109. *Physicochemical Studies of Complex Acids. Part IX. Tantalic Acid. Reactions of Alkali Niobate and Tantalate Solutions with Organic Acids.*

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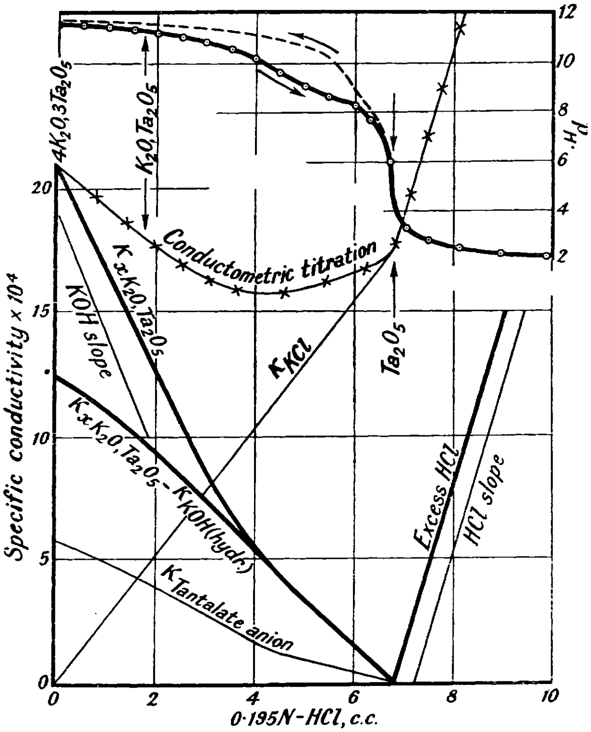
The only recorded physicochemical work on tantalic acid and alkali tantalate solutions is that by Jander and Schulz (*Z. anorg. Chem.*, 1925, **144**, 225), who carried out diffusion experiments, two colorimetric p_H measurements, and conductivity determinations of solutions of $K_7Ta_5O_{16}$ and $Na_7Ta_5O_{16}$ each at two dilutions, and by Pierce and Yntema (*J. Physical Chem.*, 1930, **34**, 1822), who made a single hydrogen-electrode titration of an alkali tantalate solution with hydrochloric acid. The present communication deals with potentiometric and conductometric investigations of the action of hydrochloric acid and typical acids of gradually diminishing strength on solutions of alkali niobate and alkali tantalate. Strong and moderately strong acids precipitate the pentoxides readily, acetic acid precipitates tantala but not niobia, whilst oxalic, lactic, tartaric, and malic acids retain both these oxides in solution.

Russ (*Z. anorg. Chem.*, **1902**, **31**, 42) found that, in contrast to the slight solubility of tantala, niobia is appreciably soluble in oxalic acid solutions; he attributed this to the different behaviours of the oxalo-acids formed. To test this view, hydrogen-electrode titrations with alkali have been performed on oxalic acid solutions containing (i) varying amounts of niobia, and (ii) the maximum quantity of tantala that could be dissolved. Russ's explanation has been found untenable, and a more valid hypothesis is now advanced.

Some observations are also recorded in regard to the precipitation of the oxides by means of ammonium hydroxide and tannic acid from oxalic acid (cf. Schoeller and Powell, *Analyst*, 1925, **50**, 485; Schoeller, *ibid.*, 1932, **57**, 750).

EXPERIMENTAL.

FIG. 1.



Solutions of K tantalate were prepared from tantalate melts after fusing Ta_2O_5 with KOH. A typical hydrogen electrode p_H curve and a corresponding conductometric curve are given in Fig. 1 for titration with HCl, some of the data of which are recorded in Table I. Col. 1 shows the vol. of HCl added. Col. 3 gives $\kappa_{obs.}$, the obs. sp. conductivities at 25°, and col. 4 the p_H values at 18° of the resulting solutions. From $\kappa_{obs.}$, the conductivity due to the KCl formed at different titres has been subtracted, giving the curve marked κ_{xK_2O,Ta_2O_5}. Further, the p_H data have been used to calculate the concns. of free KOH and the sp. conductivities due to this have been subtracted from $\kappa_{xK_2O,\ Ta_2O_5}$, giving κ_1 (col. 5), the corresponding curve, marked $\kappa_{xK_2O,\ Ta_2O_5} - \kappa_{KOH(hydr.)}$ representing the actual conductivity of the K tantalate in solution. By subtraction of the conductivity due to the K ions (the ionisation of the complex tantalate being assumed to be complete as far as these ions are concerned), κ_2 (col. 6) is found, this being the contribution of the tantalate ion to the conductivity (curve marked $\kappa_{Tantalate\ anion}$).

