# A STUDY OF THE SODIUM NIOBATES AND THEIR COMPLEXES WITH ORGANIC ACIDS.

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Thesis submitted for the degree of Ph.D.
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by

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# INTRODUCTION.

## OCCURENCE.

In its natural ores niobium is almost always associated with tantalum. Neither metal occurs naturally in the free state to any great extent but the minerals containing these metals are numerous and are generally distributed in small quantities over the earth. The metals are found mainly as the negative radicals in minerals in which the oxides of iron, manganese, calcium, titanium, and various rare earth metals form the bases.

Niobites and Tantalites are the most important ores and consist mainly of ferrous salts of meta-niobic and meta-tantalic acids in which the iron has been partially displaced by manganese. They occur mostly in igneous rocks and are black and crystalline. Niobites contain 50-70% $Nb_2O_5$ and 5-20% $Ta_2O_5$, while in Tantalites the quantities range from 40-70% $Ta_2O_5$, with 5-40% $Nb_2O_5$.

Other important ores are Pyrochlore, a crude calcium niobate, and the niobites and tantalites of the rare earth metals, e.g. Yttro-tantalite, Fergusonite, and Samarskite.

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## HISTORICAL.

Although the first pure niobium and tantalum compounds were prepared by Marignac in 1865, the existence of these elements was known at a much earlier date. In 1801, Hatchett reported the existence of a new element for which he suggested the name Columbium. In the following year, Ekeberg, while examining the ores now known as tantalite and yttro-tantalite, found what he thought was a new element, which was named Tantalum on account of the extreme difficulty experienced in dissolving its oxide in acids. It is now known that the investigations of these and subsequent chemists were carried out on a mixture of the pentoxides of niobium and tantalum.

In 1844, Rose announced that certain minerals contained, in addition to tantalic acid, the acid oxide of a new metal which he named Niobium. The earlier researches of Rose, extending over a period of nearly twenty years and contained in Pogg. Annalen, 1844-1863, have proved a valuable source of information for the chemistry of niobium and tantalum.

Marignac, (Compt. Rend., 1865, 60, 1221.), accomplished the first complete separation of niobium and tantalum, and prepared the first pure compounds of these metals. He effected this separation by fractional crystallisation of the double fluorides, $K_2NbOF_5.H_2O$, which is comparatively soluble, and ? [illegible] $\underline{K_2TaF_5}$, which is comparatively insoluble. His methods, with modifications, are still in use. The separated fluorides may be converted to the oxides by boiling with concentrated $H_2SO_4$ until free from fluorine and hydrolysing the product by boiling with water. Alternatively, the addition of ammonia to the solution of the double fluoride will precipitate the hydrated oxide.

Marignac's method has the disadvantage of being impracticable with small quantities of material, and recently a process has been evolved which avoids this difficulty. It is based on the comparative solubility of $Nb_2O_5$ and the comparative insolubility of $Ta_2O_5$ in a mixture of equal volumes of selenium oxychloride and conc. $H_2SO_4$. Hydrolysis of the extract after dilution yields niobic acid while $Ta_2O_5$ is left in the residue. (Lenher - J.A.C.S., 1921, 43, 21. ; Merrill - ibid, 1921, 43, 2378.).

In 1905, the metals were prepared in the pure state for the first time by von Bolton, (Zeitsch. Elektrochem., 1905, 11, 45, 722. ; 1907, 13, 145.). The usual method of isolation is by reduction of the pentoxide but this is difficult because of the tendency of the reducing agent to combine or alloy with any niobium formed. The method used by von Bolton was to reduce small filaments of the pentoxide to the tetroxide by heating to whiteness in carbon powder. The filaments were then heated to whiteness in a vacuum by means of an alternating current, whereupon rapid reduction to the pure metal took place.

Niobium is variously described as a dull grey, steel grey, or white metal with a yellowish tinge. It is slowly dissolved by hot HF but is not attacked by other strong acids. Alkali solutions have no effect on the metal but fusion with solid alkalies converts it into niobates.

Three oxides are definitely known, the sesquioxide,

$Nb_2O_3$; the tetroxide, $Nb_2O_4$; and the pentoxide, $Nb_2O_5$. Of these, only the pentoxide gives rise to salts, the niobates. Niobium pentoxide or niobic anhydride is probably the most common compound of niobium. It is a white amorphous solid which, after strong ignition, is practically insoluble in all acids except HF, and also in solutions of alkalies. It may be converted to niobates by fusion with alkali hydroxides or carbonates.

It does not combine directly with water to form acids of definite composition and the term niobic acid is applied to the wholly or partially hydrated pentoxide. Niobic acid is precipitated as a white gelatinous substance when solutions of alkali niobates are treated with mineral acids. When freshly precipitated, it shows a weakly amphoteric character, being soluble in excess acid, particularly conc. $H_2SO_4$, and also in caustic alkali solutions. That it is a very weak acid is shown by the readiness with which the niobates are decomposed even by weak acids with precipitation of niobic acid.

Many niobates have been prepared, showing numerous variations in the ratio of basic oxide to acidic oxide. They are mostly insoluble in water with the exception of the alkali niobates, and even some of those are very sparingly soluble. Ammonium niobates are unknown since they are decomposed by water, which instability is quite consistent with the weakness of niobic acid. The alkali niobates are most conveniently prepared by the action of caustic alkalies on niobic acid or on solutions of niobium oxytrifluoride For both potassium and sodium, a large number of niobates of varying composition have been reported.

The first systematic investigation of sodium niobates was carried out by Rose, (Pogg. Annalen, 1861, 103, 119.), who prepared several of these salts, the most important of which was the meta-niobate, which he describes as being the best crystallised and most stable of all the salts of niobic or tantalic acids. On analysis he assigned to it the formula $Na_2O.Nb_2O_5.6\text{-}9H_2O$, and gave three methods of preparation.

1. By fusing $Nb_2O_5$, an acid sodium niobate, or niobium hydroxide, with NaOH in a silver crucible. On treating the melt with water a residue was obtained, insoluble in excess NaOH but soluble in water. The neutral sodium niobate was obtained by pouring the solution into a solution of NaOH.

2. By heating a solution of NaOH containing $Nb_2O_5$ in suspension. The latter did not dissolve but after removal of excess NaOH the residue was soluble in water and could be crystallised.

3. By fusing $Nb_2O_5$ with $Na_2CO_3$. The melt was treated with water and the residue, insoluble in excess $Na_2CO_3$, was dissolved in water. After evaporation of the solution, the neutral salt often separated in the crystalline form.

These methods did not always give the meta-niobate since Rose describes a salt of composition $3Na_2O.2Nb_2O_5.24H_2O$ which he obtained once during the preparation of the meta-salt.

Other salts described by Rose were:-

$4Na_2O.5Nb_2O_5.40H_2O$. - obtained by fusing $Nb_2O_5$ with sodium carbonate at a low temperature.

$Na_2O.4Nb_2O_5.5H_2O$. - obtained as a gelatinous precipitate on passing $CO_2$ into a solution of the neutral salt.

$3Na_2O.Nb_2O_5$. - This salt was not isolated by Rose but he concluded that it was formed when $Nb_2O_5$ was fused for a long time with $Na_2CO_3$ by determining the amount of $CO_2$ expelled from the fusion. When treated with water, it decomposed giving the neutral salt and NaOH.

<u>NOTE</u>:- Rose calculated his results on the assumption that niobates were derivatives of $Nb_2O_3$. The above formulae were calculated from Rose's results by Rammelsberg, (Pogg. Annalen, 1869, 136, 177, 362.).

Of the other earlier investigators, Marignac, (Ann. Chim. Phys., 1866, [iv], 8, 20.), although he carried out much important work on niobium and tantalum, was unable to obtain any sodium salts of niobic acid.

Hermann, (J. Prakt. Chim., 1871, 3, 419.), describes a number of sodium niobates. He added NaOH to a hot solution of $K_2NbOF_5$ and obtained a salt to which he assigned the formula $5Na_2O.4Nb_2O_5.21H_2O$. This method evolved by Hermann for the preparation of sodium niobates has been used by most of the later investigators.

Santesson, (Bull. Soc. Chim., 1875, 24, [ii], 53.), obtained, by fusion of $Nb_2O_5$ with NaOH, the meta-niobate, $Na_2O.Nb_2O_5.6H_2O$. Fusion of this salt with NaOH gave another salt, $2Na_2O.3Nb_2O_5.9H_2O$, which was insoluble in water.

Holmquist, (Zeitsch. Kryst. Min., 1899, 31, 306.), fused $Nb_2O_5$ with $Na_2CO_3$ and NaF (flux). He obtained a crystalline salt, $NaNbO_3$, which he describes as insoluble in $H_2O$ and acids.

It will be seen that the work of those earlier investigators produced a confused mass of evidence for the existence of numerous sodium niobates, which showed many variations in the basic oxide - acid oxide ratio. The more recent work has been carried out more systematically, chiefly by American investigators, and those earlier experiments have been repeated.

Bedford, (J.A.C.S., 1905, 27, 1216.), repeated Hermann's experiment and added 150 gm. NaOH in concentrated solution to a solution of 50 gm. $K_2NbOF_5$ in 1000 c.c. hot water. The white, finely-divided precipitate obtained was filtered, washed with cold water, and recrystallised three times from water. The salt was very stable and was completely soluble in water. The results of his analysis were more concordant than those of Hermann and indicated the formula $7Na_2O.6Nb_2O_5.32H_2O$.

Thinking that the salt might contain an extra molecule of $Na_2O$, Bedford precipitated its aqueous solution with alcohol. The product, on analysis, proved to have the composition $7Na_2O.6Nb_2O_5.31H_2O$. He therefore concluded that the 7:6 ratio correctly represented the composition of this salt.

By precipitation from an aqueous solution of this salt, he prepared the barium, silver, and zinc salts, all of which gave the basic oxide - acid oxide ratio as 7:6.

Using Rose's method, Bedford fused 10 gm. $Nb_2O_5$ with 40 gm. NaOH in a silver crucible. The excess NaOH was washed out and the sodium niobate recrystallised twice from water. Good crystals were obtained, readily soluble in water, and having the composition $7Na_2O.6Nb_2O_5.32H_2O$. From the same preparation Rose isolated the salt $Na_2O.Nb_2O_5.6\text{-}9H_2O$.

Rose concluded that, on fusing $Nb_2O_5$ with $Na_2CO_3$ for a long time, the salt $3Na_2O.Nb_2O_5$ was formed. In imitation of this experiment, Bedford fused 8 gm. $Nb_2O_5$ with 25 gm. $Na_2CO_3$ in a platinum crucible. The excess $Na_2CO_3$ was washed from the melt and the sodium niobate dissolved in water. It was isolated by addition of $Na_2CO_3$ to the solution since it showed a great tendency to form super-saturated solutions. The salt separated as a fine crystalline powder which proved to have the composition $7Na_2O.6Nb_2O_5.36H_2O$.

Bedford concluded that the three methods used for the preparation of sodium niobate give one and the same salt, namely that in which the basic oxide - acid oxide ratio is 7:6.

This ratio is preserved in the barium, silver, and zinc salts.

In his opinion, it is possible that potassium niobates may also be reduced to one common ratio.

Balke and Smith, (J.A.C.S., 1908, 30, 1637.), state that in the general preparation of alkali niobates, by fusion of $Nb_2O_5$ with alkali carbonates, the products obtained depend on the relative quantities of oxide and carbonate used. With small amounts of carbonate, insoluble acid niobates are obtained. Ample quantities of potassium, rubidium, and caesium carbonates give clear fusions completely soluble in small amounts of water. With sodium carbonate the fusion is not clear and the resulting niobate is insoluble in excess $Na_2CO_3$ but completely soluble in water.

Balke and Smith, using Hermann's method, prepared a salt of composition $7Na_2O.6Nb_2O_5.31H_2O$. The mother liquors from the recrystallisation of this salt were allowed to evaporate spontaneously for several weeks and from these there crystallised in triclinic crystals the meta-niobate - $Na_2O.Nb_2O_5.7H_2O$. This salt, they considered, was probably the same as that prepared by Rose which he formulated as $Na_2O.Nb_2O_5.9H_2O$.

Using a solution of the 1:1 salt, Balke and Smith prepared magnesium, silver, copper, and cadmium salts, all having the 1:1 ratio.

Smith and van Haagen, (J.A.C.S., 1915, 37, 1783.), repeated the experiments of Bedford and of Balke and Smith. They dissolved $K_2NbOF_5$ in hot water and added three times its weight of NaOH in conc. solution. The heavy white precipitate obtained was dissolved in boiling water and allowed to crystallise. The resulting crystals had the composition $7Na_2O.6Nb_2O_5.31H_2O$. Superficial washing of the original precipitate increased the yield, i.e. the formation of the salt was facilitated by the presence of a small amount of free alkali.

On spontaneous evaporation, the mother liquors gave well-defined crystals of the meta-niobate, $Na_2O.Nb_2O_5.7H_2O$. Difficulty was experienced in recrystallising this salt, the product being usually amorphous and far from uniform. The one successful attempt was made by crystallising the solution over conc. $H_2SO_4$ in a $CO_2$-free atmosphere.

An attempt to prepare more acid salts from the mother liquors from the crystallisation of the 1:1 salt gave on one occasion a salt between the ratios of 3:4 and 4:5.

Smith and van Haagen describe the 7:6 salt as definite needles or slender prisms, soluble with difficulty even in hot water, and the 1:1 salt as well-defined, short, stout, triclinic crystals which, under the microscope, appear as diamond or coffin-shaped plates, and which are much more soluble than the 7:6 salt.

Bedford precipitated the 7:6 salt from aqueous solution with alcohol. In an attempt to precipitate the meta-niobate in a similar manner, Smith and van Haagen obtained a crystalline precipitate which, however, proved to be the 7:6 salt. It was noted that, if excess alcohol was used, a mixture was obtained. This peculiar change, according to Smith and van Haagen, may be expressed in the simplest form thus :-

$$7(Na_2O.Nb_2O_5) = 7Na_2O.6Nb_2O_5 + Nb_2O_5.$$

In other words, in addition to the 7:6 salt, niobic acid or, more probably, an acid niobate is formed, which will be precipitated by excess alcohol but not by a moderate amount. Other neutral substances, e.g. NaCl, likewise appear to precipitate the 7:6 salt, the less soluble compound, from solutions of the meta-niobate.

Smith and van Haagen conclude that the 7:6 and the 1:1 salts are two distinct and well-defined compounds and that they are mutually convertible. The relation may be expressed by the reversible reaction :-

$$7Na_2O.6Nb_2O_5 \rightleftarrows 6(Na_2O.Nb_2O_5) + Na_2O.$$

In aqueous solutions the change must be assumed to take the form of a partial hydrolysis as follows :-

$$7Na_2O.6Nb_2O_5 + H_2O \rightleftarrows 6(Na_2O.Nb_2O_5) + 2NaOH.$$

Smith and van Haagen are of the opinion that undoubtedly other ratios exist although it seems reasonable to suppose that some of the more improbable ratios mentioned in the literature are due to the production of mixtures.

It will be seen from the reports of these investigators that the usual method for the preparation of sodium niobate consists in fusing $Nb_2O_5$ with NaOH and, after removal of excess NaOH, crystallising the product from water. It must be noted, however, that this method, in the hands of different investigators, has yielded sodium niobates of varying composition.

It would appear from the literature that the only sodium niobates as yet isolated which can be regarded as definite chemical individuals are the meta-salt, $Na_2O.Nb_2O_5.7H_2O$, and the 7:6 salt, $7Na_2O.6Nb_2O_5.31\text{-}36H_2O$. The most common of the potassium niobates is the 4:3 salt, $4K_2O.3Nb_2O_5.16H_2O$ ; a sodium niobate of similar composition has not yet been isolated. (Schoeller and Jahn - The Analyst, 1926, 51, 613.).

The other salts mentioned in the literature are so numerous and show such large variations in the proportions of base to acid that it is probable that they are not distinct chemical identities but consist of isomorphous mixtures of simple salts.

The fact that niobic acid combines in varying proportions with basic oxides of metals suggests that niobium pentoxide forms condensed complex anions containing several niobium atoms. The niobates, however, are so sparingly soluble and are so readily hydrolysed in aqueous solution that any close investigation into their constitution and the constitution of niobic acid has been prevented.

The first part of this paper deals with an attempt to isolate definite individual sodium niobates other than the 1:1 and 7:6 salts. For this purpose it was decided to carry out fractional crystallisations on saturated solutions of sodium niobate under thermostatic control. It seemed probable that, should the crystallisation start with an acid salt, the removal of each succeeding fraction would leave the mother liquor more alkaline. By this means, it might be possible to obtain a series of salts ranging from the more acid salts in the first fractions to at least the neutral salt in the final fractions.

The preparation of such a series of salts might, it was considered, give a definite indication as to the constitution of niobic acid and a systematic basis for the formulation of the various sodium niobates.

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# PART I.

## Section 1.

## PREPARATION, FRACTIONAL CRYSTALLISATION, AND ANALYSIS OF SODIUM NIOBATES.

## Preparation of Sodium Niobate.

To carry out satisfactory fractional crystallisations it was considered desirable to work with large quantities and a considerable amount of sodium niobate was prepared as a starting material.

The method of preparation was that used by Rose - fusion of $Nb_2O_5$ with NaOH. For each fusion 6 gm. $Nb_2O_5$ and 25 gm. NaOH were thoroughly mixed and the mixture fused in a nickel crucible. The fusion took about an hour and the melt did not become clear. When cool, the crucible was immersed in 100 c.c. water and the melt removed. The aqueous extract, which contained the excess NaOH plus a small amount of sodium niobate, was filtered off and laid aside. The residue, mainly sodium niobate, was treated with 250 c.c. of hot water containing a small amount of NaOH to prevent hydrolysis of the niobate. The solution was filtered hot, and the residue was extracted again in a similar manner. The small amount of residue left after the second extraction was neglected.

The filtrates were left to stand overnight and the niobate which crystallised was filtered off, washed with cold water, and dried. The mother liquors were evaporated down to about half volume, filtered, and left to stand for some time. The salt which crystallised was collected as before. The mother liquors were combined with those from other fusions and worked up to obtain the remainder of the niobate.

The niobic acid in the first washings and final mother liquors was recovered by treatment with dilute $H_2SO_4$.

Silver crucibles were unsuitable for this work as they were not strong enough mechanically to stand the strain of repeated fusions and, since there were no platinum crucibles available which were large enough to hold the desired quantities, the fusions were carried out in nickel crucibles. This was very unsatisfactory since the nickel was readily attacked by the alkali. The use of A.R.NaOH made no appreciable difference.

Various attempts were made to prevent or modify the effect of the alkali on the nickel.

1. Several fusions were carried out under an atmosphere of nitrogen, using a device similar to a Rose crucible. It was thought that possibly the absence of air might have some effect but no perceptible difference was noted.

2. The inside of a crucible was plated with silver electrolytically, using cyanide solutions. It was found, however, that the silver blistered off, leaving the nickel open to attack as before.

3. The crucibles were nickel plated after each fusion but, although they lasted longer, a great deal of nickel got into the solutions.

Finally Monel metal crucibles were used. These were more resistant towards the molten alkali but they, too, gave traces of nickel in the niobate solutions. The nickel, which was present mostly as the finely divided metal, was very troublesome and repeated filtration was necessary to get rid of it.

In all, about 350 gm. of sodium niobate was prepared and was recrystallised from water. The salt was dissolved in boiling water, the solution evaporated to about half its original volume, filtered, and the filtrate put in a freezing mixture to start crystallisation. After standing overnight, the salt which crystallised was filtered off, drained thoroughly on the pump, washed with water, alcohol, and ether, and dried in a vacuum desiccator. The mother liquors were worked up to obtain the remainder of the niobate, which was kept separate from the first fraction as being probably less pure.

Saturated solutions of the recrystallised salt were made up, with which to start fractional crystallisation. It was observed, however, that the solutions were yellow in colour. They were tested with dimethyl glyoxime and were found to contain a small amount of nickel. A final attempt was made to remove this impurity by precipitation of the sodium niobate from solution by means of a concentrated solution of NaCl. According to Schoeller and Jahn, (The Analyst, 1926, 51, 613.), this method should give an almost quantitative precipitation of sodium niobate in a granular form which would tend to adsorb very little of any impurity present. In this case, however, a small proportion of the nickel was precipitated along with the niobate. Not only so, but an appreciable amount of niobate was not precipitated by the NaCl and was only recovered with difficulty from the NaCl solutions.

The precipitated sodium niobate was again recrystallised from water and the recrystallised salt tested with dimethyl glyoxime. Although there proved to be a small amount of nickel present, the amount found in any solution was not more than 1 in 20,000, and was usually very much less than that. This was not sufficient to account for the depth of colour of the solutions and there was obviously some other impurity present or else the colour was due to the formation of a yellow sodium niobate. The latter eventuality did not seem very probable since no mention of any such phenomenon had been noted in the literature although Joly, (Compt. Rend., 1875, 81, 268.), states that potassium meta-niobate, $K_2O.Nb_2O_5$, crystallises in straw-yellow, rectangular plates.

