# 322. *Physicochemical Studies of Complex Acids. Part VIII. Niobic Acid.*

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Niobium pentoxide, although usually considered to be an acidic oxide, is insoluble in water and only dissolves in alkalis in the fused state. From aqueous solutions of the fused niobates it is readily precipitated by mineral acids. The existing knowledge of these alkali niobate solutions is very meagre, and they have therefore been subjected to potentiometric and conductometric investigation.

## Experimental.

The alkali niobate solutions were prep. from crystals of potassium niobate which were obtained by fusing pure $Nb_2O_5$ with about 3 times its wt. of KOH in a Ag crucible, extracting the melt with hot water, and allowing it to crystallise. In one instance, the white cryst. salt was the hexaniobate, $K_8Nb_6O_{19},16H_2O$ (Found: $Nb_2O_5$, 54·57%. Calc.: 54·64%), previously isolated by Balke and Smith (*J. Amer. Chem. Soc.*, 1908, **30**, 1650), but as a rule niobates were obtained with a somewhat higher proportion of alkali than that corresponding to the 4 : 3 ratio required by the hexaniobate. The excess alkali was undoubtedly a contamination, due to insufficient washing of the crystals. Since no other impurity could be introduced thereby, this was no disadvantage. Thus, three different prepns. contained $Nb_2O_5 : K_2O = 3 : 4{\cdot}21$, 4·10, and 4·16. Several electrometric titrations were carried out with solutions made from these prepns. As the results obtained during comparable stages of the titrations were identical, the behaviour of only one solution on reaction with (*a*) KOH and (*b*) HCl is described.

Solutions of alkali niobates differ from those of the corresponding vanadates in that boiling has no ascertainable effect on niobate solutions undergoing titration with either acid or alkali.

For the direct titrations, 100 c.c. of a solution 0·0141*M* with respect to K and 0·01005*M* with respect to Nb, prep. from crystals of the 4·209 : 3 salt, were used. At 18° the $p_H$ of this solution was 11·59, and on the progressive addition of 0·1*N*-KOH increases in the $p_H$ and the specific conductivity were obs. in agreement with those calc. for free alkali, showing that the niobate does not react to form "pyroniobates," $2K_2O,Nb_2O_5$, or "orthoniobates," $3K_2O,Nb_2O_5$.

The titration of this solution with 0·2*N*-HCl gave conductometric data at 25° and potentiometric data at 18°, some of which are recorded in cols.

1—4 of Table I, and the curves plotted therefrom are shown in Fig. 1. In the table, $\kappa_1$ and $\kappa_2$ represent respectively the contributions of the salt $xK_2O,Nb_2O_5$ and the niobate anion to the conductivity. The $p_H$ data were obtained by means of the H electrode which functioned satisfactorily except in the vicinity of the point at which $Nb_2O_5$ was completely pptd. A parallel quinhydrone titration was used to determine the $p_H$ curve in this region.

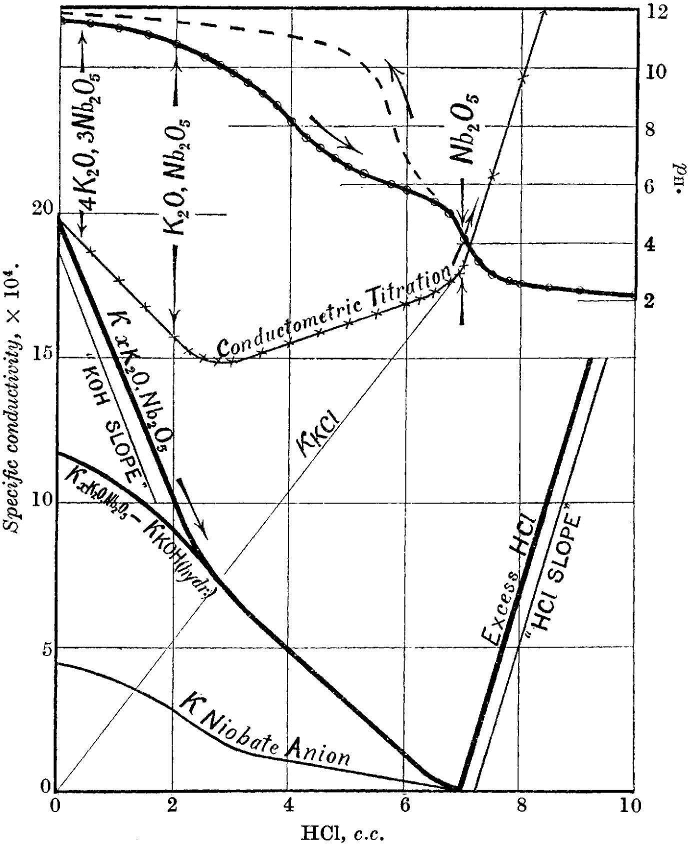

FIG. 1.

