·82°	22·80°	27·40°	34·88°	36·50°	47·86°
$[M]_{5461}^{25°}$	7·46°		13·86°	27·01°		41·22°		56·89°

Table IV (v) gives rotation data ($l = 2$; $t = 20°$) based on observations of Grossmann (*loc. cit.*) on a solution containing antimonous hydroxide in tartaric acid in the approximate molecular ratio 1 : 3, whence he considered the solution to consist of " Antimontriweinsaure." His results are plotted (curve 0·322) in Fig. 3 and are in general agreement with the other curves.

The heavy graph, " H_2T," represents the rotations at 25° (sodium D line) during the neutralisation of tartaric acid alone; in its initial section it is nearly parallel to those of the antimony hydroxide–tartaric acid graphs, showing that, in contrast to the boric and the arsenious acid curves, the influence of the antimony is reflected in a general elevation of the tartaric acid curve. With increasing amounts of boric acid, alkaline tartrate solutions became less dextrorotatory than the sodium tartrate alone, and even lævorotatory with high boric acid content. With antimonous hydroxide this effect is very much more pronounced, as seen from Fig. 3, so much so that even with 0·2 mol. of antimonous hydroxide to 1 mol. of tartaric acid there is a small lævorotation. The effect of the antimony content is more evident from the lowest curve in the inset.

FIG. 3.



Electrometric measurements. These were confined to p_{H} titrations by means of the glass electrode at room temperature. In Fig. 4 is plotted the titration curve of 100 c.c. of 0·02*M*-tartaric acid + 0·01086*M*-antimonous hydroxide [*i.e.*, $H_2T : Sb(OH)_3 = 1 : 0{\cdot}5429$] with 0·1040*N*-sodium hydroxide. Such a high antimony content could only be obtained by several hours' boiling, filtering the solution, and making it up to volume. By comparing the titration curve with that of tartaric acid alone, it is seen that the introduction of antimonous hydroxide causes the ionisation of the first stage of tartaric acid to be slightly strengthened. The main effect, however, occurred during the final portion of the second stage of neutralisation. The inflexion with 28 c.c. marks the beginning of reaction with the tartrate combined with the antimonous hydroxide, whereas the final inflexion at 37·6 c.c. not only coincides with the point at which the antimonous hydroxide began to precipitate but corresponds nearly with the complete decomposition of the antimony–tartrate complex, the theoretical end-point being 38·42 c.c. Moreover, the p_{H} range within which the complex was decomposed was abnormally high, lying between 7 and 8. A similar observation was made by Britton and Robinson (J., 1933, 422) in connexion with their work on niobium–oxalic acid complexes.

FIG. 4.

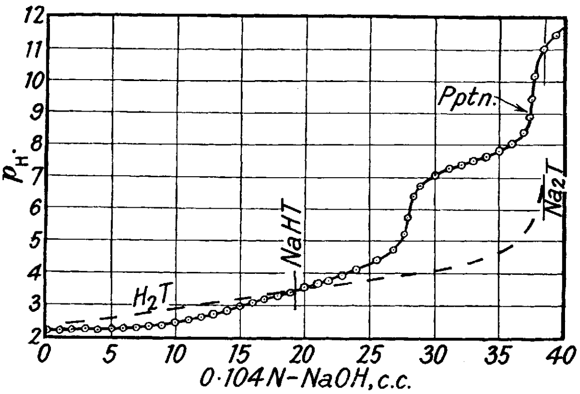


TABLE IV.

Molecular Rotations, $[M]_{\lambda}^{25°}$*, of Solutions* 0·1M-*Tartaric Acid* + xM-*Antimony Hydroxide,* $Sb(OH)_3$*, at Various Stages of Neutralisation.*

(i) $x = 0·02$.