The variations in p_H and κ were also observed when K tantalate solutions were treated with KOH. There was no evidence of the formation of $K_7Ta_5O_{16}$, as suggested by Jander and Schulz, nor of K_3TaO_4 or $K_4Ta_2O_7$. As shown in the above table, K tantalate is strongly hydrolysed. Jander and Schulz found that 0·1*N*-$K_7Ta_5O_{16}$ was hydrolysed to about 10%, yet they determined the equiv. conductivity of *N*/32- and *N*/1024-solutions in order to apply the Ostwald–Walden rule, and concluded therefrom that tantalic acid was at least sexabasic. The p_H data of the titration curve of $4K_2O,3Ta_2O_5$, obtained by Pierce and Yntema, point to considerably less hydrolysis than was found by us or by Jander and Schulz. Incidentally, their curve suggests that the p_H during the greater part of the reaction with HCl was below 7, whereas Fig. 1 indicates much higher values.

Comparison with the K niobate curve (Part VIII; J., 1932, 2265) shows that the action of HCl on this salt is very similar. There is, however, one important difference in the pptn. of Ta_2O_5 and Nb_2O_5. Whereas in the titration of the niobate solutions, a turbid unfilterable suspension was first formed which flocculated sharply at the end-point of the reaction, with the tantalate solutions the majority of the ppt. was immediately flocculated and could be filtered off, leaving only a very small suspension in the filtrate. Moreover, whilst niobate solutions

TABLE I.

Conductometric and hydrogen-electrode titrations of 100 c.c. of a solution of $0{\cdot}00663M$-K_2O and $0{\cdot}00494M$-Ta_2O_5 with $0{\cdot}195N$-HCl, at 25° and 18° respectively.

C.c.	K_2O/Ta_2O_5.	$\kappa_{obs.} \times 10^3$.	p_H.	$\kappa_1 \times 10^3$.	$\kappa_2 \times 10^4$.	Hydrolysis, %.
0	1·34	2·082	11·63	1·229	5·74	23·8
1	1·14	1·926	11·44	1·055	4·60	20·0
2	0·95	1·773	11·23	0·905	3·88	13·7
2·5	0·85	1·693	11·06	0·807	3·22	10·4
3	0·75	1·641	10·83	0·722	2·77	7·0
3·5	0·65	1·599	10·56	0·616	2·19	4·4
4	0·55	1·570	10·14	0·508	1·53	1·9
4·5	0·45	1·574	9·65	0·408	1·22	0·7
5	0·35	1·590	9·04	0·306	0·85	0·3
5·5	0·24	1·623	8·66	0·220	0·59	—
6	0·14	1·650	8·28	0·128	0·39	—

underwent little pptn. in the first half of the titration, weighing showed that the Ta_2O_5 was being pptd. at a uniform rate throughout the titration.

The broken curve at the top of Fig. 1 indicates the p_H values of the solution in which the totally pptd. tantalic acid was suspended on back-titration with KOH. It indicates that a small amount of interaction occurs between KOH and freshly pptd. Ta_2O_5. As in the pptn. of Nb_2O_5, the addition of acid beyond the amount theoretically required to ppt. Ta_2O_5 gave conductivities and p_H values which could be accounted for satisfactorily on the assumption that free HCl was present.