To discover if the absence of nickel made any appreciable difference to the colour of the solution, a fusion was carried out in a silver crucible. It was found that the melt turned green and then blue, a fact which had been noted previously but which had been attributed to the presence of nickel. The colour of the fusion pointed to the presence of manganese and the niobate obtained from the fusion, tested with sodium bismuthate, gave a positive test for this metal. The original sodium niobate solutions, tested in a similar manner, were also found to contain manganese.

On investigation, it was found that every sample of niobic anhydride on hand contained manganese. This was pointed out to the suppliers - Hopkin and Williams - and, although the later supplies were marked manganese free, these were still found to contain traces of the metal.

It was thought that the metal was present as a finely divided suspension of the hydrated oxide and attempts were made to coagulate and precipitate this suspension. The available methods were very limited, however, because of the ease with which sodium niobate is hydrolysed, and the attempts were unsuccessful.

To determine whether all the colour of the solutions was due to impurities, it was decided to prepare some manganese free niobic acid and hence some pure sodium niobate.
To purify the niobic acid the following method was used :-

The impure acid was heated with HF in a small platinum basin on the water-bath for some time. The clear liquid was decanted into a large platinum basin, more HF was added, and the process repeated several times until only a brown sludge remained undissolved. This contained the impurities (mainly $MnF_2$) and was neglected. The solution in HF was evaporated to 75% of its original volume and excess KF was added in small quantities, with constant stirring, to the hot solution. On standing overnight large crystals appeared - probably $2KF.NbOF_3$. These were filtered off and thoroughly washed. The mother liquor and washings were worked up to obtain a further crop of crystals.

The double fluoride was taken up in cold water in which it was slowly soluble. The solution was evaporated down considerably and filtered. To it was added slowly a concentrated solution of NaOH. Niobic acid was at once precipitated and, when precipitation seemed complete, it was filtered off, drained, washed with water, alcohol, and ether, and dried in a vacuum desiccator.

During this process, platinum ware was used wherever possible but, when glass-ware was used, it was coated with spermaceti.

The purified niobic acid was perfectly white and when fused with NaOH in a silver crucible gave a salt which was colorless in the solid state and in solution. It seemed clear, therefore, that the colour obtained in the previous solutions was due solely to the contamination of manganese.

Since this process for the purification of niobic acid was lengthy and difficult owing to the use of HF, and since the amounts of nickel and manganese in the solutions were much too small to affect any analysis, it was decided to continue with fractional crystallisation of the sodium niobate already prepared.

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## Analysis of Sodium Niobates.

It is, at this stage, convenient to describe the method by which the various salts, obtained by fractional crystallisation, were analysed.

The following scheme of analysis was suggested :-

Determine the percentage $H_2O$ by drying the salt at 180°C in an air oven. Dissolve the dried salt in water and precipitate the niobic acid with dilute $H_2SO_4$. Weigh the precipitate as $Nb_2O_5$ and estimate the $Na_2O$ as $Na_2SO_4$ by evaporation of the filtrate to dryness.

When this method was tried, it was found that the dried salt would not dissolve completely in water, even after heating for a day on the water-bath. Two methods of estimating the $Nb_2O_5$ and $Na_2O$ in the dried salt were attempted.

1. As much of the dried salt as was possible was

dissolved in hot water. Dilute $H_2SO_4$ was added which precipitated the niobium in solution as niobic acid and also decomposed the undissolved niobate leaving $Nb_2O_5$. The precipitate was filtered off, washed thoroughly, dried, and ignited. The filtrate was taken to dryness in a silica basin and the sodium estimated as anhydrous $Na_2SO_4$. The results obtained were not satisfactory. When compared with the concordant results obtained later, they showed a positive error for the weight of $Nb_2O_5$ and a negative error for the weight of $Na_2SO_4$, both errors being very variable. The most reasonable explanation is that some of the undissolved niobate was surrounded and protected by niobic acid and was not decomposed.

2. As in method 1., as much of the dried salt as was possible was dissolved in hot water. A small quantity of oxalic acid was added and, after heating for four hours on the water-bath, the undissolved niobate went into solution as the oxalo-complex. The solution was taken to fumes with $H_2SO_4$ to destroy the oxalic acid. On dilution niobic acid precipitated, which was filtered off, washed, ignited, and weighed as $Nb_2O_5$. The sodium in the filtrate was estimated as before. The results were again unsatisfactory and showed negative errors for the weights of $Nb_2O_5$ and positive errors for the weights of $Na_2SO_4$ as compared with later results. This was thought to be due to the presence of too much acid which caused incomplete precipitation of the niobic acid.

Since neither of these methods gave satisfactory results it was decided to use one sample for the estimation of water and another sample for the $Nb_2O_5$ and $Na_2O$. Using a uniformly ground sample of the niobate, concordant results were obtained.

## Estimation of $H_2O$.

A weighed sample of the salt was heated to constant weight in an air oven at 180°C. It was found that this did not drive off all the water present and the salt had to be heated over a bunsen flame before all the water was expelled. The amount of water left after drying at 180°C was not any definite proportion of the total water present.

## Estimation of $Nb_2O_5$ and $Na_2O$.

Another weighed sample of the salt was dissolved in 100 c.c. of hot water and the niobic acid precipitated from the hot solution by the addition of 5-10 drops of 6N. $H_2SO_4$. The precipitate was filtered off, washed thoroughly with hot water, dried, ignited, and weighed as $Nb_2O_5$. The filtrate was taken to dryness in a silica basin and the $Na_2O$ estimated as anhydrous $Na_2SO_4$ in the usual fashion.

## FRACTIONAL CRYSTALLISATION I.

The first fractional crystallisation attempted was not very successful, only two fractions being obtained, both of which proved to be the same salt.

To make up the solution, 1000 c.c. of water was boiled and niobate added until no more would dissolve. The saturation took a considerable time and the salt was found to be 10-11% soluble. The solution was filtered and put in a thermostat set at 70°C. The thermostat used was a large one of about 20 gallons capacity and gave very little variation in temperature. It was heated by an electric immersion heater and operated by the usual type of electrical thermo-regulator.

The solution was left in the thermostat for a week at 70°C and for a week at 60°C, but in neither case did any salt crystallise. The thermostat was then set at 40°C and, on standing overnight, the solution crystallised. After five days crystallisation seemed complete and the salt was filtered off and washed with cold water. When drained, the crystals were placed in an empty desiccator since they were slightly efflorescent. This proved to be the best crop of crystals obtained during this work. They appeared as clusters of large coffin-shaped plates (see reference to Smith and van Haagen, page 10.), which were slowly soluble in water giving a clear solution. Analysis proved this salt to be the meta-niobate, $Na_2O.Nb_2O_5.7H_2O$.

Analysis.

| $Nb_2O_5$ and $Na_2O$. | 1. | 2. |
|---|---|---|
| Wt. of Niobate used ---------- | 0.4360 gm. | 0.4646 gm. |
| Wt. of $Nb_2O_5$ obtained -------- | 0.2566 gm. | 0.2740 gm. |
| $Nb_2O_5$ ---------- | 58.84 % | 58.98 % |
| Wt. of $Na_2SO_4$ obtained ------- | 0.1372 gm. | 0.1473 gm. |
| $Na_2O$ ----------- | 13.73 % | 13.83 % |
| $H_2O$. | | |
| Wt. of Niobate used ---------- | 0.1718 gm. | 0.2132 gm. |
| Loss in weight --------------- | 0.0468 gm. | 0.0585 gm. |
| $H_2O$ ------------ | 27.24 % | 27.44 % |

| Oxide. | Found. | Calculated. | Formula. |
|---|---|---|---|
| $Na_2O$. | 13.78 % | 13.64 % | |
| $Nb_2O_5$. | 58.91 % | 58.65 % | $Na_2O.Nb_2O_5.7H_2O$. |
| $H_2O$. | 27.34 % | 27.71 % | |
| | 100.03 % | 100.00 % | |

The mother liquor was allowed to crystallise at ordinary temperature (16°C) but the crystals obtained did not appear to be homogeneous and were dissolved again in the mother liquor. Crystallisation was attempted at various temperatures between 40°C and 20°C but no satisfactory fraction was obtained. At

18°C, however, after standing for two days, the solution crystallised to give a homogeneous fraction. The crystals were filtered off, washed with cold water, and stored with the first fraction. This crop was also self-drying. The crystals appeared as small, very thin, transparent plates which gave a clear solution with water and had a solubility similar to that of the first fraction. Analysis proved that this salt was also the meta-niobate, $Na_2O.Nb_2O_5.7H_2O$.

Analysis.

| $Nb_2O_5$ and $Na_2O$. | 1. | 2. |
|---|---|---|
| Wt. of Niobate used ---------- | 0.3992 gm. | 0.4656 gm. |
| Wt. of $Nb_2O_5$ obtained -------- | 0.2344 gm. | 0.2750 gm. |
| $Nb_2O_5$ ---------- | 58.70 % | 59.05 % |
| Wt. of $Na_2SO_4$ obtained ------- | 0.1238 gm. | 0.1440 gm. |
| $Na_2O$ ----------- | 13.53 % | 13.49 % |
| $H_2O$. | | |
| Wt. of Niobate used ---------- | 0.2130 gm. | 0.2016 gm. |
| Loss in weight --------------- | 0.0586 gm. | 0.0552 gm. |
| $H_2O$ ------------ | 27.51 % | 27.38 % |

| Oxide. | Found. | Calculated. | Formula. |
|---|---|---|---|
| $Na_2O$. | 13.51 % | 13.64 % | |
| $Nb_2O_5$. | 58.87 % | 58.65 % | $Na_2O.Nb_2O_5.7H_2O$. |
| $H_2O$. | 27.44 % | 27.71 % | |
| | 99.82 % | 100.00 % | |

## FRACTIONAL CRYSTALLISATION II.

A concentrated solution of sodium niobate was made up in the manner previously described, using the same volume of solution (1000 c.c.). This solution was left in the thermostat at 40°C, and after several days clusters of needle-shaped crystals separated. These were filtered off, washed with cold water, drained, and stored in an empty desiccator. This salt was slightly efflorescent as, indeed, were all the other salts isolated. These white opaque clusters were very soft and broke down to a powder on drying. The salt was much more easily soluble in water than the meta-niobate but did not give a clear solution and seemed to contain a small amount of free niobic acid. On analysis this was found to be an acid salt having the composition $3Na_2O.4Nb_2O_5.19H_2O$.

Analysis.

| $Nb_2O_5$ and $Na_2O$. | 1. | 2. |
|---|---|---|
| Wt. of Niobate used ---------- | 0.4000 gm. | 0.4010 gm. |
| Wt. of $Nb_2O_5$ obtained -------- | 0.2680 gm. | 0.2687 gm. |
| $Nb_2O_5$ ---------- | 66.99 % | 67.01 % |
| Wt. of $Na_2SO_4$ obtained ------- | 0.1070 gm. | 0.1082 gm. |
| $Na_2O$ ----------- | 11.68 % | 11.78 % |
| $H_2O$. | | |
| Wt. of Niobate used ---------- | 0.4034 gm. | 0.4060 gm. |
| Loss in weight --------------- | 0.0876 gm. | 0.0880 gm. |
| $H_2O$ ------------ | 21.72 % | 21.68 % |

| Oxide. | Found. | Calculated. | Formula. |
|---|---|---|---|
| $Na_2O$. | 11.73 % | 11.66 % | |
| $Nb_2O_5$. | 67.00 % | 66.89 % | $3Na_2O.4Nb_2O_5.19H_2O$. |
| $H_2O$. | 21.70 % | 21.45 % | |
| | 100.43 % | 100.00 % | |

The mother liquor was left in the thermostat at 35°C but no crystals were obtained and the thermostat was set at 30°C. After standing for a day, a salt started to crystallise. Crystallisation was gradual but after four days it seemed complete and the crystals were filtered off, washed with cold water, drained, and stored with the first fraction. This salt was similar in appearance and in solubility to the fraction taken off at 40°C and appeared as white, needle-shaped clusters which, however, were much more crystalline than the first crop and did not break down on drying. The aqueous solution of this salt, also, was slightly turbid. Analysis proved this salt to be of the same composition as the first fraction - $3Na_2O.4Nb_2O_5.19H_2O$.

Analysis.

| $Nb_2O_5$ and $Na_2O$. | 1. | 2. |
|---|---|---|
| Wt. of Niobate used ---------- | 0.3002 gm. | 0.3118 gm. |
| Wt. of $Nb_2O_5$ obtained -------- | 0.2006 gm. | 0.2084 gm. |
| $Nb_2O_5$ ---------- | 66.82 % | 66.83 % |
| Wt. of $Na_2SO_4$ obtained ------- | 0.0808 gm. | 0.0832 gm. |
| $Na_2O$ ----------- | 11.74 % | 11.64 % |

| $H_2O$. | 1. | 2. |
|---|---|---|
| Wt. of Niobate used ---------- | 0.3064 gm. | 0.3072 gm. |
| Loss in weight --------------- | 0.0670 gm. | 0.0672 gm. |
| $H_2O$ ------------ | 21.87 % | 21.88 % |

| Oxide. | Found. | Calculated. | Formula. |
|---|---|---|---|
| $Na_2O$. | 11.69 % | 11.66 % | $3Na_2O.4Nb_2O_5.19H_2O$. |
| $Nb_2O_5$. | 66.83 % | 66.89 % | |
| $H_2O$. | 21.87 % | 21.45 % | |
| | 100.39 % | 100.00 % | |

After standing in the thermostat at 25°C for two days the mother liquor crystallised, and the crystals were filtered off, washed, drained, and stored as before. This salt was very different in appearance from the first two crops. It crystallised in small nodules which seemed to have adsorbed some of the impurities present in the solution as they were yellowish-green in colour. This salt was not quite so easily soluble in water as the 3:4 salt but gave a clear solution. On analysis it was found to have the composition $6Na_2O.7Nb_2O_5.54H_2O$.

Analysis.

| $Nb_2O_5$ and $Na_2O$. | 1. | 2. |
|---|---|---|
| Wt. of Niobate used ---------- | 0.3058 gm. | 0.2996 gm. |
| Wt. of $Nb_2O_5$ obtained -------- | 0.1788 gm. | 0.1750 gm. |
| $Nb_2O_5$ ---------- | 58.48 % | 58.39 % |

| | | |
|---|---|---|
| Wt. of $Na_2SO_4$ obtained | 0.0818 gm. | 0.0802 gm. |
| $Na_2O$ | 11.68 % | 11.68 % |

$H_2O$.

| | | |
|---|---|---|
| Wt. of Niobate used | 0.2270 gm. | 0.1424 gm. |
| Loss in weight | 0.0686 gm. | 0.0432 gm. |
| $H_2O$ | 30.22 % | 30.34 % |

| Oxide. | Found. | Calculated. | Formula. |
|---|---|---|---|
| $Na_2O$. | 11.68 % | 11.59 % | $6Na_2O.7Nb_2O_5.54H_2O$. |
| $Nb_2O_5$. | 58.44 % | 58.13 % | |
| $H_2O$. | 30.28 % | 30.28 % | |
| | 100.40 % | 100.00 % | |

The mother liquor was again left in the thermostat, this time at 20°C. After standing overnight, crystals appeared but these were mixed, part consisting of yellow nodules similar to the above fraction, and part of fine, white, silky needles. These were dissolved again in the mother liquor and, after some difficulty, the yellow nodules were crystallised alone at 24°C. These were taken off and were found to be the same as the preceding fraction.

The solution was again left to crystallise at 20°C and again a mixed crop of crystals appeared. These were dissolved in the mother liquor and the solution left to crystallise at 23°C. A small crop of fine, white, silky needles separated slowly and, after four days, these were taken off as before.

These long white needles had a solubility similar to the fractions obtained at 40°C and 30°C. They were much more crystalline in appearance, however, and gave a clear aqueous solution. Analysis showed that this salt had the same composition as the first two fractions - $3Na_2O.4Nb_2O_5.19H_2O$. It will be noted that the percentage $Nb_2O_5$ is slightly lower in this case although the $Na_2O$ - $Nb_2O_5$ ratio is not affected. This points to the presence of a small amount of free niobic acid in the first two fractions as was noted by the turbidity of their solutions.

Analysis.

| $Nb_2O_5$ and $Na_2O$. | 1. | 2. |
|---|---|---|
| Wt. of Niobate used | 0.3034 gm. | 0.3220 gm. |
| Wt. of $Nb_2O_5$ obtained | 0.2014 gm. | 0.2132 gm. |
| $Nb_2O_5$ | 66.37 % | 66.21 % |
| Wt. of $Na_2SO_4$ obtained | 0.0824 gm. | 0.0874 gm. |
| $Na_2O$ | 11.85 % | 11.84 % |
| $H_2O$. - Wt. of Niobate used | 0.1020 gm. | 0.1058 gm. |
| Loss in weight | 0.0224 gm. | 0.0232 gm. |
| $H_2O$ | 21.96 % | 21.93 % |

| Oxide. | Found. | Calculated. | Formula. |
|---|---|---|---|
| $Na_2O$. | 11.84 % | 11.66 % | $3Na_2O.4Nb_2O_5.19H_2O$. |
| $Nb_2O_5$. | 66.29 % | 66.89 % | |
| $H_2O$. | 21.94 % | 21.45 % | |
| | 100.07 % | 100.00 % | |

The mother liquor was left to crystallise at 20°C. and after two days a crop of crystals appeared which were collected as before. These crystals were small, transparent, perfectly formed cubes. They gave clear solutions in water but were much more slowly soluble than the preceding salts. On analysis they proved to be the meta-niobate, $Na_2O.Nb_2O_5.7H_2O$.

Analysis.

| $Nb_2O_5$ and $Na_2O$. | 1. | 2. |
|---|---|---|
| Wt. of Niobate used ---------- | 0.3000 gm. | 0.3634 gm. |
| Wt. of $Nb_2O_5$ obtained -------- | 0.1762 gm. | 0.2140 gm. |
| $Nb_2O_5$ ---------- | 58.73 % | 58.88 % |
| Wt. of $Na_2SO_4$ obtained ------- | 0.0944 gm. | 0.1144 gm. |
| $Na_2O$ ----------- | 13.78 % | 13.74 % |
| $H_2O$. | | |
| Wt. of Niobate used ---------- | 0.2022 gm. | 0.2030 gm. |
| Loss in weight --------------- | 0.0568 gm. | 0.0570 gm. |
| $H_2O$ ------------ | 28.08 % | 28.08 % |

| Oxide. | Found. | Calculated. | Formula. |
|---|---|---|---|
| $Na_2O$. | 13.76 % | 13.64 % | |
| $Nb_2O_5$. | 58.80 % | 58.65 % | $Na_2O.Nb_2O_5.7H_2O$. |
| $H_2O$. | 28.08 % | 27.71 % | |
| | 100.64 % | 100.00 % | |

The mother liquor was again left to crystallise, this time at room temperature, but no further salts were obtained. The solution was therefore concentrated - not to any great extent - and left to crystallise at 20°C. After three days a crop of small stout needles was obtained which were taken off as previously described. The crystals were yellowish in colour and were more readily soluble than the meta-niobate, giving clear solutions. This proved to be the 6:7 salt - $6Na_2O.7Nb_2O_5.54H_2O$.

Analysis.

| $Nb_2O_5$ and $Na_2O$. | 1. | 2. |
|---|---|---|
| Wt. of Niobate used ---------- | 0.2992 gm. | 0.4150 gm. |
| Wt. of $Nb_2O_5$ obtained -------- | 0.1746 gm. | 0.2424 gm. |
| $Nb_2O_5$ ---------- | 58.34 % | 58.41 % |
| Wt. of $Na_2SO_4$ obtained ------- | 0.0800 gm. | 0.1096 gm. |
| $Na_2O$ ----------- | 11.67 % | 11.53 % |

$H_2O$.

|  |  |  |
|---|---|---|
| Wt. of Niobate used ---------- | 0.3036 gm. | 6.2074 gm. |
| Loss in weight --------------- | 0.0920 gm. | 0.0628 gm. |
| $H_2O$ ------------ | 30.31 % | 30.28 % |

| Oxide. | Found. | Calculated. | Formula. |
|---|---|---|---|
| $Na_2O$. | 11.60 % | 11.59 % | $6Na_2O.7Nb_2O_5.54H_2O$. |
| $Nb_2O_5$. | 58.37 % | 58.13 % |  |
| $H_2O$. | 30.29 % | 30.28 % |  |
|  | 100.26 % | 100.00 % |  |

The mother liquor was left at 18°C. A small crop of white needles appeared but on standing some thick cubic plates also crystallised. The crystals were dissolved again in the mother liquor and again left at 18°C. This time the white needles were obtained alone and were taken off as before. In appearance and solubility this salt was similar to the specimens of the 3:4 salt already obtained and analysis proved it to be the same salt - $3Na_2O.4Nb_2O_5.19H_2O$.