$\frac{[NaOH]}{[H_2T]}$	0·2	0·472	0·88	1·0	1·152	1·56	2·24	2·92	3·60
$\alpha_D^{25°}$	+ 2·84°	+ 3·33°	+ 3·85°	+ 3·93°	+ 4·04°	+ 4·24°	− 0·04°	− 0·89°	− 0·88°
$[M]_D^{25°}$	+ 7·10°	+ 8·32°	+ 9·62°	+ 9·83°	+10·10°	+10·60°	− 0·10°	− 2·23°	− 2·20°

(ii) $x = 0·06$.

$\frac{[NaOH]}{[H_2T]}$	0 (0·06*M*-NaCl)	0·6	1·0	1·4	1·57	1·74	5·45	8·17
$\alpha_D^{25°}$	+ 9·84°	+10·29°	+10·96°	+10·96°	+ 8·30°	+ 5·94°	− 7·52°	− 7·52°
$[M]_D^{25°}$	+24·60°	+25·72°	+27·40°	+27·40°	+20·75°	+14·85°	−18·80°	−18·80°

(iii) $x = 0·08$.

$\frac{[NaOH]}{[H_2T]}$	0·39 (0·041*M*-NaCl)	0·80	1·0	1·072	1·344	4·88	6·24
$\alpha_D^{25°}$	+14·50°	+14·60°	+14·60°	+14·96°	+12·69°	−10·60°	−10·63°
$[M]_D^{25°}$	+36·25°	+36·50°	+36·50°	+37·40°	+31·72°	−26·50°	−26·57°

(iv) $x = 0·10$.

$\frac{[NaOH]}{[H_2T]}$	0·738 (0·0262 *M*-NaCl)	0·825 (0·0175 *M*-NaCl)	1·0	5·132	9·264	14·12
$\alpha_D^{25°}$	+18·51°	+18·70°	+19·14°	−12·49°	−12·64°	−12·03°
$[M]_D^{25°}$	+46·27°	+46·86°	+47·86°	−31·24°	−31·60°	−30·08°
$\alpha_{5461}^{25°}$			+22·76°	−14·99°	−15·17°	−14·72°
$[M]_{5461}^{25°}$			+56·90°	−37·48°	−37·93°	−36·80°

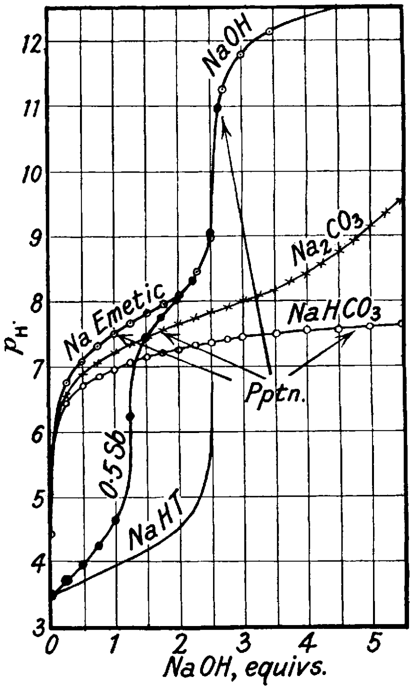
(v) $x = 0·0322$ at 20° (Grossmann).

$\frac{[NaOH]}{[H_2T]}$	0·615	0·922	1·23	1·54	1·85	2·16	2·46	3·67	6·15
$\alpha_D^{20°}$ ($l = 2$)	+ 2·56°	+ 2·80°	+ 2·92°	+ 2·92°	+ 2·04°	+ 1·32°	+ 0·74°	− 1·40°	− 1·40°
$[M]_D^{20°}$	+12·8°	+14·0°	+14·6°	+14·6°	+10·2°	+ 6·6°	+ 3·7°	− 7·0°	− 7·0°