A comparison of the p_H curves of K niobate and tantalate reveals that the first part of both titrations consists of the neutralisation of free alkali, but that the second part of the titration of the tantalate gives p_H values about 2·5 units higher than the corresponding values for the niobate. Taken in conjunction with the fact that Ta_2O_5 can be pptd. from alk. solutions of p_H 11·6, whereas Nb_2O_5 only suffers appreciable pptn. when the p_H has been lowered to about 8·0, these p_H curves throw some light on the separation of Nb from Ta by passing CO_2 through the alk. solutions (Weiss and Landecker, *Z. anorg. Chem.*, 1909, **64**, 65; Foote and Langley, *Chem. News*, 1911, **103**, 103; Hauser and Lewite, *Z. angew. Chem.*, 1912, **25**, 100), for much bicarbonate is formed and therefore the p_H is somewhat higher than 8·4. The tantalate solutions on treatment with HCl did not reach this value until nearly all the Ta_2O_5 had been pptd.

A series of hydrogen-electrode titrations of (*a*) 100 c.c. of K niobate, $0{\cdot}0137M$-K and $0{\cdot}01015M$-Nb, (*b*) 100 c.c. of K tantalate, $0{\cdot}0133M$-K and $0{\cdot}00988M$-Ta, were performed with approx. $N/10$-solutions of the following acids: monochloroacetic, formic, lactic, acetic, oxalic, tartaric, malic, and citric. In all cases, the variations in p_H during the reactions

$$4K_2O,3Nb_2O_5(Ta_2O_5) + 8HX \longrightarrow 8KX + 4H_2O + 3Nb_2O_5(Ta_2O_5)$$

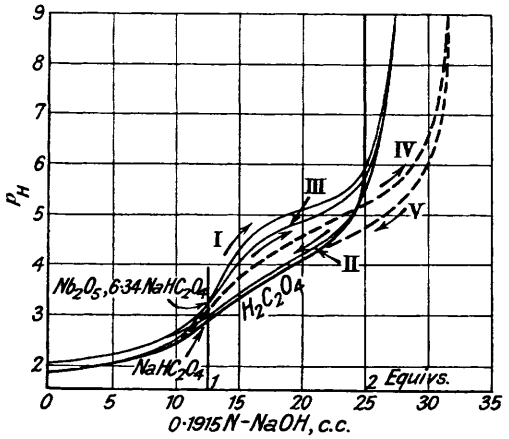
were the same as those set up when HCl was used (Part VIII, Fig. 1; this paper, Fig. 1). Both formic and monochloroacetic acids caused immediate pptn. which became complete as soon as the theo. amounts of acid had been added. This was also the case when acetic and phenylacetic acids acted upon K tantalate solutions, and the p_H values set up when excesses of these acids had been added revealed that the tantalate had been completely decomposed. Pptn. of Nb_2O_5 did not begin from K niobate solutions with acetic and phenylacetic acids until a few c.c. in excess had been added—the solutions remaining perfectly clear during the decomp. of the niobate. The buffered p_H curves corresponding to excess of these acids indicated that a small proportion of the KOH of the niobate had not been converted into KOAc and that the comp. of the K niobate remaining in solution after the stoicheiometric amounts of AcOH and $CH_2Ph{\cdot}CO_2H$ had been added were respectively $0{\cdot}36K_2O,Nb_2O_5$ and $0{\cdot}20K_2O,Nb_2O_5$. Conductometric titrations led to similar conclusions.

Neither $(CO_2H)_2$ nor the hydroxy-acids caused any pptn. from the niobate or tantalate solutions. As stated above, the initial sections of p_H curves were identical with the respective HCl curves. By assuming that each of these acids first reacted in accordance with the above equation and that the subsequent sections of the curves correspond to the addition of excess of the various acids, calculations have been made to see if the p_H values would give rise to p_K values characteristic of the respective acids. Lactic acid does not appear to have formed complex lacto-niobic or -tantalic acids, for not only did the inflexions corresponding to the end-point of the reaction occur at exactly the correct titres, but the subsequent p_H values were those set up by the K lactate and lactic acid. This is remarkable in view of the fact that the solutions remained optically clear. Oxalic acid also retained both Nb_2O_5 and Ta_2O_5 in clear solution. The p_H values corresponding to the excess of the acid in which buffering might have been controlled by the K_2 of $(CO_2H)_2$ led to $p_K = 4{\cdot}56$ in the niobate titration and $p_K = 4{\cdot}75$ in the tantalate, both values being appreciably higher than the p_{K_2} of $(CO_2H)_2$, *viz.*, 4·0. Further excess of $(CO_2H)_2$ yielded p_H values such as would be caused by the normal dissociation of $(CO_2H)_2$ in its first stage. Similar observations were made with tartaric and malic acids, but the discrepancies between the calculated and the actual p_{K_2} values were not so marked.