Analysis.

| $Nb_2O_5$ and $Na_2O$. | 1. | 2. |
|---|---|---|
| Wt. of Niobate used | 0.2978 gm. | 0.3024 gm. |
| Wt. of $Nb_2O_5$ obtained | 0.1986 gm. | 0.2020 gm. |
| $Nb_2O_5$ | 66.68 % | 66.80 % |
| Wt. of $Na_2SO_4$ obtained | 0.0800 gm. | 0.0814 gm. |
| $Na_2O$ | 11.72 % | 11.75 % |
| **$H_2O$.** | | |
| Wt. of Niobate used | 0.1926 gm. | 0.2106 gm. |
| Loss in weight | 0.0416 gm. | 0.0456 gm. |
| $H_2O$ | 21.60 % | 21.66 % |

| Oxide. | Found. | Calculated. | Formula. |
|---|---|---|---|
| $Na_2O$. | 11.74 % | 11.66 % | |
| $Nb_2O_5$. | 66.74 % | 66.89 % | $3Na_2O.4Nb_2O_5.19H_2O$. |
| $H_2O$. | 21.63 % | 21.45 % | |
| | 100.11 % | 100.00 % | |

The mother liquor was left to crystallise at 16°C. Small cubic crystals appeared but these crystallised very slowly and the solution had to be left for a month before crystallisation seemed complete. The crystals were few in number but were fairly large cubes. On analysis, the salt proved to be the meta-niobate, $Na_2O.Nb_2O_5.7H_2O$.

Analysis.

| $Nb_2O_5$ and $Na_2O$. | 1. | 2. |
|---|---|---|
| Wt. of Niobate used ---------- | 0.5638 gm. | 0.5112 gm. |
| Wt. of $Nb_2O_5$ obtained -------- | 0.3300 gm. | 0.2995 gm. |
| $Nb_2O_5$ ---------- | 58.53 % | 58.59 % |
| Wt. of $Na_2SO_4$ obtained ------- | 0.1764 gm. | 0.1598 gm. |
| $Na_2O$ ----------- | 13.66 % | 13.65 % |
| $H_2O$. | | |
| Wt. of Niobate used ---------- | 0.3004 gm. | 0.2792 gm. |
| Loss in weight --------------- | 0.0844 gm. | 0.0781 gm. |
| $H_2O$ ------------ | 28.09 % | 27.97 % |

| Oxide. | Found. | Calculated. | Formula. |
|---|---|---|---|
| $Na_2O$. | 13.65 % | 13.64 % | |
| $Nb_2O_5$. | 58.56 % | 58.65 % | $Na_2O.Nb_2O_5.7H_2O$. |
| $H_2O$. | 28.03 % | 27.71 % | |
| | 100.24 % | 100.00 % | |

The mother liquor was left in the thermostat with the heater switched off, the mean temperature being 12°C. A very small crop of white needles was obtained - not even enough for an analysis. These were taken off and the mother liquor put in a freezing mixture for several hours. The white finely-divided precipitate obtained was taken off as before. This salt was more readily soluble than the meta-niobate and gave a clear solution. It proved to have the composition - $5Na_2O.6Nb_2O_5.35H_2O$.

Analysis.

| $Nb_2O_5$ and $Na_2O$. | 1. | 2. |
|---|---|---|
| Wt. of Niobate used ---------- | 0.6162 gm. | 0.4462 gm. |
| Wt. of $Nb_2O_5$ obtained -------- | 0.3884 gm. | 0.2812 gm. |
| $Nb_2O_5$ ---------- | 63.04 % | 63.02 % |
| Wt. of $Na_2SO_4$ obtained ------- | 0.1738 gm. | 0.1258 gm. |
| $Na_2O$ ----------- | 12.30 % | 12.31 % |

$H_2O$.

| | 1. | 2. |
|---|---|---|
| Wt. of Niobate used ---------- | 0.2012 gm. | 0.2005 gm. |
| Loss in weight --------------- | 0.0496 gm. | 0.0494 gm. |
| $H_2O$ ------------ | 24.65 % | 24.63 % |

| Oxide. | Found. | Calculated. | Formula. |
|---|---|---|---|
| $Na_2O$. | 12.30 % | 12.21 % | |
| $Nb_2O_5$. | 63.03 % | 62.99 % | $5Na_2O.6Nb_2O_5.35H_2O$. |
| $H_2O$. | 24.64 % | 24.80 % | |
| | 99.97 % | 100.00 % | |

To the mother liquor an excess of NaOH was added - 50 c.c. of a 20% solution. Some salt was precipitated but this was dissolved again by heating the solution on the water-bath. The solution was then evaporated down and allowed to stand for several days. Small white needle-shaped crystals appeared which were collected as before. They were very slowly soluble in water - the least soluble of the salts prepared - and gave a clear solution. Analysis proved this salt to be the 7:6 niobate - $7Na_2O.6Nb_2O_5.32H_2O$.

Analysis.

| $Nb_2O_5$ and $Na_2O$. | 1. | 2. |
|---|---|---|
| Wt. of Niobate used ---------- | 0.2950 gm. | 0.2612 gm. |
| Wt. of $Nb_2O_5$ obtained -------- | 0.1585 gm. | 0.1600 gm. |
| $Nb_2O_5$ ---------- | 61.19 % | 61.27 % |
| Wt. of $Na_2SO_4$ obtained ------- | 0.0998 gm. | 0.1002 gm. |
| $Na_2O$ ----------- | 16.74 % | 16.75 % |
| $H_2O$. | | |
| Wt. of Niobate used ---------- | 0.2014 gm. | 0.2008 gm. |
| Loss in weight --------------- | 0.0444 gm. | 0.0442 gm. |
| $H_2O$ ------------ | 22.05 % | 22.07 % |

| Oxide. | Found. | Calculated. | Formula. |
|---|---|---|---|
| $Na_2O$. | 16.74 % | 16.63 % | |
| $Nb_2O_5$. | 61.23 % | 61.30 % | $7Na_2O.6Nb_2O_5.32H_2O$. |
| $H_2O$. | 22.06 % | 22.07 % | |
| | 100.03 % | 100.00 % | |

Attempts to obtain further salts from the mother liquor were unsuccessful.

Another sample of the 7:6 salt was prepared by dissolving crude sodium niobate in water and adding excess NaOH. The solution was evaporated down and allowed to crystallise. The crystals obtained had the composition $7Na_2O.6Nb_2O_5.30H_2O$.

Analysis.

| $Nb_2O_5$ and $Na_2O$. | 1. | 2. |
|---|---|---|
| Wt. of Niobate used ---------- | 0.4214 gm. | 0.3974 gm. |
| Wt. of $Nb_2O_5$ obtained -------- | 0.2606 gm. | 0.2474 gm. |
| $Nb_2O_5$ ---------- | 61.84 % | 62.26 % |
| Wt. of $Na_2SO_4$ obtained ------- | 0.1624 gm. | 0.1550 gm. |
| $Na_2O$ ----------- | 16.82 % | 17.02 % |

$H_2O$.

| | 1. | 2. |
|---|---|---|
| Wt. of Niobate used ---------- | 0.3002 gm. | 0.2534 gm. |
| Loss in weight --------------- | 0.0636 gm. | 0.0536 gm. |
| $H_2O$ ------------ | 21.18 % | 21.15 % |

| Oxide. | Found. | Calculated. | Formula. |
|---|---|---|---|
| $Na_2O$. | 16.92 % | 16.87 % | |
| $Nb_2O_5$. | 62.05 % | 62.15 % | $7Na_2O.6Nb_2O_5.30H_2O$. |
| $H_2O$. | 21.17 % | 20.98 % | |
| | 100.14 % | 100.00 % | |

## GUANIDINE NIOBATES.

Since guanidine, as a rule, gives more fully substituted products in this type of compound than do the alkali metals, it was thought that the preparation of guanidine niobates might be of some interest. No record could be found in the literature of any previous preparation of such compounds.

10 gm. of sodium niobate was dissolved in 200 c.c. of water and a slight excess of guanidine hydrochloride solution, just alkaline to methyl orange, was added. The white precipitate obtained was filtered off, drained, and washed with cold water. The salt was dissolved in hot water and was very sparingly soluble. The solution, which, when filtered, was clear, was allowed to stand for three days. Crystals appeared in clusters of small pearly plates and these were filtered off, drained, and washed with cold water. Analysis proved the salt to be of composition - $6(CN_3H_6)_2O.7Nb_2O_5.16H_2O$.

The mother liquor was evaporated down to about half-volume and left to stand for some time. A small crop of crystals separated, very similar in appearance to the first fraction, and these were taken off as before. The analysis for this salt corresponded approximately to the formula $4(CN_3H_6)_2O.5Nb_2O_5.12H_2O$.

On further concentration the mother liquor gave a very small crop of crystals, not even enough for an analysis. These were similar in appearance to the first two fractions.

### Analysis.

Ignition of a known amount of the guanidine niobate removed the water and decomposed the guanidine leaving $Nb_2O_5$, which was weighed. The guanidine was estimated by micro-combustion for nitrogen and the water was obtained by difference.

## Results.

### Fraction I.

| $Nb_2O_5$. | 1. | 2. |
|---|---|---|
| Wt. of Niobate used ---------- | 0.2532 gm. | 0.3020 gm. |
| Wt. of $Nb_2O_5$ obtained -------- | 0.1594 gm. | 0.1902 gm. |
| $Nb_2O_5$ ---------- | 62.96 % | 62.98 % |

$(CN_3H_6)_2O$.

Nitrogen by micro-combustion ---------- 16.90 %

$(CN_3H_6)_2O$ --------------- 27.40 %

## Fraction I. (contd.).

| Oxide. | Found. | Calculated. | Formula. |
|---|---|---|---|
| $(CN_3H_6)_2O$. | 27.40 % | 27.48 % | |
| $Nb_2O_5$. | 62.97 % | 62.83 % | $6(CN_3H_6)_2O.7Nb_2O_5.16H_2O$. |
| $H_2O$. | 9.63 % | 9.69 % | |
| | 100.00 % | 100.00 % | |

## Fraction II.

### $Nb_2O_5$.

| | 1. | 2. |
|---|---|---|
| Wt. of Niobate used ---------- | 0.1996 gm. | 0.1774 gm. |
| Wt. of $Nb_2O_5$ obtained -------- | 0.1280 gm. | 0.1142 gm. |
| $Nb_2O_5$ ---------- | 64.12 % | 64.37 % |

### $(CN_3H_6)_2O$.

Nitrogen by micro-combustion ---------- 15.80 %

$(CN_3H_6)_2O$ --------------- 25.60 %

| Oxide. | Found. | Calculated. | Formula. |
|---|---|---|---|
| $(CN_3H_6)_2O$. | 25.60 % | 25.98 % | |
| $Nb_2O_5$. | 64.24 % | 63.71 % | $4(CN_3H_6)_2O.5Nb_2O_5.12H_2O$. |
| $H_2O$. | 10.16 % | 10.31 % | |
| | 100.00 % | 100.00 % | |

Two attempts were made to discover something of the composition of these guanidine salts but these were unsuccessful.

## 1. Application of the Ostwald Basicity Rule (see page 105).

An attempt to apply this rule to guanidine niobate failed because of the small solubility of the salt. It was found that the salt would not dissolve at 32 litres dilution and, although it did so at 64 litres dilution on heating, it crystallised again on cooling. Since it has been observed that, as a general rule, the differences in equivalent conductivity at the various dilutions vary considerably and without any regularity, it was considered that to dissolve the salt at 128 litres dilution and extrapolate for 64 and 32 litres dilution would not give dependable results. The attempt was therefore abandoned.

## 2. Progressive Dehydration.

An attempt was made to distinguish between water of constitution and water of crystallisation by drying the salt to constant weight in an air oven at 110°C. The attempt was not successful, however, since the results obtained indicated decomposition of the guanidine.

* * *

## DISCUSSION.

The results of the second fractional crystallisation may be tabulated as follows :-

40°C - $3Na_2O.4Nb_2O_5.19H_2O$.

↓

30°C - $3Na_2O.4Nb_2O_5.19H_2O$.

↓

25°C - $6Na_2O.7Nb_2O_5.54H_2O$.

↓

23°C - $3Na_2O.4Nb_2O_5.19H_2O$.

↓

20°C - $Na_2O.Nb_2O_5.7H_2O$.

Concentration.

↓

20°C - $6Na_2O.7Nb_2O_5.54H_2O$.

↓

18°C - $3Na_2O.4Nb_2O_5.19H_2O$.

↓

16°C - $Na_2O.Nb_2O_5.7H_2O$.

Freezing.

↓

$5Na_2O.6Nb_2O_5.35H_2O$.

Addition of NaOH.

↓

$7Na_2O.6Nb_2O_5.32H_2O$.

It would appear that the concentration of the solution after crystallisation at 20°C has upset the balance of the solution and that the crystallisation has been thrown back by two stages. This seems to have happened also when the solution was frozen. At this stage it was expected that an alkaline salt, probably the 7:6 niobate, would crystallise but an acid salt was actually obtained.

It will be seen that the series of salts isolated show a gradual increase in the proportion of alkali oxide present, ranging from the 3:4 salt to the 7:6 salt. Although the most common and most stable potassium niobate is the 4:3 salt, it does not seem possible to prepare the sodium analogue. Attempts were made to do so by adding excess caustic soda to a solution of sodium niobate and crystallising the resulting solution but these were unsuccessful and in each case the 7:6 salt was obtained.

The solubility in water of the sodium niobates prepared shows a gradual decrease proceeding from the more acid to the more alkaline salts and the 7:6 salt is very sparingly soluble. It is quite probable that the failure of many investigators to prepare a 4:3 sodium niobate is due to the low solubility of the 7:6 salt which will crystallise from solution before the formation of the 4:3 salt has been accomplished.

The solutions in water of these salts were, in most cases, clear and apparently free from any colloidal niobic acid. In one or two instances, however, the solutions were turbid, particularly in the case of the 3:4 salt crystallised at 40°C.

Of the various salts obtained, little need be said concerning the 1:1 and the 7:6 sodium niobate, which have been described by numerous investigators and have long been regarded as definite chemical identities.

The 5:6 salt, obtained by freezing the solution of sodium niobate, might possibly have been regarded as a mixture of the meta-niobate with niobic acid since it was really forced out of solution and appeared as a white, finely-divided powder. Its solution in water, however, was clear and gave no evidence of the presence of any free niobic acid. If not homogeneous, therefore, it must consist of a mixture of more acid and more alkaline salts which dissolve freely in water. This is not very probable since the analysis approximates very closely to the formula which has been noted.

The appearance of the 3:4 and the 6:7 sodium niobates suggests that these are definite salts. The 3:4 salt made its appearance as long, white, slender needles and was definitely crystalline in two of the three samples obtained. The 6:7 salt was crystalline in both samples isolated and appeared as short, stout needles or as small nodules. The fact that these salts were obtained more than once during the fractional crystallisation seems to point to their being individual substances.

The parallelism shown in the three fractions at 25°C, 23°C, and 20°C before the concentration of the solution and the three fractions at 20°C, 18°C, and 16°C after concentration is remarkable and suggests that the results obtained from this fractional crystallisation might be reproducible. Against this, however, there is the fact that the first fractional crystallisation attempted, which was carried out under approximately the same conditions as the second, gave very different results and yielded only two fractions, both of which proved to be the meta-niobate.

No record has been found in the literature of any niobate having the basic oxide - acid oxide ratio as 5:6 or as 6:7, but two instances have been noted where the ratio was 3:4.

Hermann, (loc. cit.), describes a 3:4 sodium niobate* which he prepared by adding NaOH to a hot solution of $K_2NbOF_5$, (see page 6).

Also, a rubidium niobate, described as fine silky needles and having the composition $3Rb_2O.4Nb_2O_5.9\frac{1}{2}H_2O$., has been reported by Balke and Smith, (loc. cit.).

*Note - Hermann describes this salt as a 5:4 sodium niobate with 21 molecules of water, but this formula was calculated on the assumption that the salt was a derivative of "unterniobsäure" - $Nb_2O_3$ or $Nb_2O_2$. Using the percentages of the various oxides found by Hermann in his analysis, the composition was recalculated for $Nb_2O_5$ and was found to be $3Na_2O.4Nb_2O_5.28H_2O$. Bedford, (loc. cit.), notes the composition of this salt as $3Na_2O.4Nb_2O_5.21H_2O$, while Balke and Smith, (loc. cit.), mention it as having the formula $5Na_2O.4Nb_2O_5.21H_2O$.

## Guanidine Salts.

The guanidine niobates obtained were acid salts and not, as might be expected, salts containing a large proportion of basic oxide. It is suggested that this may be due to solubility differences. The sodium niobates show solubilities which decrease with increasing proportions of basic oxide. If the guanidine salts, which are much less soluble than the sodium salts, show a similar gradation in solubility, then it is possible that the least soluble guanidine niobate may be an acid salt, such as the 6:7 salt isolated here, and that it may be impossible to prepare any salts with a higher proportion of alkali because of this small solubility. This is in accordance with the view expressed concerning the formation of a 4:3 sodium niobate, (see page 43).

The general opinion arising from this work was that the salts prepared and described did not exist in solution as such and that each salt did not give rise to a complex anion corresponding to its particular composition. In other words, it was considered that the behaviour of these salts in solution was the same in each case and that the various salts obtained were merely forced out of solution by abnormal circumstances, the composition of the salt depending entirely on the conditions under which it crystallised. It seemed probable that the isolation of any particular salt depended mainly on the solubility factor.

It seems impossible to suggest any common basis for the formulation of the various sodium niobates. With sodium tungstates, for example, the case is much more simple, since the basic oxide - acid oxide ratio is never greater than one. With sodium niobates, however, a common basis for, say, the 6:7 and 7:6 salts would demand the consideration of a 42-basic acid, which does not seem at all probable.

It was decided to investigate the behaviour in solution of the various salts prepared, and to carry out a series of conductometric and potentiometric titrations on their solutions, which might either confirm or disprove the existence of different complex niobate anions.

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# PART I.

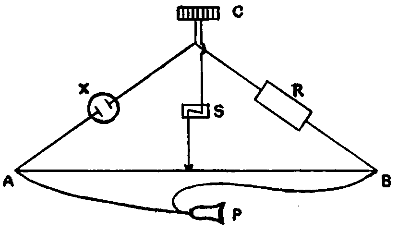
## Section 2.

## CONDUCTOMETRIC AND POTENTIOMETRIC TITRATIONS OF VARIOUS SODIUM NIOBATE SOLUTIONS WITH HYDROCHLORIC ACID.

## CONDUCTOMETRIC TITRATIONS.

Conductometric titrations were carried out on solutions of the various sodium niobates titrated with dilute HCl.

The usual apparatus for the determination of the conductivity of solutions was employed, wired as in diagram :-



AB - Wire Bridge.
S - Switch.
P - Phones.
C - Ruhmkorff Coil.
R - Resistance Box.
X - Cell with Unknown.

The cell used was of the pipette type and had a capacity of about 25 c.c. The electrodes were pieces of platinum foil about 1 cm. square, mounted on platinum wire, and these were sealed into the sides of the pipette bulb. They were coated with platinum black by filling the cell with a solution of platinum chloride and passing a current of 4 volts - $\frac{1}{4}$ amp. for ten minutes in each direction.

The constant of the cell was found in the usual manner, using $\frac{N}{50}$ KCl solution and taking readings of the conductivity at various resistances.

The niobate solutions were made up in each case by dissolving .4 gm. of the salt in 100 c.c. of cold water. To give a start to the conductivity curve, 1 c.c. of free alkali (.2228 N. NaOH) was added to each solution.

The solution to be titrated was placed in a beaker into which the cell dipped and was mechanically stirred throughout the titration. The HCl, which was .2301 N., was added to the solution very slowly, drop by drop, from a micro-burette and the conductivity was noted for each .4 c.c. of acid added. Each reading was taken as follows :-

After addition of .4 c.c. of acid, the solution was stirred for a minute. The cell was then flushed out twice and a reading taken. The solution was stirred for five minutes, the cell flushed again, and another reading taken. This made certain that the solution had reached equilibrium before a further quantity of acid was added.

After each titration the niobic acid adhering to the cell and electrodes was removed by washing with oxalic acid solution. When not in use, the cell was kept filled with water.

Satisfactory null-points were obtained as long as the electrodes had a reasonable coating of platinum black. This had to be renewed once or twice and a new value for the cell constant determined.

---

## POTENTIOMETRIC TITRATIONS.

Potentiometric titrations, similar to the conductometric titrations, were carried out on solutions of the various niobates. Two series of determinations were made.

1. Using a Hydrogen Electrode - Saturated Calomel Electrode Cell.
2. Using a Quinhydrone - Quinhydrone Cell.

### 1. Hydrogen Electrode - Saturated Calomel Electrode Cell.

Pt., $H_2$(1 atmos.) | Unknown Solution. | Saturated KCl, HgCl | Hg.

### The Hydrogen Electrode.

The hydrogen electrode used was of the Hildebrand type, the electrode itself being a strip of platinum foil which was cleaned with nitric acid and coated with platinum black by electrolysis of a 10% solution of platinum chloride, using the electrode as cathode. The anode was another piece of platinum foil of the same size. The two electrodes were placed parallel to each other and platinum black deposited by passing a current of 4 volts - ¼ amp. for fifteen minutes. The other face of the cathode was turned opposite the anode and given a similar treatment. After several trials, a uniform and firm coating of platinum black was obtained.

When not in use, the electrode was kept under water. If left to stand for more than a few days, it had to be saturated with hydrogen before using. This was done by electrolysing a dilute solution of HCl using the electrode as cathode.