The curve, "Na Emetic," in Fig. 5, which refers to the electro-titration of 50 c.c. of 0·1*M*-sodium emetic with 0·2*M*-sodium hydroxide, shows that the initial solution has p_H 4·42, and that on treatment with alkali a rapid increase in p_H occurs, until the same range, p_H 7—8, is reached, and then when the stoicheiometrical amount of alkali has been added to convert all the sodium hydrogen tartrate contained in the sodium emetic into normal sodium tartrate, the final inflexion, indicating the presence of free alkali in the solution, is produced. Precipitation of antimonous hydroxide, however, began at p_H 7·50, when 10 c.c., instead of the 25 c.c. required for complete decomposition of the complex, had been added. The curve 0·5 Sb is that of the titration of 50 c.c. of 0·1*M*-sodium hydrogen tartrate + 0·05*M*-antimonous hydroxide with 0·2*M*-sodium hydroxide. The p_H of the solution was 3·47, which is also that of a sodium hydrogen tartrate solution of the same concentration. (The lowest curve in Fig. 5 shows the change in p_H on neutralisation if no antimonous hydroxide is present.) As in Fig. 4, there occurs a well-defined inflexion indicating the beginning of attack on the antimony–tartrate complex. Decomposition again takes place, mainly between p_H 7 and 8, but owing to the relatively small antimony content, precipitation is delayed until the solution has reached p_H 11, and slightly more than the correct amount of alkali has been added to convert the hydrogen tartrate into the neutral tartrate.

It appears from the position of the inflexions in the alkali titration curves that 1 mol. of antimonous hydroxide must enter into some type of combination with 1 mol. of alkali hydrogen tartrate. Such combination seems to be complete and to be independent of the concentrations of the reactants. In other words, the formation of the complex is not determined by equilibria governed by the law of mass action, which seems to apply in the case of boric and arsenious acids. This might possibly account for the more rapid increase in rotation of sodium hydrogen tartrate produced by antimonous hydroxide than by arsenious acid, as shown by the curves inset in Fig. 1. It is probably owing to the stability of the antimony complex that its decomposition does not begin until all the uncombined sodium hydrogen tartrate (present in the solution because the amount of antimonous hydroxide is insufficient to convert it wholly into the 1 : 1 complex) has reacted with the added alkali. This explanation would also account for the fact that the maximum rotations, in the case of tartaric acid solutions containing less than one mol. of antimonous hydroxide, lie further towards the sodium tartrate point as the antimony ratio is lessened.

Fig. 5.



Grossmann (*loc. cit.*) specially emphasises the fact that both sodium carbonate and sodium hydrogen carbonate when added to potassium emetic solutions did not cause them to become lævorotatory, but merely less dextrorotatory. This is undoubtedly due to the fact that these reactants are salts of carbonic acid, which in its first stage undergoes neutralisation between $p_{\rm H}$ 4·5 and 8·5, p_{K_1} being 6·5. Any reaction between potassium emetic and sodium hydrogen carbonate must therefore result in the liberation of free carbonic acid, and buffer action will occur within this range, which happens to be that wherein the emetic itself suffers decomposition. This explains why the buffer action shown by the curve, $NaHCO_3$, in Fig. 5, corresponding to the titration of 50 c.c. of 0·1*M*-sodium emetic with 0·2*M*-sodium hydrogen carbonate, should lie between $p_{\rm H}$ 7 and 8, and also why precipitation should be delayed until nearly 5 equivs. of sodium hydrogen carbonate are added. Owing to the greater weakness of the second stage of carbonic acid, $p_{K_2} = 10·2$, and the consequent hydrolysis of sodium carbonate solutions, it might be expected that the decomposition effected by sodium carbonate would be greater, as higher $p_{\rm H}$ values would be more quickly established. This is illustrated by the curve, Na_2CO_3, in Fig. 5, which gives the change in $p_{\rm H}$ when 50 c.c. of 0·1*M*-sodium emetic are titrated with 0·1*M*-sodium carbonate.

The fact that Grossman was unable to obtain lævorotatory solutions with sodium carbonate and hydrogen carbonate must be attributed to the fact that the solutions are not rendered sufficiently alkaline. It appears certain that the complex formation existing in alkaline solutions is different in nature from that in acid solutions. It seems quite definite that the latter complex is composed of 1 mol. each of sodium hydrogen tartrate and antimonous hydroxide.

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