The addition of the smallest amount of acid produced a faint turbidity which became a ppt. when about half the amount of acid required completely to ppt. the $Nb_2O_5$ had been added. Until then, however, the ppt. remained in equil. with a turbid colloidal suspension which could not be destroyed by boiling or ageing. Complete flocculation of the hydrated $Nb_2O_5$ occurred almost immediately after adding the stoicheiometrical amount of acid. Once the $Nb_2O_5$ had been pptd. it could not be redissolved in alkali, though H electrode titrations of such ppts. with alkali showed that some of the alkali was absorbed, apparently as the result of chemical combination. The curves so obtained are

### TABLE I.

*Conductometric and potentiometric titrations of* 100 c.c. *of a solution* 0·00705M-$K_2O$ *and* 0·00503M-$Nb_2O_5$ *with* 0·2N-HCl.

| C.c. | $\frac{K_2O}{Nb_2O_5}$. | $\kappa \times 10^3$. | $p_H$. | $\kappa_1 \times 10^3$. | $\kappa_2 \times 10^4$. | Hydrolysis, %. |
|---|---|---|---|---|---|---|
| 0 | 1·40 | 1·961 | 11·59 | 1·178 | 4·54 | 20·4 |
| 1·0 | 1·20 | 1·761 | 11·32 | 1·065 | 3·88 | 13·4 |
| 2·0 | 1·00 | 1·580 | 10·80 | 0·939 | 3·09 | 3·8 |
| 2·5 | 0·90 | 1·501 | 10·31 | 0·797 | 2·13 | 1·7 |
| 3·0 | 0·80 | 1·484 | 9·83 | 0·650 | 1·54 | 0·5 |
| 3·5 | 0·69 | 1·514 | 9·12 | 0·577 | 1·28 | 0·1 |
| 4·0 | 0·59 | 1·550 | 8·11 | 0·488 | 1·05 | — |
| 5·0 | 0·39 | 1·620 | 6·60 | 0·307 | 0·57 | — |
| 6·0 | 0·20 | 1·685 | 5·81 | 0·123 | 0·03 | — |
| 6·5 | 0·09 | 1·731 | 5·39 | 0·047 | 0·00 | — |

| *Excess acid.* | | | | | |
|---|---|---|---|---|---|
| HCl, c.c. .......... | 7·25 | 7·5 | 8·0 | 10·0 | 15·0 |
| $\kappa \times 10^3$ .......... | 1·966 | 2·122 | 2·469 | 3·806 | 7·166 |
| $p_H$ (obs.) .......... | 3·30 | 3·06 | 2·79 | 2·31 | 1·84 |
| $p_H$ (calc.) .......... | 3·41 | 3·07 | 2·75 | 2·27 | 1·85 |

not reproducible on account of the heterogeneous nature of the reaction, but the typical back-titration curve given as a broken line at the top of Fig. 1 illustrates the extent of the reaction that occurs with freshly pptd. $Nb_2O_5$. The last col. of Table I gives the % amounts of KOH produced by hydrolysis from the potassium niobate in solution at different titres: these were calc. from the $p_H$ data. The line marked $\kappa_{KCl}$ in Fig. 1 gives the specific conductivities due to the KCl formed during the titration. By subtracting the contribution made by the KCl from the obs. specific conductivities at different titres, the specific conductivity of the potassium niobate can be computed. These values are given in col. 5 of Table I and are also shown in Fig. 1 by means of a heavy line marked $\kappa_{xK_2O,Nb_2O_5}$.

The analysis of the conductometric curve can be carried a stage further. The last-mentioned curve is the component of the conductivities of $K^{\bullet}$ kations, niobate anions, and KOH formed by hydrolysis. The conductivity due to the last can be calc. and subtracted from that of the niobate, giving the curve in Fig. 1 marked $\kappa_{xK_2O,Nb_2O_5}-\kappa_{KOH(hydr.)}$. Further, deducting from this curve the conductivity due to the $K^{\bullet}$ ions derived from the niobate, conductivities are obtained (shown by the bottom curve of Fig. 1 and in col. 6 of Table I) of the soluble niobate anions at different titres.

Finally, the last part of Table I gives the obs. specific conductivities and $p_H$ values of the solution to which an excess of HCl had been added beyond that required to ppt. the $Nb_2O_5$.

## *Discussion.*

The reactants and products of the above titration are represented by the equation:

$$4{\cdot}21K_2O,3Nb_2O_5 + 8{\cdot}42HCl \longrightarrow 3Nb_2O_5 + 8{\cdot}42KCl + 4{\cdot}21H_2O,$$

the reaction being complete at 6·93 c.c. The reaction of $4{\cdot}21K_2O,3Nb_2O_5$ with alkali affords no evidence of the formation of salts corresponding to the "pyro-" or "ortho-niobate."

Fig. 1 shows that at the end-point of the above reaction (6·93 c.c.) the conductivity of the solution is accounted for entirely by the KCl formed, in accordance with the fact that the $Nb_2O_5$ is then quant. pptd. Beyond this titre a very rapid increase occurs in the specific conductivity, almost identical with that produced by free HCl, as is shown by the calculated slope on the right of Fig. 1 (displaced somewhat to the right for the sake of clearness). Further, knowing that the conductivity of the solution is due to a fixed amount of KCl and an increasing amount of HCl, the concentration of the latter can be found from the conductometric data. Such calculations are in good agreement with one another and show that beyond 7·04 c.c. the added acid remains free. Moreover, $p_H$ values, calculated on this basis and recorded at the end of Table I, agree with the observed. The extra 0·11 c.c. of acid is probably adsorbed by the precipitate.