## The Saturated Calomel Electrode.

The calomel electrode used was of the Rideal pattern. The end of the connecting tube was drawn out to a very fine bore, which reduced to a minimum the diffusion of any solution into the electrode. A reservoir on top of the connecting tube held saturated KCl solution which flushed the electrode on turning a stop-cock.

## Preparation of Calomel.

The mercury used in the preparation of the calomel for the calomel electrode was thoroughly cleaned and twice distilled before using. The calomel was prepared in two ways, chemically and electrolytically.

### Chemical preparation of Calomel.

Some of the purified mercury was taken up in nitric acid, there being always excess mercury to ensure mercurous nitrate only. HCl was added and the precipitated calomel allowed to settle. It was washed by decantation, filtered off, and drained thoroughly.

## Electrolytic preparation of Calomel.

(See Clark - "Determination of Hydrogen Ion Concentration" - page 307). An HCl solution was electrolysed using a platinum cathode and an anode of the purified mercury. Current was passed while the mercury was kept constantly stirred. The final product obtained was calomel containing a fair amount of finely-divided mercury. This was washed by decantation as before, using conductivity water, filtered off, and drained thoroughly.

Both samples of calomel were stored in stoppered flasks under a saturated solution of potassium chloride.

## Preparation of KCl Solution.

A.R. KCl was recrystallised from water, filtered, and drained thoroughly. It was shaken up with conductivity water until no more would dissolve. Chemically prepared calomel was added to the solution, which was then shaken for a day on a mechanical shaker. This solution was always kept in contact with solid KCl to ensure its being fully saturated.

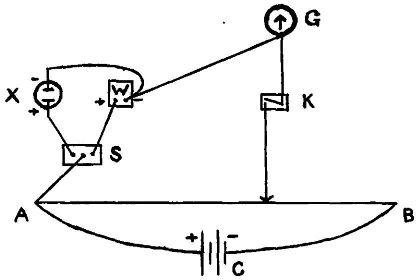
The platinum wire of the calomel electrode was amalgamated by electrolysing a solution of mercurous nitrate in the electrode, using the platinum wire as cathode. Electrolysis was continued until a large bead of mercury had formed round the cathode. Equal parts of chemically and electrolytically prepared calomel were mixed together in a paste and about half an inch of this mixture was put in the electrode, which was then filled with saturated KCl solution.

The calomel electrode was rather troublesome since, on standing, the saturated KCl solution crystallised, especially in the capillary end of the side-arm, and it was only with difficulty that this tube could be cleared again. There seemed to be no way of preventing this and, from this point of view, the use of normal KCl seems desirable. The saturated calomel electrode has, however, the advantage that it does not need careful protection from the saturated KCl solution usually employed as a liquid junction, as do the normal and tenth-normal half-cells. It has the further advantage of being more sensitive because of the high conductivity of the saturated KCl solution.

## Hydrogen.

Cylinders of electrolytic hydrogen, supplied by the British Oxygen Company, were used. The hydrogen proved satisfactory throughout, except on one occasion where it was found to be mixed with oxygen.

The circuit for the measurement of the E.M.F. was wired as shown in diagram :-



X - Hydrogen Electrode Cell.

W - Weston Normal Cell.

G - Mirror Galvanometer.

C - Two-volt Accumulator.

AB - Wire Bridge. S - Two-way Switch. K - Tapping Key.

Since the accumulator is apt to vary during a titration, it had to be balanced against the Weston normal cell after each reading. This was most conveniently done by introducing a two-way switch which brought the unknown cell or the Weston cell into circuit as desired. A switch was also introduced for the accumulator, in order to save current, but this led to erratic results and had to be dispensed with.

Before using, the apparatus was checked against solutions of known hydrogen ion concentration made up from acid potassium phthalate and from Prideaux and Ward's universal buffer mixture. The $p_H$ values obtained for these solutions were found to be low, the error being a constant one. The calomel electrode was checked against a silver electrode made up from a silver wire in $\frac{N}{10}$ $AgNO_3$ solution. The E.M.F. of the calomel electrode - silver electrode cell was found experimentally and that of the silver half-cell by calculation. Subtraction gave the E.M.F. of the calomel half-cell, which proved to be lower than the correct value. This was allowed for when calculating the $p_H$ values and fairly accurate and reproducible results were obtained for the buffer solutions.

An additional check was made by running a titration of sodium tungstate with HCl. The results obtained were very similar to those of Britton and German, (J.C.S., 1930, 1, 1251).

It was now felt that the apparatus was working satisfactorily and titrations were carried out on solutions of the various niobates with HCl. For each titration, .4 gm. of the salt was dissolved in 100 c.c. water and 1 c.c. of .2228 N. NaOH added. The solution was saturated with hydrogen until a constant reading was obtained - this took about 20-30 minutes - and titrated with .2310 N. HCl, which was added from a micro-burette. A reading was taken for each .4 c.c. of acid added. The acid was added very slowly, drop by drop, and, during its addition and for several minutes afterwards, the solution was mechanically stirred. The stirrer was switched off and the solution left for five minutes to come to equilibrium. The calomel electrode was flushed and a reading taken. The Weston cell was then balanced against the accumulator and then a final reading of the unknown was taken to ensure its being constant before further addition of acid.

After each titration the hydrogen electrode was steeped for some time in oxalic acid solution which removed the adherent niobic acid, after which it was thoroughly washed with water.

## 2. Quinhydrone - Quinhydrone Cell.

It was considered that the precipitated niobic acid which adhered to the hydrogen electrode was bound to have some effect on the results obtained, the platinum foil being coated with the gelatinous precipitate before the end of the titration. It was decided, therefore, to carry out a series of titrations using a quinhydrone cell and thus avoid this interference.

The quinhydrone cell was made up as follows :-

| | | | | |
|---|---|---|---|---|
| Au | Unknown Solution<br>sat. with quinhydrone | Sat. KCl | .09N. HCl - .01N. KCl<br>sat. with quinhydrone | Pt. |

The quinhydrone half-cell used was a calomel electrode vessel of the ordinary type, having the usual platinum wire connection. The vessel was filled with a solution .09 N. in HCl and .01 N. in KCl, saturated with quinhydrone, in which there was always a quantity of solid quinhydrone.

The quinhydrone half-cell was connected to the test solution by means of a salt bridge, saturated KCl solution being used as a liquid junction.

The other electrode was a gold wire which dipped into the test solution. Before using, the wire was cleaned with nitric acid, washed, and dried in an alcohol flame.

The same circuit was used as is shown on page 54. The apparatus was tested out as for the hydrogen electrode, using buffer solutions, and gave satisfactory results. A titration of sodium tungstate with HCl gave results practically identical with those obtained using the hydrogen electrode except, of course, in the regions where the $p_H$ value was greater than eight.

Solutions of the various niobates were made up as previously, containing .4 gm. of the salt plus 1 c.c. .2228 N. NaOH in 100 c.c. water. The solution to be titrated was saturated with quinhydrone; this took about twenty minutes with constant stirring. The titrations were carried out exactly as described for the hydrogen electrode.

## RESULTS.

The results obtained from these conductometric and potentiometric titrations are drawn up in tabular form, each set of results being accompanied by a graph.

The conductivities were calculated from the formula -

$$K = \frac{N \times L}{(1000-L) \times R.} \quad \text{where} \quad \begin{cases} N = \text{Cell Constant.} \\ L = \text{Bridge Reading.} \\ R = \text{Resistance.} \end{cases}$$

The $p_H$ values for the hydrogen electrode were calculated from the formula -

$$p_H = \frac{E - \text{Value for Sat. Calomel Electrode.}}{RT/F.}$$

$$\text{where } E = \frac{\text{Bridge Reading (Unknown).}}{\text{Bridge Reading (Weston).}} \times \text{E.M.F. of Weston Cell.}$$

and for the quinhydrone cell from the formula -

$$p_H = 2.03 + \frac{E}{RT/F.}$$

The values for the saturated calomel electrode and for the factor RT/F were taken from the "Chemists' Year Book".

In the following tables of results, the first column gives the amounts of HCl added. Column 2 gives the observed specific conductivities from which has been subtracted the conductivity of the water used. These values are shown on the graphs as the line marked 'conductometric titration'.

In column 3 are noted the specific conductivities due to the sodium chloride formed during the titration. These were calculated by drawing a graph of specific conductivity against concentration for NaCl from data taken from Landolt-Börnstein's "Tabellen". From the amounts of HCl added, the concentration of the NaCl in the solution at each titre could be calculated and, from the graph, the specific conductivity obtained. These conductivities are shown on the graphs by the line marked $K_{NaCl}$.

By subtracting the contribution made by the NaCl to the observed specific conductivities, the conductivities due to sodium niobate plus NaOH were obtained. These are noted in column 4 of the tables and as the line marked $K_{Na\ Niobate\ +\ NaOH}$ on the graphs.

Beyond the equivalence point the specific conductivity of the NaCl remains constant and the increase in conductivity should be due to the addition of free HCl. This is noted at the foot of columns 3 and 4.

The conductivity which would be produced if 1, 2, and 3 c.c. of .2310 N. HCl were diluted to the same volume as is contained in the solutions at the equivalence point, e.g. 110.3 c.c. in the case of the 7:6 salt, was found by calculating the normality of HCl in each case and hence the specific conductivity by means of data taken from "Tabellen". These values are noted in the small table at the bottom right-hand corner and are shown on the graphs by the line marked 'HCl Slope', which is slightly displaced to the right for the sake of clearness.

Columns 5 and 6 in the tables give the $p_H$ values obtained by means of the hydrogen electrode and the quinhydrone cell respectively. These are shown in the upper parts of the graphs, the hydrogen electrode values by a continuous line and the quinhydrone values by a broken line.

From the $p_H$ values and data found in Clark, (loc. cit. - page 673), the normality of free NaOH in the initial stages was calculated. This in turn gave the specific conductivity of free NaOH which is noted in column 7 of the tables.

By subtracting the specific conductivity of NaOH from the conductivity of sodium niobate plus NaOH, the specific conductivity of sodium niobate alone was obtained. This is given in column 8 and is shown on the graphs by the line marked $K_{\text{Na Niobate}}$.

The results for the two $Na_2WO_4$ - HCl potentiometric titrations carried out as checks for the hydrogen electrode and quinhydrone cells are given in Table 6 and Figure 6. They have been included for the sake of comparison.

## TABLE 1.

### $3Na_2O.4Nb_2O_5.19H_2O$.

.4 gm. salt in 100 c.c. water. 1 c.c. .2228 N. NaOH added.

Titrated with .2310 N. HCl.

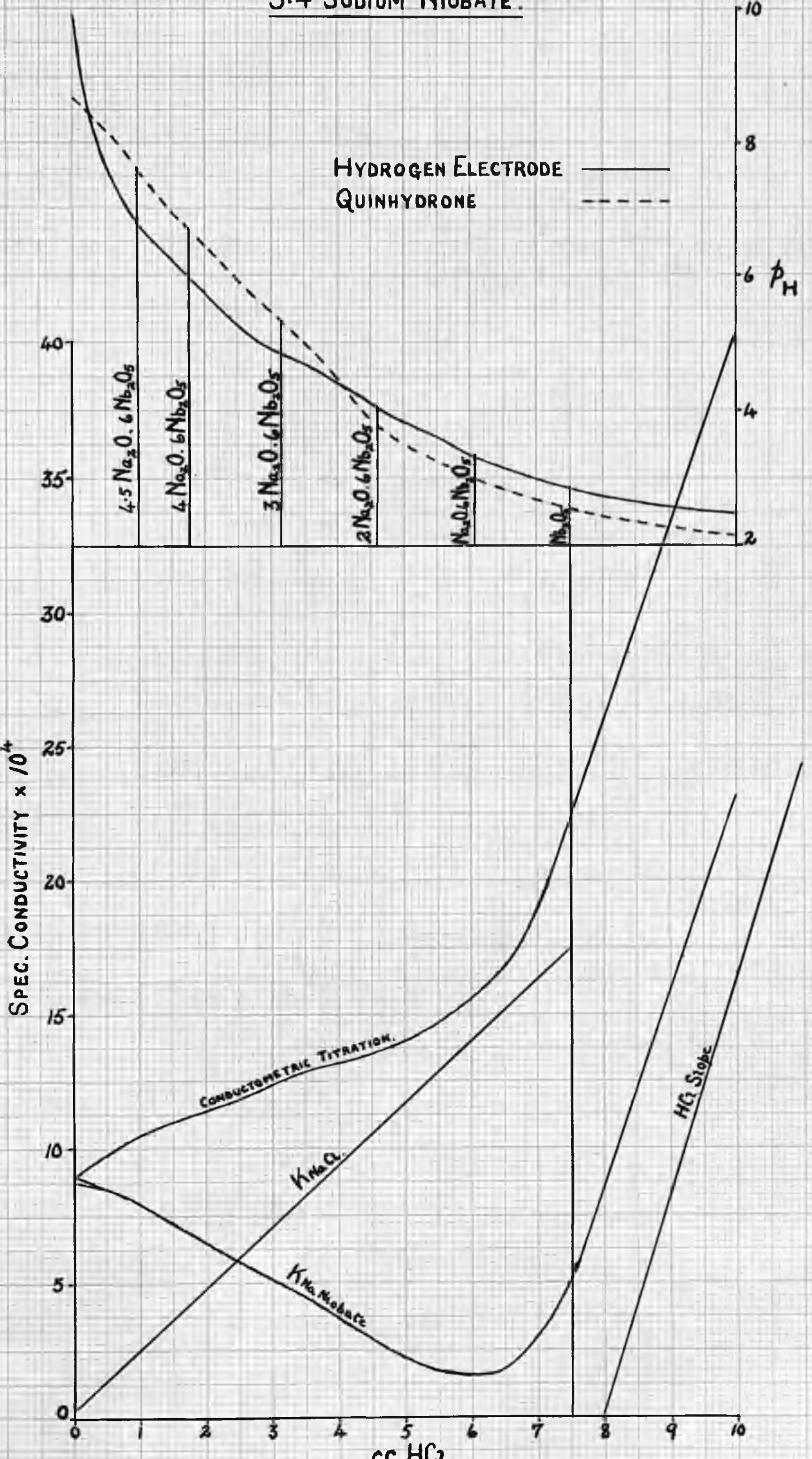
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| C. C. Acid | Total Conductivity x $10^4$ | Conductivity of NaCl x $10^4$ | Conductivity of NaOH + Na Niobate x $10^4$ | $p_H$ [Hydrogen Electrode] | $p_H$ [Quin-hydrone] | Conductivity of NaOH x $10^4$. | Conductivity of Na Niobate x $10^4$. |
| 0.0 | 8.95 | 0.00 | 8.95 | 9.90 | 8.70 | 0.16 | 8.79 |
| 0.4 | 9.65 | 1.08 | 8.57 | 8.02 | 8.30 | 0.00 | 8.57 |
| 0.8 | 10.24 | 1.98 | 8.26 | 7.07 | 7.86 | 0.00 | 8.26 |
| 1.2 | 10.67 | 3.00 | 7.67 | 6.47 | 7.29 | | 7.67 |
| 1.6 | 11.02 | 3.94 | 7.08 | 6.09 | 6.81 | | 7.08 |
| 2.0 | 11.34 | 4.89 | 6.45 | 5.76 | 6.43 | | 6.45 |
| 2.4 | 11.72 | 5.83 | 5.89 | 5.38 | 6.05 | | 5.89 |
| 2.8 | 12.11 | 6.76 | 5.35 | 5.02 | 5.58 | | 5.35 |
| 3.2 | 12.53 | 7.68 | 4.85 | 4.81 | 5.25 | | 4.85 |
| 3.6 | 12.95 | 8.59 | 4.36 | 4.65 | 4.91 | | 4.36 |
| 4.0 | 13.17 | 9.51 | 3.66 | 4.43 | 4.50 | | 3.66 |
| 4.4 | 13.44 | 10.42 | 3.02 | 4.19 | 3.98 | | 3.02 |
| 4.8 | 13.79 | 11.34 | 2.45 | 3.92 | 3.63 | | 2.45 |
| 5.2 | 14.20 | 12.23 | 1.97 | 3.70 | 3.38 | | 1.97 |

## TABLE 1 (contd.).

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| C. C. Acid | Total Conductivity $\times 10^4$ | Conductivity of NaCl $\times 10^4$ | Conductivity of NaOH + Na Niobate $\times 10^4$ | $p_H$ [Hydrogen Electrode] | $p_H$ [Quinhydrone] | Conductivity of NaOH $\times 10^4$ | Conductivity of Na Niobate $\times 10^4$ |
| 5.6 | 14.82 | 13.06 | 1.76 | 3.58 | 3.20 | | 1.76 |
| 6.0 | 15.54 | 13.97 | 1.57 | 3.33 | 3.01 | | 1.57 |
| 6.4 | 16.59 | 14.86 | 1.73 | 3.19 | 2.86 | | 1.73 |
| 6.8 | 18.21 | 15.77 | 2.44 | 3.05 | 2.74 | | 2.44 |
| 7.2 | 20.33 | 16.62 | 3.71 | 2.93 | 2.61 | | 3.71 |
| 7.5 | Equivalence Point | 17.26 | Conductivity of HCl. | | | | |
| 7.6 | 22.92 | 17.26 | 5.66 | 2.84 | 2.52 | Calculated Conductivity of HCl. | |
| 8.0 | 25.71 | 17.26 | 8.45 | 2.75 | 2.43 | Equivalence Point = 7.5 c.c. | |
| 8.4 | 28.58 | 17.26 | 11.32 | 2.67 | 2.37 | 1 c.c. | 8.41 |
| 8.8 | 31.59 | 17.26 | 14.33 | 2.61 | 2.31 | 2 c.c. | 16.59 |
| 9.2 | 34.67 | 17.26 | 17.41 | 2.55 | 2.24 | 3 c.c. | 24.53 |
| 9.6 | 37.56 | 17.26 | 20.30 | 2.51 | 2.18 | | |
| 10.0 | 40.30 | 17.26 | 23.04 | 2.48 | 2.15 | | |

FIGURE 1.

3:4 SODIUM NIOBATE.



## TABLE 2.

### $6Na_2O.7Nb_2O_5.54H_2O.$

.4 gm. salt in 100 c.c. water. 1 c.c. .2228 N. NaOH added.

Titrated with .2310 N. HCl.