The foregoing observations reveal that complex formation between organic acids and the earths, Nb_2O_5 and Ta_2O_5, inasmuch as the acids are able to hold these relatively insol. oxides in clear solution, is not confined solely to hydroxy-acids, for acetic, phenylacetic, and oxalic acids also possess such a property in various degrees. It is just possible that the magnitude of the dissociation const. may in some way be involved.

Oxalic Acid Solutions of Niobic and Tantalic Oxides.—In order to render Nb_2O_5 sol. in H_2O, it was necessary to form K niobate by fusing the pure oxide with K_2CO_3, extracting the melt with H_2O, and pptg. with HCl, impurities being removed by washing with hot H_2O. Curve I in Fig. 2 shows the variations in p_H when 100 c.c. of a solution of 0·3 g. of $(CO_2H)_2,2H_2O$ and 0·1 g. of Nb_2O_5 (*i.e.*, 0·02381*M*-$H_2C_2O_4$ and 0·00751*M*-Nb) were titrated with 0·1915*N*-NaOH. The lower curve in Fig. 2 is the corresponding p_H curve of 100 c.c. of 0·02381*M*-$H_2C_2O_4$ titrated with 0·1915*N*-NaOH. Comparison reveals that the p_H values set up during the neutralisation of the first equiv. of the acid in both solutions were identical; those during the neutralisation of the next equiv. were, however, very different, the presence of the Nb_2O_5 causing much higher p_H values to be established.

FIG. 2.



The fact that the final inflexion of curve I appears 2·5 c.c. later than in the $(CO_2H)_2$ curve is not to be attributed to complex formation, for it will be seen from the curves given in Part VIII (*loc. cit.*), showing the effect of alkali on Nb_2O_5, that a certain amount of alkali reacts with Nb_2O_5 in the region of p_H 5—6. Curve II is that of a back-titration of the Nb_2O_5–$(CO_2H)_2$ solution with 0·1915*N*-HCl. This curve almost duplicates the $(CO_2H)_2$ curve, and thus it would appear that the complex had suffered decomp. in spite of the fact that the HCl added was insufficient to cause pptn. of the Nb_2O_5. The slightly higher p_H values during the final stage of the titration are due solely to the increased dilution. Curve III is that of a titration of the resulting solution—the HCl added being equiv. to the NaOH in the first titration—with 0·1915*N*-NaOH. It is significant that high p_H values should have again been produced during the addition of the second equiv. of NaOH.

The ratio $Nb_2O_5/(CO_2H)_2$ in the above solution was 1/6·34. It corresponds very nearly to the max. amount of Nb_2O_5 that can be dissolved in an oxalic acid solution of the concn. used. Titrations of solutions containing smaller amounts of Nb_2O_5 yielded curves that were identical with the parent acid curve during the neutralisation of the first equiv., but the higher p_H values during the second stage were largely confined to the portion immediately before the solution became alk., the magnitude of this section depending on the amount of Nb_2O_5 present.

A similar p_H titration of a $(CO_2H)_2$ solution of Ta_2O_5 was made, but, probably owing to the relatively small solubility of that oxide in the acid, the amount dissolved was such as to have no perceptible effect on the p_H values set up throughout the whole neutralisation. The Ta_2O_5 was first fused with K_2CO_3, pptd. with HCl, and washed. To dissolve 0·3 g. of Ta_2O_5, a solution containing no less than 9 g. of $(CO_2H)_2,2H_2O$ was necessary. The solution titrated contained 0·015 g. of Ta_2O_5 and 0·45 g. of $(CO_2H)_2,2H_2O$, *i.e.*, 52·6 mols. of acid to 1 mol. of Ta_2O_5. Addition of NaOH did not cause pptn.