The precipitation of the pentoxide from the 4·21 : 3 salt proceeds in two stages. In the first stage, occupying the first 2·5 c.c. of the titration, the hydroxyl-ion concentration fell from 0·0029*M* to 0·00015*M*, the contribution of the hydroxyl ion to the total conductivity decreasing from 0·783 to $0{\cdot}031 \times 10^{-3}$ mho, and the conductivity of the niobate ion from 0·454 to $0{\cdot}213 \times 10^{-3}$ mho. Also, during the first 2·0 c.c. the hydroxyl-ion concentration is exactly proportional to the titre. In this respect, the system differs from the neutralisation of a very weak acid, *e.g.*, phosphoric acid in its third stage of dissociation, and a mass-action equilibrium of the usual form is obviously inapplicable. This neutralisation of free alkali accords with the initially rapid diminution in conductivity, which is compared with the calculated change in conductivity for the removal of an equivalent amount of potassium hydroxide, shown by the line on the left of Fig. 1. The slopes of the two lines are very nearly but not quite identical.

Hauser and Lewite (*Z. angew. Chem.*, 1912, **25**, 100) showed that alkali niobate solutions can be dialysed through parchment membranes, yielding a stable niobium pentoxide sol that is practically free from alkali. It is probable then that the niobate solution contains potassium ions, colloidal niobate anions, and free alkali. The first addition of acid results in the uniform neutralisation of the alkali, only a small fraction of the acid being used in precipitating the pentoxide. At first, little change occurs in the conductivity of the niobate anion, but then a very rapid diminution occurs to $0{\cdot}154 \times 10^{-3}$ mho at 3·0 c.c., after which the conductivity decreases slowly but regularly during the remainder of the titration. Since, at first, little diminution occurs in the concentration of niobium, the first decrease in the anionic conductivity must be attributed to some aggregation, probably the first stage towards precipitation, caused by the withdrawal of the stabilising hydroxyl ions. Finally, at about 3·0 c.c. the hydroxyl-ion concentration becomes too low to retain the sol in solution, and thereafter precipitation occurs uniformly.

It was impossible to estimate the amount of pentoxide precipitated at different titres, for much of the precipitate remained in colloidal suspension and could not be filtered off, but approximate nephelometric estimates were made by comparison with suspensions of known niobium pentoxide concentrations. The following results were obtained :

| HCl, c.c. .......... | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|---|
| %$Nb_2O_5$ pptd. .... | 0 | 5 | 10 | 18 | 35 | 57 | 80 | 100 |
| $K_2O/Nb_2O_5$ in soln. | 1·11 | 1·10 | 1·05 | 0·94 | 0·90 | 0·88 | 0·82 | — |
| $\lambda_{\text{Nb anion}}$ .......... | 45 | 41 | 34 | 19 | 16 | 13 | 14 | — |

These figures give an approximate estimate of the amount of niobium pentoxide in solution at different titres; since the concentration of that part of the potassium which is not present as either the chloride or the hydroxide is calculable, it is possible to find the ratio $K_2O/Nb_2O_5$ of the soluble salt at various stages, given in the third line. Although these calculations must necessarily be very rough, they indicate that the composition of the soluble salt did not differ much from that of the 1 : 1 salt. This appears to be the salt present during the first 2·0 c.c., after which it undergoes decomposition :

$$K_2O,Nb_2O_5 + 2HCl \longrightarrow 2KCl + H_2O + Nb_2O_5,$$

precipitation not being abundant until another c.c. of acid is added, causing sufficient diminution in the $p_H$ and aggregation of the niobate sol to initiate precipitation. This aggregation is illustrated by the last line of the table giving the molecular conductivities of the anion (per mol. of $Nb_2O_5$).

Between 3·0 and 6·5 c.c., the potassium niobate conductivity curve is rectilinear, becoming zero if continued to 6·7 c.c. At 6·5 c.c., however, the curve becomes slightly concave, reaching zero at 6·93 c.c. This probably means that the precipitated pentoxide is mixed with some adsorbed alkali, giving a composition of $0{\cdot}05K_2O,Nb_2O_5$ for the precipitate, the alkali being removed by the last 0·4 c.c. of the titration.

There is no evidence for the existence of any ion in the solution corresponding to the 4 : 3 salt which is the stable solid niobate.

Pierce and Yntema (*J. Physical Chem.*, 1930, **34**, 1822) have recently titrated a potassium niobate ($K_8Nb_6O_{19}$) solution with hydrochloric acid in the presence of the hydrogen electrode. Their curve is similar to that in Fig. 1 in that the inflexion occurred when the 2 : 3 potassium niobate had been formed. Their $p_H$ values corresponding to the first section were somewhat irregular and lay between 10·4 and 8·0, whereas those now obtained are appreciably higher and have, moreover, been found to be in accord with the conductivity data. The two curves, however, are in agreement in the second section, during which precipitation of niobium pentoxide occurs.

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