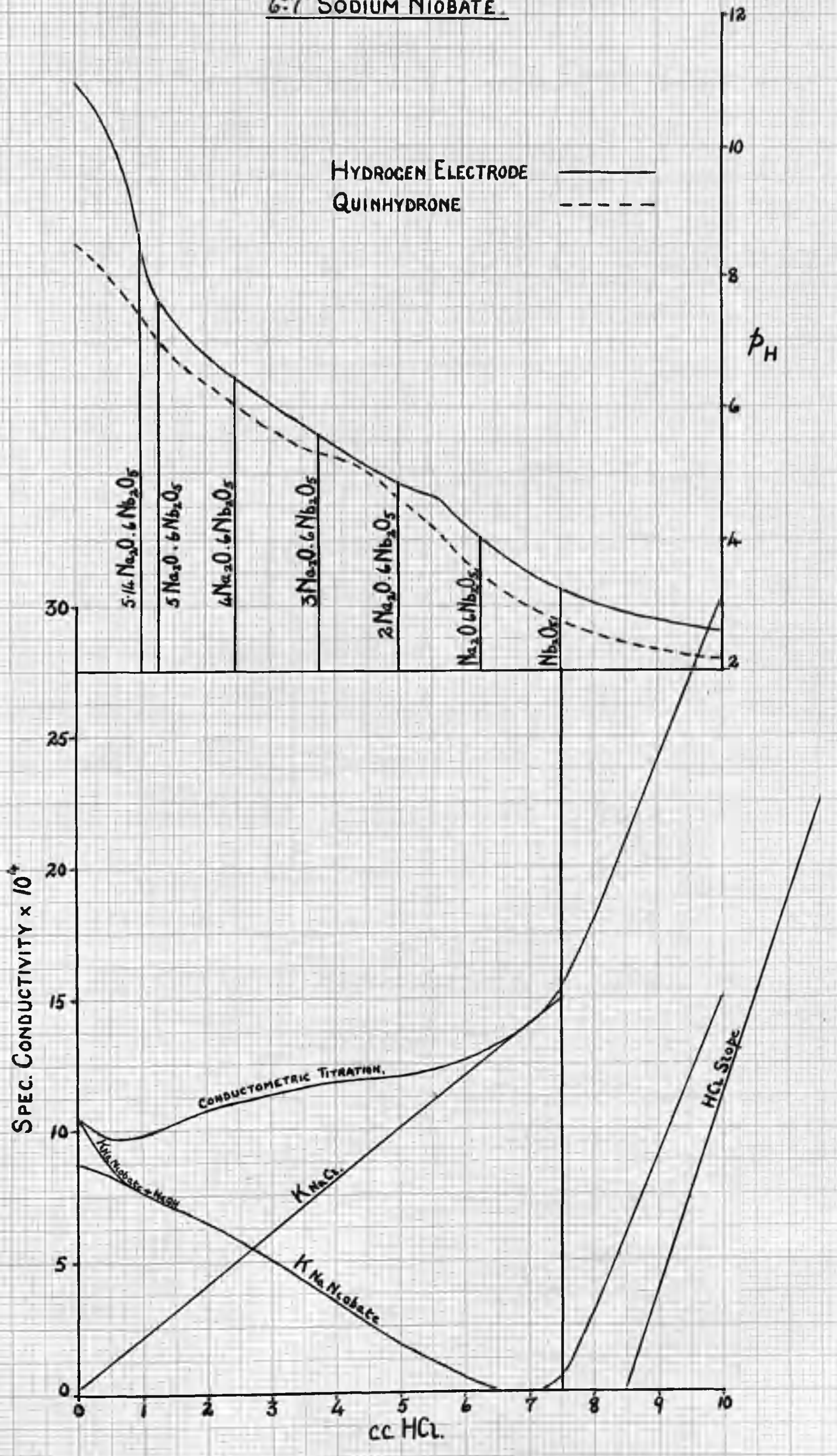
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| c. c. Acid | Total Conductivity x $10^4$ | Conductivity of NaCl x $10^4$ | Conductivity of NaOH + Na Niobate x $10^4$ | $p_H$ [Hydrogen Electrode] | $p_H$ [Quinhydrone] | Conductivity of NaOH x $10^4$ | Conductivity of Na Niobate x $10^4$ |
| 0.0 | 10.55 | 0.00 | 10.55 | 10.95 | 8.47 | 1.82 | 8.73 |
| 0.4 | 9.88 | 0.94 | 8.94 | 10.39 | 8.11 | 0.50 | 8.44 |
| 0.8 | 9.75 | 1.77 | 7.98 | 9.44 | 7.60 | 0.06 | 7.92 |
| 1.2 | 9.97 | 2.60 | 7.37 | 7.72 | 7.07 | 0.00 | 7.37 |
| 1.6 | 10.36 | 3.42 | 6.94 | 7.18 | 6.63 |  | 6.94 |
| 2.0 | 10.72 | 4.24 | 6.48 | 6.78 | 6.36 |  | 6.48 |
| 2.4 | 10.96 | 5.06 | 5.90 | 6.47 | 6.09 |  | 5.90 |
| 2.8 | 11.20 | 5.87 | 5.33 | 6.21 | 5.81 |  | 5.33 |
| 3.2 | 11.38 | 6.67 | 4.71 | 5.91 | 5.55 |  | 4.71 |
| 3.6 | 11.58 | 7.45 | 4.13 | 5.66 | 5.34 |  | 4.13 |
| 4.0 | 11.77 | 8.25 | 3.52 | 5.46 | 5.25 |  | 3.52 |
| 4.4 | 11.82 | 9.04 | 2.78 | 5.14 | 5.08 |  | 2.78 |
| 4.8 | 11.97 | 9.84 | 2.13 | 4.97 | 4.81 |  | 2.13 |
| 5.2 | 12.12 | 10.62 | 1.50 | 4.77 | 4.45 |  | 1.50 |

## TABLE 2 (contd.).

| 1 c.c. Acid | 2 Total Conductivity x $10^4$ | 3 Conductivity of NaCl x $10^4$ | 4 Conductivity of NaOH + Na Niobate x $10^4$ | 5 $p_H$ [Hydrogen Electrode] | 6 $p_H$ [Quinhydrone] | 7 Conductivity of NaOH x $10^4$ | 8 Conductivity of Na Niobate x $10^4$ |
|---|---|---|---|---|---|---|---|
| 5.6 | 12.38 | 11.33 | 1.05 | 4.61 | 4.16 | | 1.05 |
| 6.0 | 12.64 | 12.13 | 0.51 | 4.25 | 3.70 | | 0.51 |
| 6.4 | 13.01 | 12.90 | 0.11 | 3.93 | 3.40 | | 0.11 |
| 6.8 | 13.61 | 13.69 | -0.08 | 3.64 | 3.11 | | -0.08 |
| 7.2 | 14.42 | 14.43 | -0.01 | 3.39 | 2.88 | | -0.01 |
| 7.5 | Equivalence Point | 14.98 | Conductivity of HCl. | | | | |
| 7.6 | 15.83 | 14.98 | 0.85 | 3.22 | 2.72 | Calculated Conductivity of HCl. | |
| 8.0 | 17.94 | 14.98 | 2.96 | 3.04 | 2.58 | Equivalence Point = 7.5 c.c. | |
| 8.4 | 20.18 | 14.98 | 5.20 | 2.92 | 2.45 | 1 c.c. | 7.30 |
| 8.8 | 22.73 | 14.98 | 7.75 | 2.82 | 2.36 | 2 c.c. | 15.26 |
| 9.2 | 25.21 | 14.98 | 10.33 | 2.73 | 2.29 | 3 c.c. | 22.57 |
| 9.6 | 27.67 | 14.98 | 12.69 | 2.66 | 2.23 | | |
| 10.0 | 30.03 | 14.98 | 15.05 | 2.60 | 2.19 | | |

# FIGURE 2.

6:7 SODIUM NIOBATE.



## TABLE 3.

### $5Na_2O.6Nb_2O_5.35H_2O.$

.4 gm. salt in 100 c.c. water. 1 c.c. .2228 N. NaOH added.

Titrated with .2310 N. HCl.

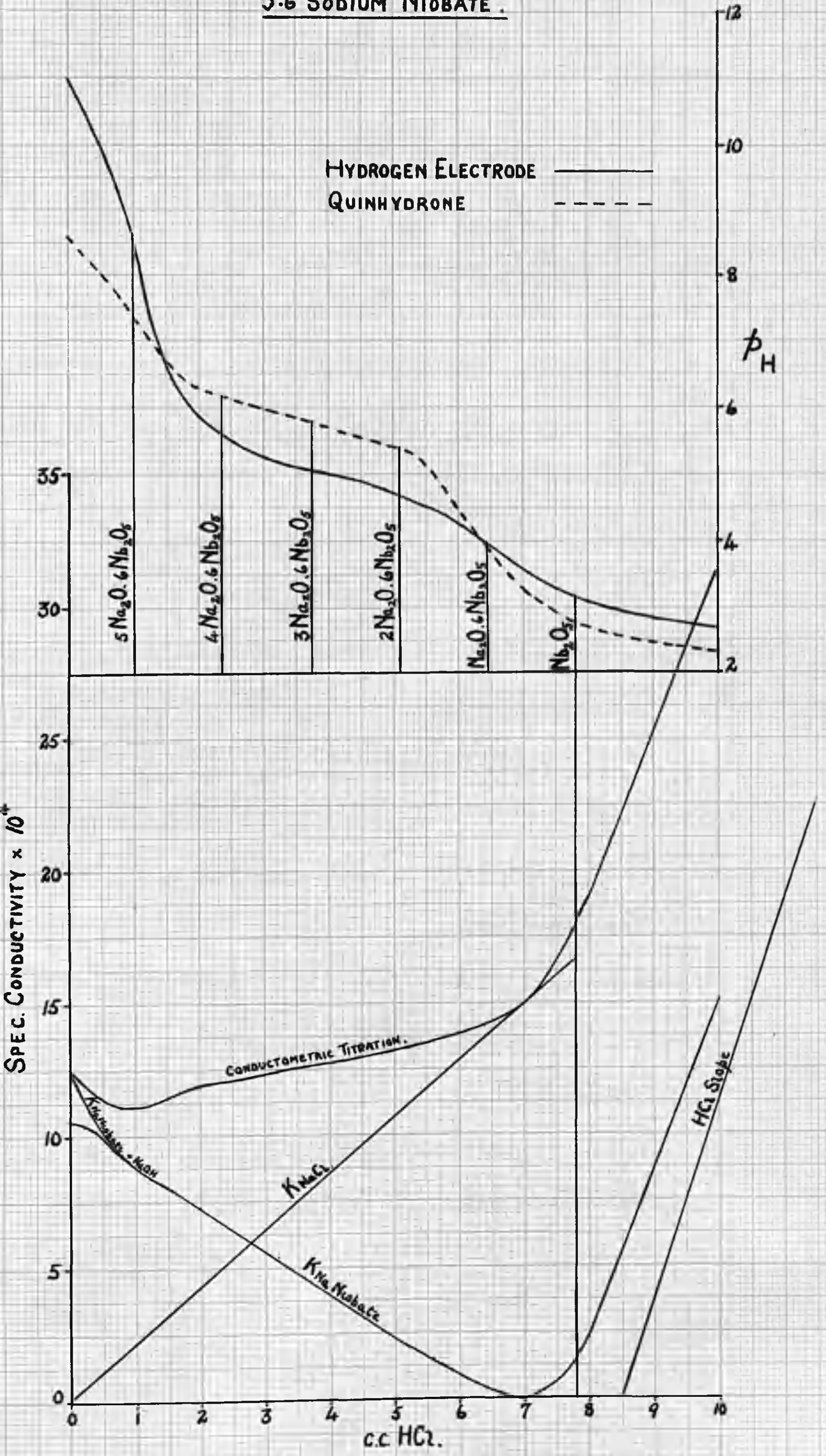
| 1 c.c. Acid. | 2 Total Conductivity x $10^4$ | 3 Conductivity of NaCl. x $10^4$ | 4 Conductivity of NaOH + Na Niobate x $10^4$ | 5 $p_H$ [Hydrogen Electrode] | 6 $p_H$ [Quin-hydrone] | 7 Conductivity of NaOH x $10^4$ | 8 Conductivity of Na Niobate x $10^4$ |
|---|---|---|---|---|---|---|---|
| 0.0 | 12.55 | 0.00 | 12.55 | 10.98 | 8.58 | 1.95 | 10.60 |
| 0.4 | 11.57 | 1.00 | 10.57 | 10.22 | 8.13 | 0.34 | 10.23 |
| 0.8 | 11.13 | 1.88 | 9.25 | 9.27 | 7.62 | 0.04 | 9.21 |
| 1.2 | 11.18 | 2.77 | 8.41 | 7.43 | 7.03 | 0.00 | 8.41 |
| 1.6 | 11.51 | 3.66 | 7.85 | 6.63 | 6.58 | | 7.85 |
| 2.0 | 11.81 | 4.52 | 7.29 | 5.86 | 6.27 | | 7.29 |
| 2.4 | 12.02 | 5.39 | 6.63 | 5.56 | 6.14 | | 6.63 |
| 2.8 | 12.23 | 6.25 | 5.98 | 5.31 | 6.03 | | 5.98 |
| 3.2 | 12.44 | 7.10 | 5.34 | 5.17 | 5.92 | | 5.34 |
| 3.6 | 12.59 | 7.94 | 4.65 | 5.07 | 5.81 | | 4.65 |
| 4.0 | 12.75 | 8.79 | 3.96 | 5.00 | 5.70 | | 3.96 |
| 4.4 | 12.92 | 9.63 | 3.29 | 4.93 | 5.58 | | 3.29 |
| 4.8 | 13.08 | 10.49 | 2.59 | 4.79 | 5.44 | | 2.59 |
| 5.2 | 13.30 | 11.31 | 1.99 | 4.61 | 5.35 | | 1.99 |

## TABLE 3 (contd.).

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| C.C. Acid. | Total Conductivity x $10^4$ | Conductivity of NaCl x $10^4$ | Conductivity of NaOH + Na Niobate x $10^4$ | $p_H$ [Hydrogen Electrode] | $p_H$ [Quinhydrone] | Conductivity of NaOH x $10^4$ | Conductivity of Na Niobate x $10^4$ |
| 5.6 | 13.58 | 12.07 | 1.51 | 4.49 | 5.03 |  | 1.51 |
| 6.0 | 13.81 | 12.92 | 0.89 | 4.28 | 4.49 |  | 0.89 |
| 6.4 | 14.10 | 13.74 | 0.36 | 4.00 | 3.99 |  | 0.36 |
| 6.8 | 14.60 | 14.58 | 0.02 | 3.72 | 3.48 |  | 0.02 |
| 7.2 | 15.44 | 15.39 | 0.07 | 3.44 | 3.13 |  | 0.07 |
| 7.6 | 17.01 | 16.15 | 0.86 | 3.25 | 2.88 |  | 0.86 |
| 7.8 | Equivalence Point. | 16.54 | Conductivity of HCl. |  |  |  |  |
| 8.0 | 18.97 | 16.54 | 2.43 | 3.10 | 2.72 | Calculated Conductivity of HCl. |  |
| 8.4 | 21.34 | 16.54 | 4.80 | 2.99 | 2.60 | Equivalence Point = 7·8c.c. |  |
| 8.8 | 23.92 | 16.54 | 7.38 | 2.90 | 2.50 | 1 c.c. | 7.74 |
| 9.2 | 26.61 | 16.54 | 10.07 | 2.80 | 2.44 | 2 c.c. | 15.29 |
| 9.6 | 29.19 | 16.54 | 12.65 | 2.72 | 2.39 | 3 c.c. | 22.60 |
| 10.0 | 31.66 | 16.54 | 15.12 | 2.67 | 2.34 |  |  |

# FIGURE 3.

## 5:6 SODIUM NIOBATE.



## TABLE 4.

## $Na_2O.Nb_2O_5.7H_2O.$

.4 gm. salt in 100 c.c. water. 1 c.c. .2228 N. NaOH added.

Titrated with .2310 N. HCl.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| C.C. Acid. | Total Conductivity $\times 10^4$ | Conductivity of NaCl. $\times 10^4$ | Conductivity of NaOH + Na Niobate $\times 10^4$ | $p_H$ [Hydrogen Electrode] | $p_H$ [Quinhydrone] | Conductivity of NaOH $\times 10^4$ | Conductivity of Na Niobate $\times 10^4$ |
| 0.0 | 13.04 | 0.00 | 13.04 | 10.88 | 8.59 | 1.55 | 11.49 |
| 0.4 | 12.98 | 0.99 | 11.99 | 10.54 | 8.22 | 0.71 | 11.28 |
| 0.8 | 13.04 | 1.86 | 11.18 | 10.08 | 7.89 | 0.25 | 10.93 |
| 1.2 | 13.16 | 2.76 | 10.40 | 9.62 | 7.59 | 0.08 | 10.32 |
| 1.6 | 13.27 | 3.61 | 9.66 | 9.05 | 7.37 | 0.02 | 9.64 |
| 2.0 | 13.50 | 4.47 | 9.03 | 8.10 | 7.20 | 0.00 | 9.03 |
| 2.4 | 13.67 | 5.34 | 8.33 | 7.37 | 7.03 | 0.00 | 8.33 |
| 2.8 | 13.84 | 6.19 | 7.65 | 7.06 | 6.88 |  | 7.65 |
| 3.2 | 14.02 | 7.03 | 6.99 | 6.88 | 6.75 |  | 6.99 |
| 3.6 | 14.19 | 7.86 | 6.33 | 6.76 | 6.72 |  | 6.33 |
| 4.0 | 14.32 | 8.70 | 5.62 | 6.58 | 6.69 |  | 5.62 |
| 4.4 | 14.43 | 9.54 | 4.89 | 6.31 | 6.66 |  | 4.89 |
| 4.8 | 14.55 | 10.38 | 4.17 | 5.96 | 6.62 |  | 4.17 |
| 5.2 | 14.62 | 11.19 | 3.43 | 5.38 | 6.60 |  | 3.43 |

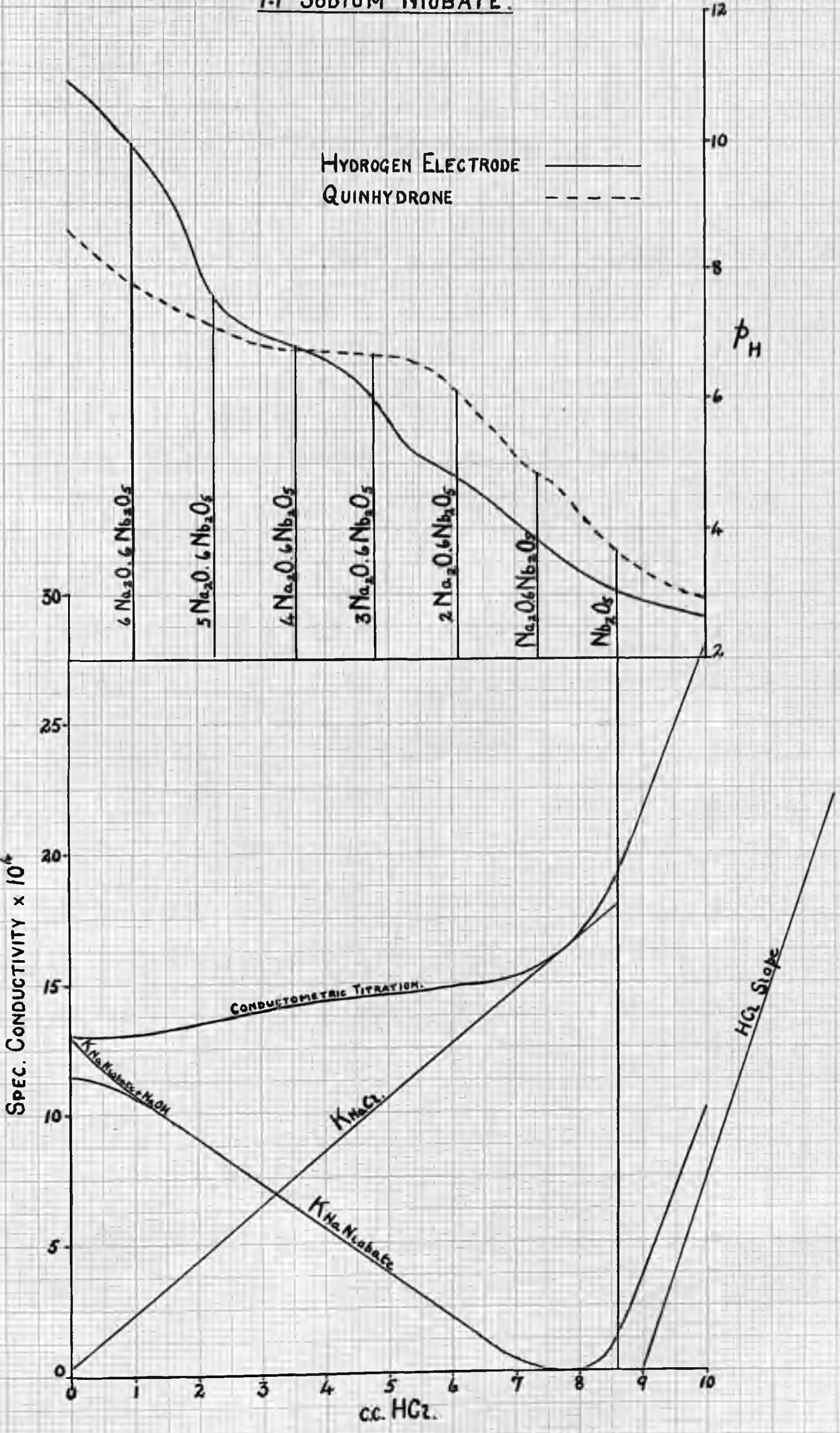
## TABLE 4 (contd.).

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| C.C. Acid. | Total Conductivity x $10^4$ | Conductivity of NaCl. x $10^4$ | Conductivity of NaOH + Na Niobate x $10^4$ | $p_H$ [Hydrogen Electrode] | $p_H$ [Quinhydrone] | Conductivity of NaOH x $10^4$ | Conductivity of Na Niobate x $10^4$ |
| 5.6 | 14.74 | 11.95 | 2.79 | 5.04 | 6.44 | | 2.79 |
| 6.0 | 14.86 | 12.78 | 2.08 | 4.82 | 6.18 | | 2.08 |
| 6.4 | 14.99 | 13.60 | 1.39 | 4.58 | 5.77 | | 1.39 |
| 6.8 | 15.12 | 14.43 | 0.69 | 4.29 | 5.39 | | 0.69 |
| 7.2 | 15.43 | 15.21 | 0.22 | 3.94 | 4.94 | | 0.22 |
| 7.6 | 16.01 | 15.99 | 0.02 | 3.64 | 4.68 | | 0.02 |
| 8.0 | 16.75 | 16.76 | -0.01 | 3.35 | 4.26 | | -0.01 |
| 8.4 | 18.10 | 17.54 | 0.56 | 3.15 | 3.83 | | 0.56 |
| 8.6 | Equivalence Point. | 17.93 | Conductivity of HCl. | | | | |
| 8.8 | 20.35 | 17.93 | 2.42 | 2.95 | 3.50 | | |
| 9.2 | 22.89 | 17.93 | 4.96 | 2.83 | 3.24 | | |
| 9.6 | 25.44 | 17.93 | 7.51 | 2.71 | 3.05 | | |
| 10.0 | 28.05 | 17.93 | 10.12 | 2.62 | 2.91 | | |

| Calculated Conductivity of HCl.<br>Equivalence Point = 8·6 c.c. | |
|---|---|
| 1 c.c. | 7.63 |
| 2 c.c. | 15.02 |
| 3 c.c. | 22.19 |

# FIGURE 4

1:1 SODIUM NIOBATE.



# TABLE 5.

## $7Na_2O.6Nb_2O_5.32H_2O$.

.4 gm. salt in 100 c.c. water. 1 c.c. .2228 N. NaOH added.

Titrated with .2310 N. HCl.