Russ (*loc. cit.*) found that evaporation of complex alkali niobioxalate solutions yielded salts of the formula $Nb_2O_5,3R_2O,6C_2O_3,xH_2O$ where R = NH_4, Na, K, Rb. Conductivity measurements of solutions of these salts at dilutions of 16—2048 l./mol. showed, except in the very dil.

solutions, that Λ was but very slightly less than that of the corresponding solutions of the respective hydrogen oxalate. Application of Ostwald basicity rule led to values ranging from 48·9 to 53·3, and this led Russ to represent the constitution of his salt in solution as $R_4Nb_2O_2(C_2O_4)_6$. Curve I in Fig. 2 shows that the complexity of the niobioxalic acid solutions is connected with the second stage of dissociation of $(CO_2H)_2$. It has already been shown (p. 421) that the weakness of acetic and phenylacetic acids may be responsible for the delay of pptn. when alkali niobate solutions are subjected to their attack. It appears likely that the weakness of the second ionisation of $(CO_2H)_2$ may be responsible for the complex formation which that acid promotes, though it must not be overlooked that $H{\cdot}CO_2H$, which is but slightly stronger, shows no tendency to form complex solutions with Nb_2O_5. Russ's salt might be considered as $Nb_2O_5,6RHC_2O_4$. The solute present at the mid-point of the titration (curve I) is comparable, as it corresponds to the formation of $Nb_2O_5,6{\cdot}34NaHC_2O_4$. The difference between the p_H of the solution at this point and that at the mid-point of the $(CO_2H)_2$ titration explains why the complex Nb solutions have a smaller Λ than the corresponding alkali hydrogen oxalate solutions. Although towards strong acids, Nb_2O_5 exhibits scarcely any basic tendencies, it would appear from the titration curve that H ions originating from HC_2O_4' ions had reacted with $Nb(OH)_5$, thus

$$x\mathrm{H}^{\cdot} + x\mathrm{HC_2O_4}' + \mathrm{Nb(OH)_5} \rightleftharpoons x\mathrm{H}^{\cdot} + \left[\mathrm{Nb}^{\mathrm{(OH)}_{5-x}}_{(\mathrm{C_2O_4})_x}\right]^{'x} + x\mathrm{H_2O}$$

Excluding the possibility of covalent linkages, such a combination would seem possible only if the complex so formed were unable to ionise. In view of the very small solubility of Nb_2O_5 in strong acids, it appears that its dissolution in $(CO_2H)_2$ is more probably of a colloidal nature, in spite of the fact that the solutions are optically clear. The formation of Russ's salt could then be accounted for by

$$3\mathrm{KHC_2O_4} + \mathrm{Nb(OH)_5} \rightleftharpoons 3\mathrm{K} + \left[\mathrm{Nb}^{\mathrm{(OH)}_2}_{(\mathrm{C_2O_4})_3}\right]^{'''} + 3\mathrm{H_2O}.$$

This equilibrium would also explain the smaller conductivity of the niobioxalates, and also why the equiv. conductivities of the niobioxalates and hydrogen oxalates are of similar magnitude. It also affords an explanation of the higher p_H values prevailing in Curve I. The niobioxalate complex in entering into hydrolytic equilibrium with H_2O,

$$\left[\mathrm{Nb}^{\mathrm{(OH)}_{5-x}}_{(\mathrm{C_2O_4})_x}\right]^{'x} + y\mathrm{H_2O} \longrightarrow \left[\mathrm{Nb}^{\mathrm{(OH)}_{(5-x+y)}}_{(\mathrm{C_2O_4})_{(x-y)}}\right]^{'(x-y)} + y\mathrm{H}^{\cdot}$$