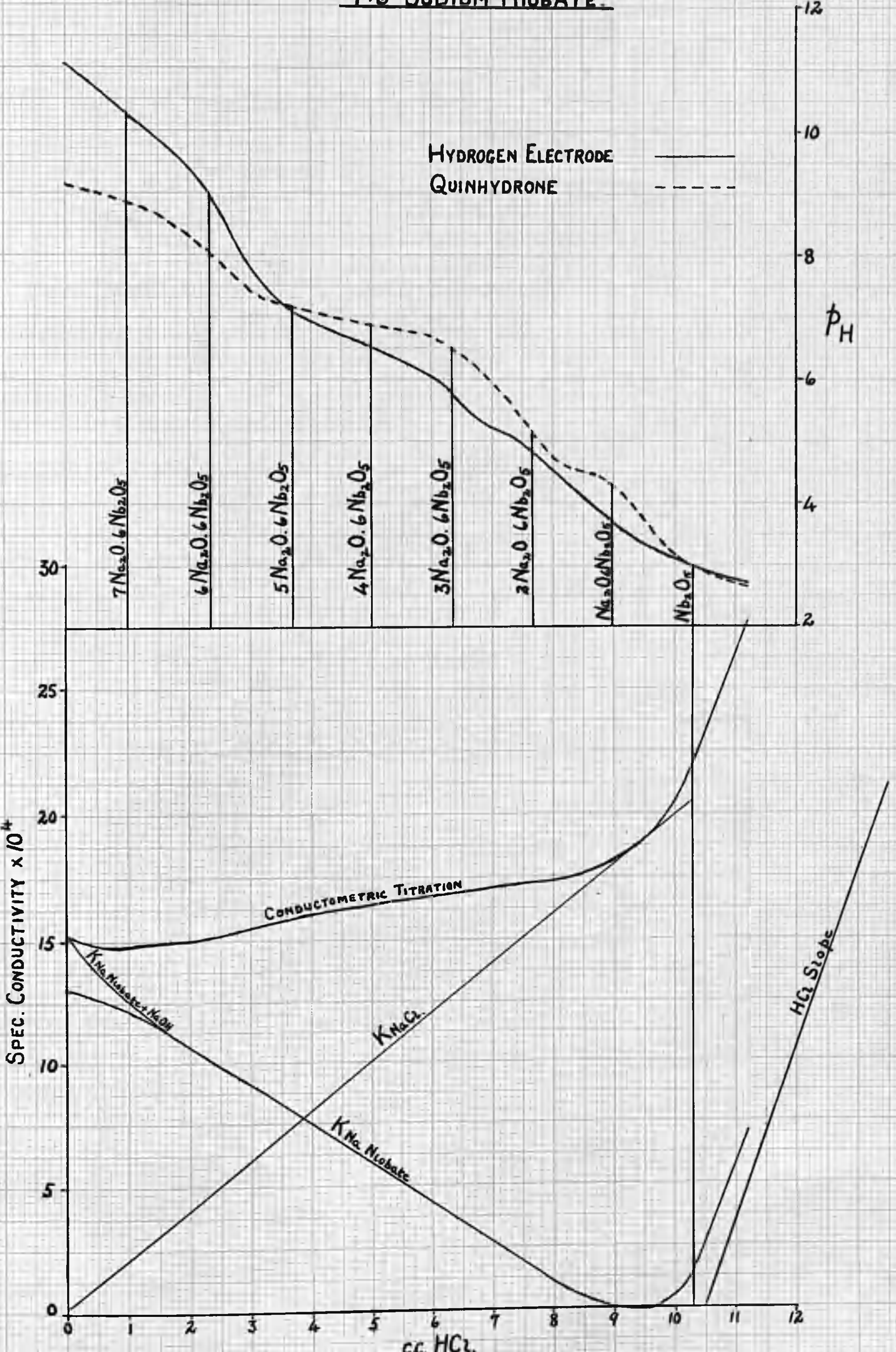
| 1 C.C. Acid | 2 Total Conductivity x $10^4$ | 3 Conductivity of NaCl x $10^4$ | 4 Conductivity of NaOH + Na Niobate x $10^4$ | 5 $p_H$ [Hydrogen Electrode] | 6 $p_H$ [Quin-hydrone] | 7 Conductivity of NaOH x $10^4$ | 8 Conductivity of Na Niobate x $10^4$ |
|---|---|---|---|---|---|---|---|
| 0.0 | 15.25 | 0.00 | 15.25 | 11.03 | 9.14 | 2.19 | 13.06 |
| 0.4 | 14.94 | 0.96 | 13.98 | 10.79 | 9.04 | 1.26 | 12.72 |
| 0.8 | 14.82 | 1.81 | 13.01 | 10.43 | 8.91 | 0.55 | 12.46 |
| 1.2 | 14.88 | 2.66 | 12.22 | 10.13 | 8.78 | 0.28 | 11.94 |
| 1.6 | 14.94 | 3.50 | 11.44 | 9.79 | 8.58 | 0.13 | 11.31 |
| 2.0 | 15.00 | 4.33 | 10.67 | 9.42 | 8.31 | 0.05 | 10.62 |
| 2.4 | 15.13 | 5.17 | 9.96 | 8.92 | 7.98 | 0.02 | 9.94 |
| 2.8 | 15.31 | 6.00 | 9.31 | 8.15 | 7.62 | 0.00 | 9.31 |
| 3.2 | 15.60 | 6.81 | 8.79 | 7.53 | 7.31 | 0.00 | 8.79 |
| 3.6 | 15.79 | 7.61 | 8.18 | 7.13 | 7.18 | 0.00 | 8.18 |
| 4.0 | 15.95 | 8.43 | 7.52 | 6.91 | 7.08 |  | 7.52 |
| 4.4 | 16.14 | 9.24 | 6.90 | 6.76 | 6.98 |  | 6.90 |
| 4.8 | 16.28 | 10.06 | 6.22 | 6.62 | 6.91 |  | 6.22 |
| 5.2 | 16.41 | 10.85 | 5.56 | 6.44 | 6.83 |  | 5.56 |

## TABLE 5 (contd.).

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| C.C. Acid. | Total Conductivity $\times 10^4$ | Conductivity of $NaCl$. $\times 10^4$ | Conductivity of $NaOH$ + Na Niobate $\times 10^4$ | $p_H$ [Hydrogen Electrode] | $p_H$ [Quinhydrone] | Conductivity of $NaOH$ $\times 10^4$ | Conductivity of Na Niobate $\times 10^4$ |
| 5.6 | 16.54 | 11.58 | 4.96 | 6.21 | 6.76 | | 4.96 |
| 6.0 | 16.67 | 12.39 | 4.28 | 6.03 | 6.68 | | 4.28 |
| 6.4 | 16.85 | 13.18 | 3.67 | 5.70 | 6.42 | | 3.67 |
| 6.8 | 16.99 | 13.99 | 3.00 | 5.34 | 6.12 | | 3.00 |
| 7.2 | 17.09 | 14.74 | 2.35 | 5.12 | 5.73 | | 2.35 |
| 7.6 | 17.20 | 15.49 | 1.71 | 4.87 | 5.21 | | 1.71 |
| 8.0 | 17.30 | 16.24 | 1.06 | 4.53 | 4.75 | | 1.06 |
| 8.4 | 17.51 | 17.00 | 0.51 | 4.18 | 4.52 | | 0.51 |
| 8.8 | 17.87 | 17.75 | 0.12 | 3.84 | 4.42 | | 0.12 |
| 9.2 | 18.46 | 18.50 | -0.04 | 3.54 | 4.09 | | -0.04 |
| 9.6 | 19.22 | 19.25 | -0.03 | 3.28 | 3.60 | | -0.03 |
| 10.0 | 20.42 | 20.00 | 0.42 | 3.11 | 3.17 | | 0.42 |
| 10.3 | Equivalence Point | 20.57 | Conductivity of $HCl$. | | | | |
| 10.4 | 22.51 | 20.57 | 1.94 | 2.94 | 2.94 | Calculated Conductivity of $HCl$. | |
| 10.8 | 25.04 | 20.57 | 4.47 | 2.81 | 2.78 | Equivalence Point = 10·3 c.c. | |
| 11.2 | 27.65 | 20.57 | 7.08 | 2.72 | 2.65 | 1 c.c. | 7.28 |
| | | | | | | 2 c.c. | 14.32 |
| | | | | | | 3 c.c. | 21.19 |

# FIGURE 5

## 7:6 SODIUM NIOBATE.



## TABLE 6.

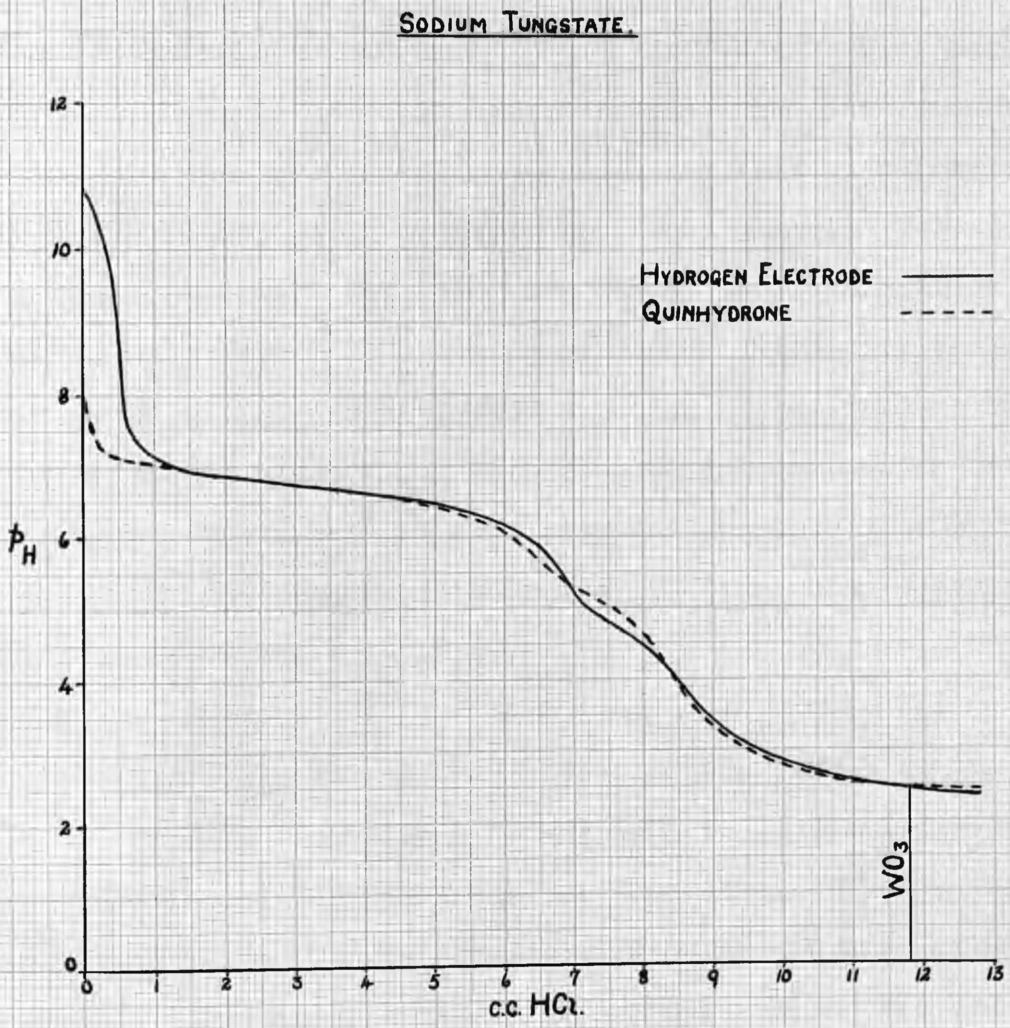
### Sodium Tungstate.

.4 gm. salt in 100 c.c. water. 1 c.c. .2228 N. NaOH added.

Titrated with .2310 N. HCl.

| c.c. Acid. | $p_H$ [Hydrogen Electrode] | $p_H$ [Quinhydrone] |
|---|---|---|
| 0.0 | 10.86 | 8.04 |
| 0.4 | 9.64 | 7.15 |
| 0.8 | 7.30 | 7.05 |
| 1.2 | 6.99 | 7.00 |
| 1.6 | 6.92 | 6.92 |
| 2.0 | 6.87 | 6.88 |
| 2.4 | 6.82 | 6.83 |
| 2.8 | 6.78 | 6.78 |
| 3.2 | 6.70 | 6.73 |
| 3.6 | 6.63 | 6.68 |
| 4.0 | 6.58 | 6.61 |
| 4.4 | 6.56 | 6.54 |
| 4.8 | 6.51 | 6.46 |
| 5.2 | 6.42 | 6.37 |
| 5.6 | 6.33 | 6.23 |
| 6.0 | 6.17 | 6.06 |
| 6.4 | 5.93 | 5.79 |
| 6.8 | 5.53 | 5.41 |
| 7.2 | 4.99 | 5.19 |
| 7.6 | 4.72 | 4.97 |
| 8.0 | 4.48 | 4.62 |
| 8.4 | 4.10 | 4.07 |
| 8.8 | 3.60 | 3.52 |
| 9.2 | 3.22 | 3.17 |
| 9.6 | 3.01 | 2.95 |
| 10.0 | 2.82 | 2.78 |
| 10.4 | 2.72 | 2.68 |
| 10.8 | 2.63 | 2.57 |
| 11.2 | 2.55 | 2.52 |
| 11.6 | 2.50 | 2.48 |
| 11.8 | Equivalence Point. | |
| 12.0 | 2.45 | 2.46 |
| 12.4 | 2.39 | 2.44 |
| 12.8 | 2.34 | 2.44 |

# FIGURE 6.


SODIUM TUNGSTATE.
HYDROGEN ELECTRODE
QUINHYDRONE
$p_H$
0
2
4
6
8
10
12
0
1
2
3
4
5
6
7
8
9
10
11
12
13
c.c. HCl.
$WO_3$

## DISCUSSION.

During this work it was noted that niobic acid was thrown out right from the start of each titration. The addition of the smallest amounts of acid produced a faint turbidity in the solutions although it was thought that the free alkali which had been added would have been neutralised before any decomposition of the sodium niobate took place. This decomposition, however, may have been due to the localisation of the acid, although it occurred no matter how slowly the acid was added or how violently the solution was stirred. The niobic acid remained as a turbid colloidal suspension until about half the amount of acid required completely to precipitate the niobic acid had been added, after which coagulation and precipitation took place.

The character of the conductometric curves is the same in all cases. There is a slight drop in conductivity during the addition of approximately the first c.c. of acid, which should correspond to the neutralisation of the free alkali added. This does not appear in the case of the 3:4 salt (figure 1), where the specific conductivity starts to increase immediately. It would appear that, in this case, the free NaOH added had been absorbed by the sodium niobate, this being the most acid of the salts.

After this slight drop, the specific conductivities increase gradually and fairly regularly until the equivalence point is reached. The slope of this portion of the curves is steepest for the 3:4 salt and becomes less steep with decreasing acidity of the salts.

Beyond the equivalence point the specific conductivity increases rapidly, the increase being very similar to that which would be produced by free HCl, which is shown in the 'HCl Slope'.

The equivalence points in each case are slightly displaced but it will be observed that the specific conductivity of the sodium niobate shows a regular decrease until it reaches zero at the equivalence point. In other words, the total specific conductivity of the solution at the equivalence point is due entirely to the NaCl present, being practically the same as the specific conductivity calculated for NaCl at that point. This is in accordance with the fact that niobic acid is quantitatively precipitated from solutions of sodium niobate by dilute acids.

It will be noted, however, that the 3:4 salt proved exceptional in this respect. The graph for the 3:4 salt (figure 1) shows clearly that the specific conductivity of the solution at the equivalence point is distinctly higher than that calculated for the amount of NaCl present. Three determinations of the conductivity data for this salt gave the same result. In this respect the conductometric titration of the 3:4 sodium niobate with HCl bears a distinct resemblance to that noted by Britton for sodium tungstate with HCl (H. T. S. Britton - "Conductometric Analysis" - page 125). Britton attributes this excess of conductivity to the formation of the salt of a strong acid, in this case a poly-tungstate, probably sodium meta-tungstate, which is not decomposed by HCl.

In the case of the 3:4 sodium niobate also, then, this phenomenon may be due to the formation of a complex acid or acid salt, stronger than niobic acid, which keeps some of the niobium in solution. It seems peculiar, however, that this should occur in one case only and with none of the other sodium niobates titrated under the same conditions. The only difference noted between the 3:4 salt and the others was that this salt only gave a turbid solution and contained a small amount of free niobic acid.

The specific conductivities of the sodium niobates, then, appear in all the graphs as almost straight lines and show no evidence whatsoever of the change of one niobate anion to another or, for that matter, of the existence of different niobate anions at all.

The $p_H$ values do not indicate any extensive hydrolysis. After subtraction of the acid required to neutralise the added alkali, the $p_H \div 10$ for the 7:6 and 1:1 salts, 8.5 for the 6:7 and 5:6 salts, and 7.5 for the 3:4 salt. The small extent of hydrolysis is also seen in the conductivity curves, there being only a slight branching in the lines $K_{\text{Na Niobate + NaOH}}$ and $K_{\text{Na Niobate}}$.

For the 3:4 niobate (figure 1), the $p_H$ values (hydrogen electrode) start from just above the neutral point and drop regularly in a fairly smooth curve to the equivalence point. These values show that the solution is acid very early in the titration and becomes steadily more acid up to the equivalence point. This shows a certain agreement with the conductometric data for this salt if the assumption be made that the excess conductivity is due to the formation of an acid or an acid salt considerably stronger than niobic acid. The quinhydrone values for the 3:4 salt show a slight suggestion of a 'break' in the curve corresponding to the well-defined 'breaks' shown by the 5:6, 1:1, and 7:6 salts.

The 6:7 salt (figure 2) gives $p_H$ curves quite similar to those of the 3:4 salt. The values in this case are higher and there is shown in both the hydrogen electrode and quinhydrone results the beginnings of the 'breaks' which are much more prominent in the three successive salts

The 5:6, 6:6 (or 1:1), and 7:6 salts are of interest because they give a series of salts with a regular gradation in the alkali - acid ratio. These salts give $p_H$ curves (figures 3, 4, and 5) which are quite similar although they show the effect of the additional alkali in each case. The hydrogen electrode results show a rapid drop down to about, or slightly below, the neutral point, at which stage the curves straighten out. This 'break' is much more distinct with the quinhydrone results which are in all three cases considerably higher than those obtained with the hydrogen electrode. The $p_H$ in this region decreased very slowly during the addition of approximately 3.5 c.c. of .2310 N. HCl.

It was noted that in this region the solutions took much longer than usual to come to equilibrium. At other stages of the titrations 10-15 minutes was ample for the hydrogen electrode and even less for the quinhydrone cell but at this particular stage 30-40 minutes elapsed before equilibrium was reached and a constant reading obtained. On addition of the acid the $p_H$ value decreased and then gradually rose again on standing. This phenomenon was was noted also during the conductometric titrations but not to such a marked degree.

After this 'break' the $p_H$ values fall rapidly at first and then by decreasing amounts until the equivalence point is reached. For the 5:6 salt (figure 3) this drop shows as a smooth curve but in the case of the 1:1 and 7:6 salts there appears another small 'break' at $p_H = 4.4-4.8$

which was noted in all the potentiometric titrations carried out for those two salts. It is very slight in the case of the 1:1 salt (figure 4) but is clearly defined for the 7:6 salt (figure 5).

The $p_H$ curves of these salts have been compared with those of Pierce and Yntema, (J. Physical Chem., 1930, 34, 1822.) and of Britton and Robinson (J. C. S., 1932, 2265.), who carried out potentiometric titrations on solutions of potassium hexa-niobate, $4K_2O.3Nb_2O_5$, with HCl. The first stages of the curves shown here are comparable with the results obtained by Pierce and Yntema, showing a rapid drop in $p_H$ down to the first 'break'. Britton and Robinson's values for the corresponding section are much higher and the drop in $p_H$ is much more gradual. For the later stages both pairs of investigators give results which are in agreement with each other but which differ considerably from those obtained here. While they show the first 'break' mentioned here, it is not nearly so well-defined and occurs much later in the titration, almost at the equivalence point. It is followed by a rapid inflection at the equivalence point corresponding to the precipitation of niobic acid. The present graphs show a well-defined 'break' much earlier in the titration followed by a gradual falling off in $p_H$ value down to the equivalence point.

In order to find if the change in alkali metal was responsible for those differences, it was decided to prepare some potassium niobate and to carry out potentiometric titrations on solutions of this salt with HCl.

The potassium niobate was prepared by fusion of $Nb_2O_5$ with $K_2CO_3$. The melt dissolved almost completely in hot water and the solution was filtered and left to crystallise. The salt crystallised after two days, the crystals being small flat plates. These were filtered off, washed with cold water, and dried. The analysis was carried out in the manner previously described and proved the salt to be the 7:6 potassium niobate - $7K_2O.6Nb_2O_5.20H_2O$.

Analysis.

| $Nb_2O_5$ and $K_2O$. | 1. | 2. |
|---|---|---|
| Wt. of Niobate used ---------- | 0.4850 gm. | 0.5468 gm. |
| Wt. of $Nb_2O_5$ obtained -------- | 0.2960 gm. | 0.3326 gm. |
| $Nb_2O_5$ ---------- | 61.03 % | 60.82 % |
| Wt. of $K_2SO_4$ obtained -------- | 0.2262 gm. | 0.2556 gm. |
| $K_2O$ ------------ | 25.23 % | 25.28 % |
| $H_2O$. | | |
| Wt. of Niobate used ---------- | 0.3224 gm. | 0.3014 gm. |
| Loss in weight --------------- | 0.0444 gm. | 0.0417 gm. |
| $H_2O$ ------------ | 13.77 % | 13.83 % |

| Oxide. | Found. | Calculated. | Formula. |
|---|---|---|---|
| $K_2O$. | 25.25 % | 25.19 % | |
| $Nb_2O_5$. | 60.92 % | 61.07 % | $7K_2O.6Nb_2O_5.20H_2O$. |
| $H_2O$. | 13.80 % | 13.74 % | |
| | 99.97 % | 100.00 % | |

Solutions of potassium niobate were made up, each containing .4 gm. of the salt in 100 c.c. water, and potentiometric titrations were carried out on these solutions with HCl. The quinhydrone - quinhydrone cell was used and the titrations were carried out in the manner previously described. The results of two determinations are given in Table 7 and are shown on the graph (figure 7) by a continuous and a dotted line.

The results are very similar to those obtained for the 7:6 sodium niobate. The main 'break' occurs at approximately the same $p_H$ value and for the same titre of HCl. The small secondary 'break' noted for the 7:6 and 1:1 sodium niobates is also noted for the potassium salt in one of the determinations but not in the other. Small discrepancies such as this were noted several times during this work and it would appear that the equilibrium is very complex and is not always identical.

## TABLE 7.

## $7K_2O.6Nb_2O_5.20H_2O.$

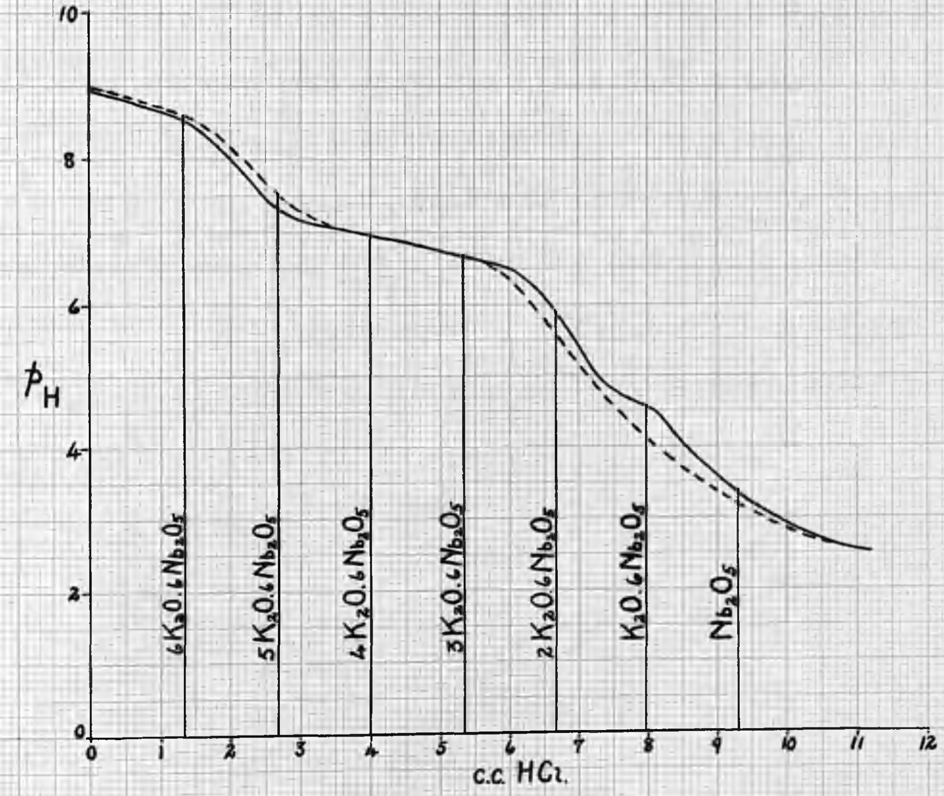
.4 gm. salt in 100 c.c. water.   Titrated with .2310 N. HCl.

| C.C. Acid. | $p_H$ | $p_H$ |
|---|---|---|
| 0.0 | 8.95 | 9.00 |
| 0.4 | 8.85 | 8.91 |
| 0.8 | 8.73 | 8.77 |
| 1.2 | 8.59 | 8.65 |
| 1.6 | 8.37 | 8.48 |
| 2.0 | 8.01 | 8.19 |
| 2.4 | 7.59 | 7.80 |
| 2.8 | 7.26 | 7.42 |
| 3.2 | 7.10 | 7.19 |
| 3.6 | 7.04 | 7.03 |
| 4.0 | 6.97 | 6.96 |
| 4.4 | 6.90 | 6.89 |
| 4.8 | 6.80 | 6.81 |
| 5.2 | 6.70 | 6.73 |
| 5.6 | 6.60 | 6.61 |

| C.C. Acid. | $p_H$ | $p_H$ |
|---|---|---|
| 6.0 | 6.50 | 6.38 |
| 6.4 | 6.21 | 5.93 |
| 6.8 | 5.72 | 5.43 |
| 7.2 | 5.09 | 4.95 |
| 7.6 | 4.74 | 4.50 |
| 8.0 | 4.55 | 4.12 |
| 8.4 | 4.16 | 3.81 |
| 8.8 | 3.78 | 3.50 |
| 9.2 | 3.43 | 3.25 |
| 9.3 | EQUIVALENCE POINT. | |
| 9.6 | 3.14 | 3.03 |
| 10.0 | 2.92 | 2.87 |
| 10.4 | 2.73 | 2.69 |
| 10.8 | 2.59 | 2.58 |
| 11.2 | 2.51 | 2.50 |

# FIGURE 7

**POTASSIUM NIOBATE.**



The results obtained, then, are not the same as those of Britton and Robinson. Their $p_H$ curve, showing a gradual decrease in $p_H$ value followed by a slight flattening of the curve in the region of $p_H = 7-5$ and an abrupt inflection at the equivalence point corresponding to the precipitation of niobic acid, is more of the order of a simple neutralisation than are the curves obtained here, although it should be noted that Britton and Robinson had a larger amount of alkali present in their original solutions. The curves noted here show a much more complex reaction, indicating the formation of an acid or an acid salt, stronger than niobic acid, which compound is gradually decomposed again to give complete precipitation of niobic acid at the equivalence point.

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# PART II.

# SODIUM NIOBATE AND ORGANIC ACIDS.

## INTRODUCTION.

It has long been known that, although the addition of very weak acids to niobate solutions causes the precipitation of niobic acid, the addition of oxalic, tartaric, malonic, malic, or citric acid has no such effect. Also, freshly precipitated niobic acid can be dissolved in solutions of oxalic or tartaric acid or of the alkali acid oxalates or tartrates.

These facts have been regarded as evidence for the existence of soluble complexes of niobates with these organic acids.

## Nioboxalates.

The first systematic investigation of nioboxalates was carried out by Russ, (Zeitsch. anorg. Chemie, 1902, 31, 42-91.), who prepared a series of alkali nioboxalates by fusing $Nb_2O_5$ with alkali carbonates, dissolving the melt in water, and adding oxalic acid to the solution. He obtained thus the sodium, rubidium, and potassium salts and assigned to them the general formula - $3R_2O.Nb_2O_5.6C_2O_3.xH_2O$. An ammonium salt of similar composition was prepared by dissolving freshly precipitated niobic acid in $NH_4HC_2O_4$.

From a solution of niobic acid in excess $H_2C_2O_4$, Russ crystallised a niob-oxalic acid of composition $Nb(C_2O_4H)_5$ which, however, was decomposed by water. By treatment with alcohol an unstable compound of composition $Nb_2O_5.C_2O_3.4H_2O$ was obtained.

With solutions of barium, strontium, and calcium salts, Russ obtained precipitates on addition of potassium nioboxalate. The precipitated barium salt had the composition $5BaO.Nb_2O_5.10C_2O_3.20H_2O$.

Of the alkali nioboxalates prepared by Russ, only the potassium salt was recrystallised from water. The others were precipitated from concentrated solution by acetone and it must be noted that these concentrated solutions contained the relative proportions of alkali niobate and oxalic acid required for the formula assigned by Russ to the salts which he obtained. It is considered, therefore, that these salts, with the exception of the potassium salt, must be regarded with suspicion, as being possibly mixtures of alkali niobate and oxalic acid in the proportions required to satisfy Russ's formulae. It seems probable that the other alkali metals will give salts analogous to the potassium salt but this need not necessarily follow, since sodium salts, in particular, sometimes differ from those of the other alkali metals as, for example, in the sodium niobates themselves.

Edmister and Albritton, (J.A.C.S., 1932, 54, 438.), found that freshly precipitated niobic acid was readily and completely soluble in a boiling solution of oxalic acid. The resulting solution, on addition of ammonia or alkali hydroxides, gave an incomplete precipitation of hydrated $Nb_2O_5$.

Attempts made by Edmister and Albritton to prepare double oxalates with the heavy metals proved unsuccessful. When the solution was treated with the salt of a heavy metal, the oxalate of the reagent metal was precipitated, c.f. Russ - formation of barium nioboxalate.

From ionic migration tests of the oxalate solution, Edmister and Albritton conclude that the niobium is joined with the oxalate ions, forming a complex. They are of the opinion that this may be similar to the analogous chromium complex. According to Werner, chromium forms with oxalic acid the complex chromo-oxalic acid, $H_6Cr_2(C_2O_4)_6$, where the chromium is joined with the oxalate ion, forming a complex anion. Edmister and Albritton point out that, in agreement with this theory, niobium would form the compound $H_5Nb(C_2O_4)_5$, c.f. Russ's niob-oxalic acid.

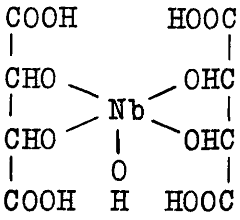
Note. - It does not seem probable that a fully-substituted compound such as this - a compound of ortho-niobic acid - will exist.

## Niobtartrates.

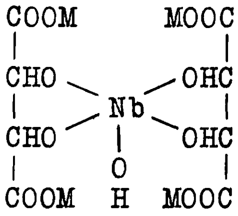
According to Edmister and Albritton, (loc. cit.), the dissolving of niobic acid in solutions of tartaric acid or of the alkali tartrates takes place rather slowly as if dependent on an organic type rather than an ionic type of reaction. They state that niobic acid is not precipitated from tartrate solutions by ammonia or alkali hydroxides, thus differing from the complex oxalate solutions. Strong mineral acids precipitate the metal as the hydrated oxide.

Edmister and Albritton prepared a specimen of niobtartaric acid by saturating an aqueous solution of tartaric acid with freshly precipitated niobic acid and crystallising the resulting solution over $H_2SO_4$. The solution became viscous and finally fine white tetrahedral crystals appeared which were very soluble in hot water and which were not tartaric acid. Ionic migration tests showed the presence of a complex acid and analysis gave the ratio of two molecules of tartaric acid to one atom of niobium. Titration of a solution of this complex acid with NaOH showed that there was no change in the total hydrogen equivalent of the tartaric acid. The dissolving of the niobic acid evidently did not involve the reaction of double decomposition, with simple salt formation, in which the hydrogen ions take part.

From these results Edmister and Albritton assign to this compound the composition $(C_4H_4O_6)_2NbOH$. They consider that its formation involves the replacement of the hydrogen of the alcoholic hydroxyl groups and not of the carboxyl groups. This agrees with the slowness of formation, which resembles an organic type of reaction, and with the composition and properties of the acid. They therefore assign the following constitutional formulae :-



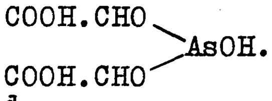
and



Niobtartaric Acid.

Alkali salt where M represents the alkali metal.

This conclusion is in accordance with that of G. G. Henderson, (J.C.S., 1895, 67, 102.), concerning the action of tartrates on arsenious oxide, where the formula



$$\begin{matrix} COOH.CHO \\ COOH.CHO \end{matrix} > AsOH.$$

was assigned to the so-called tartrarsenious acid.

While the action of other organic acids on niobate solutions has not been investigated, there is, as has been stated, some slight evidence for the existence of complexes with malonic, malic, and citric acids.

## EXPERIMENTAL.

### Conductometric Titrations.

It was thought that, in the event of complex formation between sodium niobate and oxalic or tartaric acids, with the production of large complex anions, there would be an appreciable effect on the electrical conductivity of the solutions which might give some suggestion as to the composition of such complexes. It was decided, therefore, to carry out a series of conductometric titrations of sodium niobate solutions with oxalic and tartaric acids.

In each case the meta-niobate, $Na_2O.Nb_2O_5.7H_2O$, was used, the solutions consisting of .4 gm. of the salt in 100 c.c. water. These solutions were titrated with N. $H_2C_2O_4$ or $H_6C_4O_6$ and the specific conductivity determined for each .5 c.c. of acid added. The titrations were carried out in the manner previously described, using the same apparatus.

As a parallel in each case a 'blank' titration was carried out on a solution containing, per 100 c.c. water, free NaOH equivalent to the weight of $Na_2O$ in .4 gm. sodium meta-niobate.

The results of these determinations are shown in Tables 8 and 9 and in Figure 8.

The 'blank' determinations show a decrease in specific

## TABLE 8.

## $Na_2O.Nb_2O_5.7H_2O.$

.4 gm. salt in 100 c.c. water. Titrated with N. Oxalic Acid.

| C.C. Acid. | Specific Conductivity x $10^4$ | |
|---|---|---|
| | Equivalent of Free Alkali. | Na Niobate. |
| 0.0 | 23.92 | 10.56 |
| 0.5 | 19.05 | 11.32 |
| 1.0 | 15.23 | 10.90 |
| 1.5 | 14.22 | 10.49 |
| 2.0 | 14.63 | 11.18 |
| 2.5 | 14.69 | 11.32 |
| 3.0 | 14.00 | 11.43 |
| 3.5 | 13.60 | 11.50 |
| 4.0 | 13.71 | 11.55 |
| 4.5 | 14.92 | 11.84 |
| 5.0 | 17.66 | 12.49 |
| 5.5 | 21.33 | 13.67 |
| 6.0 | 25.14 | 15.53 |

| C. C. Acid. | Specific Conductivity x $10^4$ | |
|---|---|---|
| | Equivalent of Free Alkali. | Na Niobate. |
| 6.5 | 29.16 | 17.80 |
| 7.0 | 32.97 | 20.16 |
| 7.5 | 36.77 | 23.43 |
| 8.0 | 40.61 | 26.43 |
| 8.5 | 44.37 | 29.28 |
| 9.0 | 47.89 | 32.67 |
| 9.5 | 51.59 | 36.10 |
| 10.0 | 54.79 | 39.27 |
| 10.5 | 57.97 | 42.64 |
| 11.0 | 61.08 | 47.42 |
| 11.5 | 64.48 | 51.59 |
| 12.0 | 67.74 | 55.72 |

## TABLE 9.

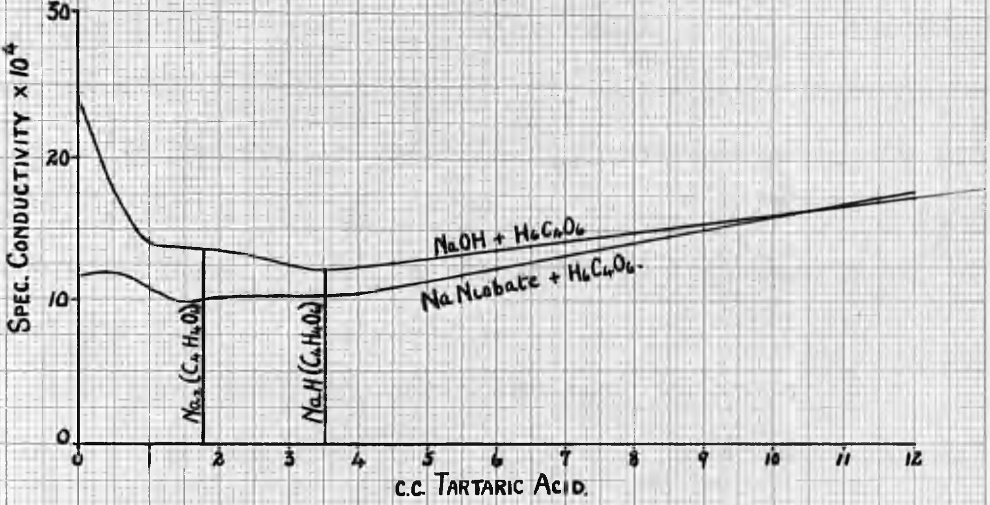
## $Na_2O.Nb_2O_5.7H_2O$.

.4 gm. salt in 100 c.c. water. Titrated with N. Tartaric Acid.

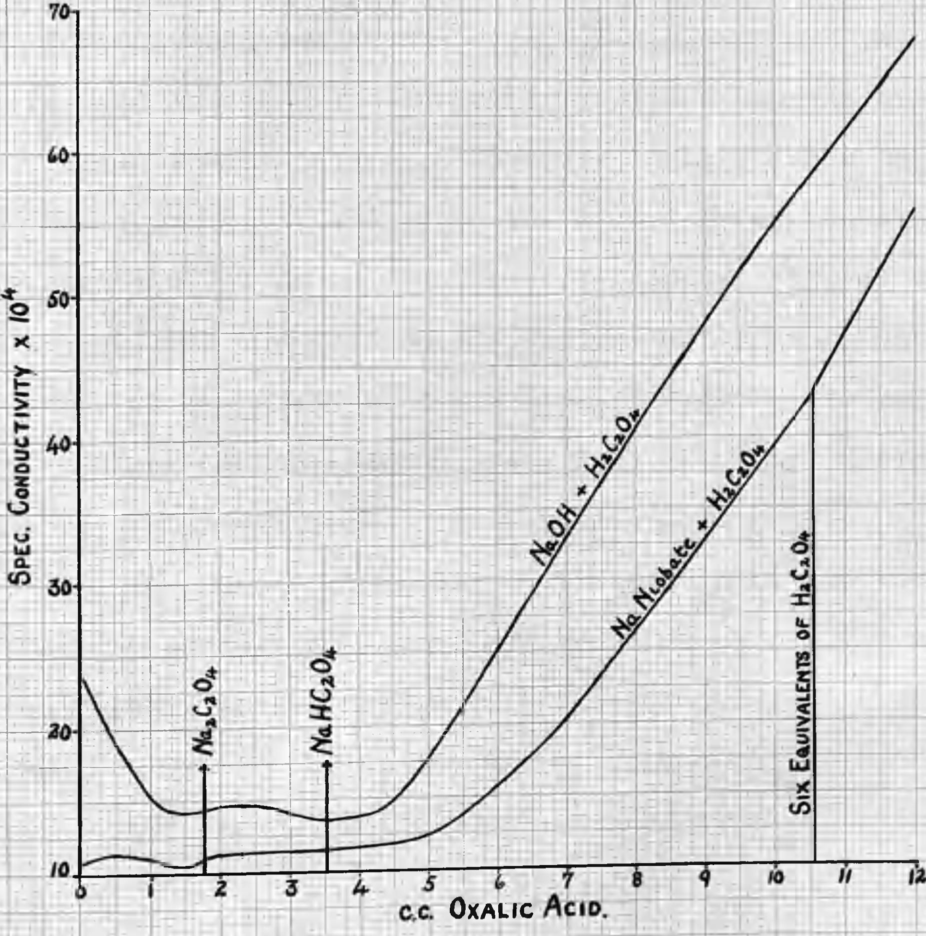
| C.C. Acid. | Specific Conductivity x $10^4$ | |
|---|---|---|
| | Equivalent of Free Alkali. | Na Niobate |
| 0.0 | 24.52 | 11.68 |
| 0.5 | 17.66 | 11.84 |
| 1.0 | 14.11 | 10.72 |
| 1.5 | 13.71 | 9.76 |
| 2.0 | 13.55 | 10.09 |
| 2.5 | 13.01 | 10.13 |
| 3.0 | 12.49 | 10.18 |
| 3.5 | 12.34 | 10.23 |
| 4.0 | 12.44 | 10.38 |
| 4.5 | 12.65 | 10.76 |
| 5.0 | 12.90 | 11.22 |
| 5.5 | 13.17 | 11.69 |
| 6.0 | 13.50 | 12.19 |
| 6.5 | 13.82 | 12.70 |
| 7.0 | 14.17 | 13.20 |
| 7.5 | 14.51 | 13.71 |
| 8.0 | 14.87 | 14.22 |
| 8.5 | 15.17 | 14.74 |
| 9.0 | 15.47 | 15.23 |
| 9.5 | 15.85 | 15.66 |
| 10.0 | 16.17 | 16.07 |
| 10.5 | 16.50 | 16.50 |
| 11.0 | 16.83 | 16.90 |
| 11.5 | 17.17 | 17.31 |
| 12.0 | 17.46 | 17.73 |

# FIGURE 8.

SODIUM NIOBATE WITH TARTARIC ACID.