liberates H˙ ions, which, as the alkali is added, become replaced and so, in disturbing the equilibrium, ultimately bring about the decomp. of complex oxalate. As already stated, no pptn. occurred. The lower p_H values recorded in Curve II suggest that the more active acid, HCl, prevented the complete re-formation of the complex oxalate until the $(CO_2H)_2$ had been released. Whatever may be the true explanation of the complex niobium–oxalate formation, Fig. 2 shows definitely that Russ's conclusions from conductivity data cannot be valid. The explanation given above is not without objections, but it is probably the only one that will fit the electrometric data; the true explanation will not be forthcoming until we have greater knowledge of solutions that are intermediate between true and obviously colloidal solutions. The fact that both solutions can be pptd. in the presence of tannin and an electrolyte (*vide infra*) by the addition of NH_3 aq. seems to indicate that they are colloidal.

Note on Powell and Schoeller's Method of separating Tantalum from Niobium.—Powell and Schoeller (*locc. cit.*) have devised a method by which Ta_2O_5 may be separated from Nb_2O_5 by the careful addition of NH_3 aq. to a boiling solution of the oxides in a mixture of $(NH_4)_2C_2O_4$ and $(CO_2H)_2$ containing sufficient tannin, coagulation of the Ta_2O_5–tannin complex being assisted by means of NH_4Cl. The foregoing work shows that in order to dissolve Ta_2O_5 a relatively large proportion of $(CO_2H)_2$ is necessary compared with that required for Nb_2O_5. In the cold, it is possible to neutralise the Nb and Ta–$(CO_2H)_2$ solutions containing tannin with NaOH without the appearance of a ppt. The broken curve IV refers to a titration similar to that represented by Curve I, with the exception that the solution contained 0·25 g. of tannin per 100 c.c. Curve V is that of the back-titration with HCl at 18°. No ppts. were obtained. The extra alkali required is due to the tannic acid. Similar titrations of Ta–$(CO_2H)_2$ solutions gave no ppt. In the presence of NH_4Cl, however, both Nb_2O_5 and Ta_2O_5–tannin adsorption complexes were pptd. Powell and Schoeller emphasise the necessity of fractional pptn., evidently because the p_H at which Ta is pptd. is very close to that at which Nb begins to separate.

A series of p_H titrations with NH_4OH of $(CO_2H)_2$–NH_4Cl–tannin solutions containing either Nb_2O_5 or Ta_2O_5 have been carried out at 18°. The same solutions were titrated with NH_4OH at 100°, and the p_H values at which pptn. occurs were very similar and depended largely on the ratio of the particular " earth " to $(CO_2H)_2$: in a typical titration, at 18°, of 100 c.c. of a solution containing 0·3 g. of $(CO_2H)_2$, 0·03 g. of Nb_2O_5, 5 g. of NH_4Cl, and 0·2 g. of tannin with 0·233*N*-NH_4OH, cloudiness appeared at p_H 1·75 and coagulation at p_H 4·4, whereas at 100° pptn. was delayed until p_H 3·0. By trebling the amount of Nb_2O_5, pptn. on boiling began at p_H 2·2. From 100 c.c. of a solution containing 0·45 g. of $(CO_2H)_2$, 0·015 g. of Ta_2O_5, 5 g. of NH_4Cl, and 0·2 g. of tannin, pptn. begins with 0·233*N*-NH_4OH at p_H 3·2 at 18°, but on boiling it occurs earlier—at p_H 2·1. It would appear, therefore, that the success of the method lies in the amount of NH_3 that can be added in bringing about the pptn. of Ta_2O_5 without pptg. Nb_2O_5, *i.e.*, without increasing the p_H appreciably. As Powell and Schoeller state, a more satisfactory separation can be effected if the amount of Ta_2O_5 present is high. In this case H_2SO_4 and a considerably larger amount of $(NH_4)_2C_2O_4$ are necessary, and this enables greater amounts of NH_3 to be added without materially affecting the p_H. The control of $[H^\cdot]$ is thus of no service in performing the separation. We have found the separation of Ta from Nb to be extremely difficult, requiring considerable experience and skill before accurate results can be obtained. It seems that the only method of controlling the separation is, as stated by Schoeller, the difference in the colours of the pptd. adsorption complexes.

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