SODIUM NIOBATE WITH OXALIC ACID.



conductivity down to a point which approximates to the formation of neutral sodium oxalate or tartrate. There is then little variation in the specific conductivity until the acid oxalate or tartrate stage is reached after which there is a steady increase due to the addition of free oxalic or tartaric acid.

The conductivity curves obtained for the niobate solutions resemble those for the 'blank' determinations and show 'breaks' approximating to neutral and acid salt formation. The specific conductivities of the niobate are smaller, as would be anticipated. The slight rise in specific conductivity for the addition of the first .5 c.c. of acid is peculiar and occurred in every determination carried out.

After the addition of two equivalents of acid there is a considerable difference in the behaviour of the oxalate and tartrate solutions. The specific conductivity of the sodium niobate - tartaric acid solution increases gradually and, although the slope of the graph is slightly steeper than for the 'blank' determination, this increase would appear to be due to the addition of free tartaric acid.

For the sodium niobate - oxalic acid solution, however, the specific conductivity does not increase as rapidly as for the 'blank' determination until the addition of 10.5 c.c. of $H_2C_2O_4$. At this point the curve shows a slight inflection and thereafter resembles the addition of free oxalic acid.

Between the titres of 3.5 c.c. and 10.5 c.c. of acid, however, the behaviour of the solution indicated an abnormal equilibrium. It was found to be very difficult to obtain constant readings, the solution having to stand for a considerable time before equilibrium was attained. The specific conductivity rose sharply on addition of acid and then gradually decreased, taking 30-45 minutes to become constant. For this part of the titration, indeed, the values given for the specific conductivities may be regarded as being only approximate, the balancing of the solution being so slow that it was difficult to tell when equilibrium had been reached. After the addition of 10.5 c.c. of acid no such phenomenon was noted nor was it evident at any stage in the sodium niobate - tartaric acid titrations, where the solution came to equilibrium almost immediately.

The addition of 10.56 c.c. of N. $H_2C_2O_4$ solution corresponds to the addition of six equivalents of the acid. Since the observed inflection on the curve is practically identical with this titre, these titrations would seem to indicate the formation of a sodium nioboxalate which contains six $C_2O_4$ groups per molecule.

It seemed probable that, should the formula assigned by Russ to sodium nioboxalate be correct, i.e. $3Na_2O.Nb_2O_5.6C_2O_3.8H_2O$, the presence of additional alkali in the niobate solutions would promote the formation of such a complex. Accordingly, another series of conductometric titrations was carried out for sodium niobate with oxalic acid, the initial niobate solutions in this case containing an additional one or two equivalents of NaOH. The corresponding 'blank' determinations were also made. The graphs of the specific conductivities obtained from these titrations, however, showed nothing definite except the 'breaks' corresponding to the formation of $Na_2C_2O_4$ and $NaHC_2O_4$ and the results have not been included here.

From the sodium niobate - tartaric acid titrations no definite conclusion could be drawn, but it seemed evident, at least, that there was no complex formation beyond the stage corresponding to the addition of two equivalents of $H_6C_4O_6$, and that any complex which might be formed would contain not more than two molecules of $H_6C_4O_6$ per molecule.

It was thought that, in this case, conditions might not be favourable for the formation of a complex. Accordingly, titrations were carried out using normal solutions of sodium tartrate and of sodium hydrogen tartrate instead of tartaric acid. It was found that the specific conductivities of the niobate solutions increased steadily with addition of $Na_2C_4H_4O_6$ or $NaHC_4H_4O_6$, the graphs being practically straight lines. No evidence of complex formation was observed and the results of these titrations, also, have been omitted. It was noted, however, that the sodium niobate - sodium hydrogen tartrate titration was similar to the sodium niobate - oxalic acid titration in that the solution took a long time to come to equilibrium.

## Potentiometric Titrations.

Potentiometric titrations, similar to the conductometric titrations, were carried out on solutions of sodium meta-niobate, consisting of .4 gm. of the salt in 100 c.c. water, which were titrated with normal oxalic and tartaric acids. The hydrogen electrode was used, there being, in this case, no interference due to the precipitation of niobic acid. A parallel titration was run in each case for comparison, using sodium tungstate in place of sodium niobate. The titrations were carried out as previously described, using the hydrogen electrode - saturated calomel electrode cell.

Britton and Robinson, (J.C.S., 1933, 1, 419-424.), carried out a series of hydrogen electrode titrations on solutions containing known amounts of freshly precipitated niobic acid and of oxalic acid titrated with standard NaOH. 'Blank' determinations with the same amount of oxalic acid alone were also made. Comparison revealed that the $p_H$ curves were identical during the neutralisation of the first equivalent of acid. For the next equivalent, however, the values obtained were much higher in the presence of $Nb_2O_5$ than for the 'blank' titrations.

According to Britton and Robinson, their $p_H$ curves show that the complexity of the nioboxalic acid solutions is connected with the second stage of dissociation of oxalic acid. It appeared to them probable that the weakness of the second ionisation of oxalic acid might be responsible for the complex formation which that acid promotes, although it was noted that formic acid, which is but slightly stronger, shows no tendency to form complex solutions with $Nb_2O_5$.

Britton and Robinson are of the opinion that the conclusion drawn by Russ from conductometric data (see page 108), from which he assigns to nioboxalates the formula $R_6Nb_2O_2(C_2O_4)_6$, cannot be valid in the light of their potentiometric data. The solute present at the mid-point of Britton and Robinson's titration corresponds to the formula $Nb_2O_5 \cdot 6.34 NaHC_2O_4$, and they are of the opinion that Russ's salt might be considered as $Nb_2O_5 \cdot 6RHC_2O_4$.

They consider that, in view of the very small solubility of $Nb_2O_5$ in strong acids, the solubility in oxalic acid is probably of a colloidal nature in spite of the fact that the solutions are optically clear. The fact that niobic acid can be precipitated in presence of tannin and an electrolyte by the addition of ammonia seems to indicate that the solutions are colloidal.[*]

The following suggestions are put forward by Britton and Robinson :-

If the solutions are of a colloidal nature, the formation of Russ's salt would be accounted for by the equation :-

$$3KHC_2O_4 + Nb(OH)_5 \rightleftharpoons 3K + \left[Nb \begin{matrix}(OH)_2 \\ (C_2O_4)_3\end{matrix}\right]^{\prime\prime\prime} + 3H_2O.$$

The nioboxalate complex may then enter into hydrolytic equilibrium with water thus :-

$$\left[Nb \begin{matrix}(OH)_{5-x} \\ (C_2O_4)_x\end{matrix}\right]^{\prime x} + yH_2O \longrightarrow \left[Nb \begin{matrix}(OH)_{5-x+y} \\ (C_2O_4)_{x-y}\end{matrix}\right]^{\prime x-y} + yH^{\cdot}.$$

The $H^{\cdot}$ ions liberated would become replaced on addition of alkali and so, disturbing the equilibrium, ultimately bring about decomposition of the complex oxalate.

---

[*] Note :- This need not necessarily follow. Precipitation of hydrated niobic acid might be due in this case to secondary ionisation of the nioboxalate, giving a small concentration of niobic acid. This is precipitated as the tannin adsorption complex by tannin plus $NH_4OH$ with progressive withdrawal of the niobic acid from the complex oxalate. Even the relatively stable ferri- and chrom-oxalates are not completely

stable to alkali. The conductivity differences obtained in the Ostwald basicity determinations (see page 109) point to partial hydrolytic dissociation of the complex.

The results of the present potentiometric titrations are given in Tables 10 and 11 and in Figure 9.

The $p_H$ curves for sodium niobate with $H_2C_2O_4$ and $H_6C_4O_6$ resemble each other closely as do the sodium tungstate curves. The niobate curves show some resemblance to those obtained by Britton and Robinson although the titrations were carried out in the reverse direction.

The tungstate $p_H$ values, after a small preliminary drop for the first .2 c.c. of acid added, decrease very gradually during the addition of 1.5 - 1.6 c.c. of acid, the values in this region ranging from 7.3 to 6.5. Beyond this point the values decrease in a smooth curve which gradually becomes less steep.

The niobate $p_H$ values decrease rapidly until the neutral point is reached. There is then a slight inflection at $p_H = 6.5$ which corresponds to the addition of approximately 0.9 c.c. of acid. Beyond this point the $p_H$ values decrease steadily, the rate of decrease becoming less and less.

If it is assumed that these titrations represent the simple neutralisation of the alkali of the niobate and tung-

## TABLE 10.

### $Na_2O.Nb_2O_5.7H_2O$.

and

### $Na_2WO_4$.

.4 gm. salt in 100 c.c. water.   Titrated with N. Oxalic Acid.

| c.c. Acid. | $p_H$ Value. | |
|---|---|---|
| | Na Tungstate. | Na Niobate. |
| 0.0 | 7.53 | 9.90 |
| 0.2 | 7.16 | 8.66 |
| 0.4 | 7.09 | 7.40 |
| 0.6 | 7.03 | 6.93 |
| 0.8 | 6.95 | 6.68 |
| 1.0 | 6.89 | 6.33 |
| 1.2 | 6.76 | 5.96 |
| 1.4 | 6.63 | 5.58 |
| 1.6 | 6.36 | 5.34 |
| 1.8 | 5.99 | 5.14 |

| c.c. Acid. | $p_H$ Value. | |
|---|---|---|
| | Na Tungstate | Na Niobate. |
| 2.0 | 5.60 | 5.01 |
| 2.2 | 5.20 | 4.91 |
| 2.4 | 4.96 | 4.81 |
| 2.6 | 4.79 | 4.73 |
| 2.8 | 4.65 | 4.64 |
| 3.0 | 4.51 | 4.51 |
| 3.5 | 4.08 | 4.11 |
| 4.0 | 3.69 | 3.77 |
| 4.5 | 3.37 | 3.47 |
| 5.0 | 3.10 | 3.21 |

## TABLE 11.

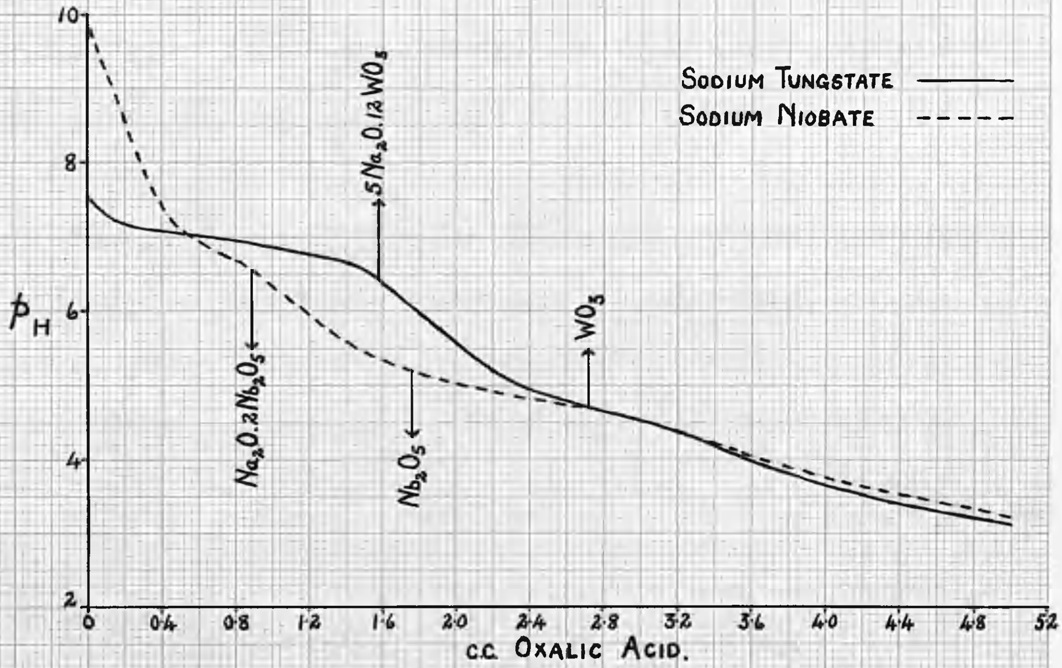
### $Na_2O.Nb_2O_5.7H_2O$.
### and
### $Na_2WO_4$.

.4 gm. salt in 100 c.c. water. Titrated with N. Tartaric Acid.

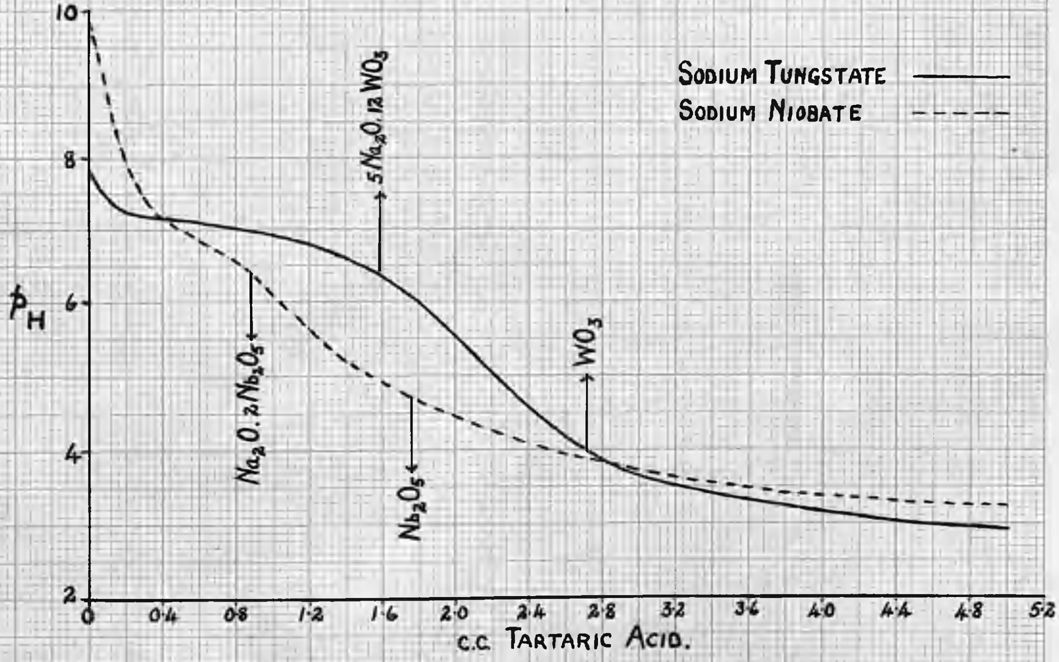
| c.c. Acid. | $p_H$ Value. | |
|---|---|---|
| | Na Tungstate | Na Niobate |
| 0.0 | 7.86 | 9.83 |
| 0.2 | 7.26 | 7.97 |
| 0.4 | 7.17 | 7.13 |
| 0.6 | 7.10 | 6.83 |
| 0.8 | 7.00 | 6.53 |
| 1.0 | 6.91 | 6.07 |
| 1.2 | 6.80 | 5.63 |
| 1.4 | 6.60 | 5.19 |
| 1.6 | 6.34 | 4.92 |
| 1.8 | 6.00 | 4.67 |
| 2.0 | 5.53 | 4.45 |
| 2.2 | 5.04 | 4.25 |
| 2.5 | 4.39 | 4.00 |
| 3.0 | 3.65 | 3.71 |
| 3.5 | 3.34 | 3.51 |
| 4.0 | 3.15 | 3.37 |
| 4.5 | 3.00 | 3.27 |
| 5.0 | 2.93 | 3.21 |

## FIGURE 9.

SODIUM NIOBATE AND SODIUM TUNGSTATE WITH OXALIC ACID.



SODIUM NIOBATE AND SODIUM TUNGSTATE WITH TARTARIC ACID.



state, accompanied by peptization of the niobic and tungstic acid set free, the equivalence point for the tungstate would be represented by the addition of 2.72 c.c. of acid, at which titre the $p_H = 4.6$ . For sodium niobate the titre would be 1.76 c.c. of acid, where the $p_H = 4.4$ . These values are higher than those observed for sodium niobate and tungstate with HCl.

The inflections on the tungstate curves correspond to the addition of approximately 1.6 c.c. of acid, which is 7/12 of the amount required to neutralise the alkali present in the solutions. The inflections therefore coincide with the formation of sodium para-tungstate, $5Na_2O.12WO_3$. On the same basis, the inflections on the niobate curves, occurring at the addition of half the total acid required, would represent the formation of an acid sodium niobate - $Na_2O.2Nb_2O_5$.

The inflections noted on the niobate curves, although much smaller in this case, correspond approximately to those noted for sodium niobate with HCl. The curves also show a resemblance in becoming acid quite early in the titration. This early acidity may have some significance in view of the suggestion put forward by Britton and Robinson that sodium nioboxalates may enter into hydrolytic equilibrium with water with liberation of $H^{\cdot}$ ions (see page 95).

The results obtained from these potentiometric titrations show little or no evidence of complex formation between sodium niobate and oxalic or tartaric acid. It is quite possible, however, that complexes may be formed since solutions containing such compounds might not show a great variation in hydrogen ion concentration from solutions containing sodium oxalate or tartrate with peptized niobic acid.

## Optical Rotations.

The fact that tartaric acid is optically active suggested a simple and reliable method by which could be studied the behaviour of tartaric acid in presence of sodium niobate. It was decided, therefore, to determine the optical rotations of a solution of sodium niobate containing varying amounts of tartaric acid.

Gernez, (Compt. Rend., 1888, 106, 1527.), determined the rotations of solutions containing neutral sodium tungstate and tartaric acid. A fixed amount of tartaric acid (1.25 gm.) was used for each solution and the amounts of sodium tungstate varied from 1/48 - 17 equivalents.

Gernez found that the rotations increased regularly and in proportion to the weight of sodium tungstate used, up to one equivalent of sodium tungstate. They continued to increase, but by diminishing amounts, up to the addition of two equivalents of sodium tungstate, where the rotation reached a maximum. After this point the rotations decreased regularly by amounts which became less and less.

Gernez concluded that the first amounts of sodium tungstate combined completely with tartaric acid to form a complex containing one equivalent of both $Na_2WO_4$ and $H_6C_4O_6$, which showed a rotation much larger than that of the corresponding amount of free tartaric acid. On addition of larger amounts of $Na_2WO_4$, another complex was formed containing two equivalents of $Na_2WO_4$ to one equivalent of $H_6C_4O_6$. The formation of this compound was complete at the maximum observed rotation, which corresponded with the weight of $Na_2WO_4$ equal to two equivalents and which was 22 times greater than that produced by the corresponding amount of tartaric acid. This compound was dissociated by successive additions of $Na_2WO_4$.

A similar series of determinations, using potassium tungstate, gave similar results. The maximum observed rotation was, in this case, 23 times greater than that produced by a corresponding amount of free tartaric acid.

In the present experiments, a solution of sodium metaniobate, $Na_2O.Nb_2O_5.7H_2O$, was titrated with normal tartaric acid and the optical rotations determined for various titres of the acid. The rotations being small, larger amounts of sodium niobate and tartaric acid were used than in previous titrations. 0.8 gm. of the salt was dissolved in 50 c.c. water and the rotation observed for each 0.5 c.c. of $H_6C_4O_6$ added. A series of 'blank' determinations was also carried out by titrating 50 c.c. of water alone with normal tartaric acid and measuring the optical rotations. In this case readings were taken for every 1 c.c. of acid added, the increase in rotation per 0.5 c.c. of acid being too small to be accurately determined.

A Lippich polarimeter was used, consisting of a polarising Nicol prism in front of which are two smaller prisms arranged so as to give a triple field. Behind the carrier for the polarimeter tube is placed an analysing Nicol prism which is turned until the three fields are at a minimum equal illumination, giving the zero. The solution is introduced and the analyser turned to restore equal illumination, the angle through which it is turned giving the rotation. The half-shadow angle, i.e. the angle between the large prism and one of the smaller ones, was, in this case, adjusted to 1°, which gave a sensitive reading. A two-decimetre polarimeter tube was used. The source of light was a mercury vapour lamp fitted with a yellow screen.

The titrations were carried out as follows :-

The polarimeter tube was filled with the test solution, which was contained in a small beaker, and the rotation measured. The solution was then transferred from the polarimeter tube to the beaker and the required amount of tartaric acid added from a micro-burette. The polarimeter tube was washed out with the resulting solution several times to ensure thorough mixing of all the niobate and tartaric acid present. The tube was then filled and the rotation again observed. The process was repeated for the various amounts of acid added. For each titre of acid three determinations of the rotation were made and a mean value taken.

The results obtained are shown in Table 12 and in Figure 10.

It will be seen that the rotation for tartaric acid in the presence of sodium niobate is much greater than for tartaric acid alone. The 'blank' titration shows a slight uniform increase in rotation for each addition of acid, the graph obtained being almost a straight line. In the sodium niobate - tartaric acid titration, however, the rotation increases rapidly and regularly until one equivalent of tartaric acid has been added. It continues to increase up to the addition of two equivalents of tartaric acid but the rate of increase becomes gradually less and the curve becomes less steep. Just beyond the addition of two equivalents of acid (= 7.04 c.c.), there is a drop in rotation which may be due to a slight decomposition of the complex formed. This is followed by the slight increase in rotation due to the addition of free tartaric acid.

## TABLE 12.

## $Na_2O.Nb_2O_5.7H_2O$.

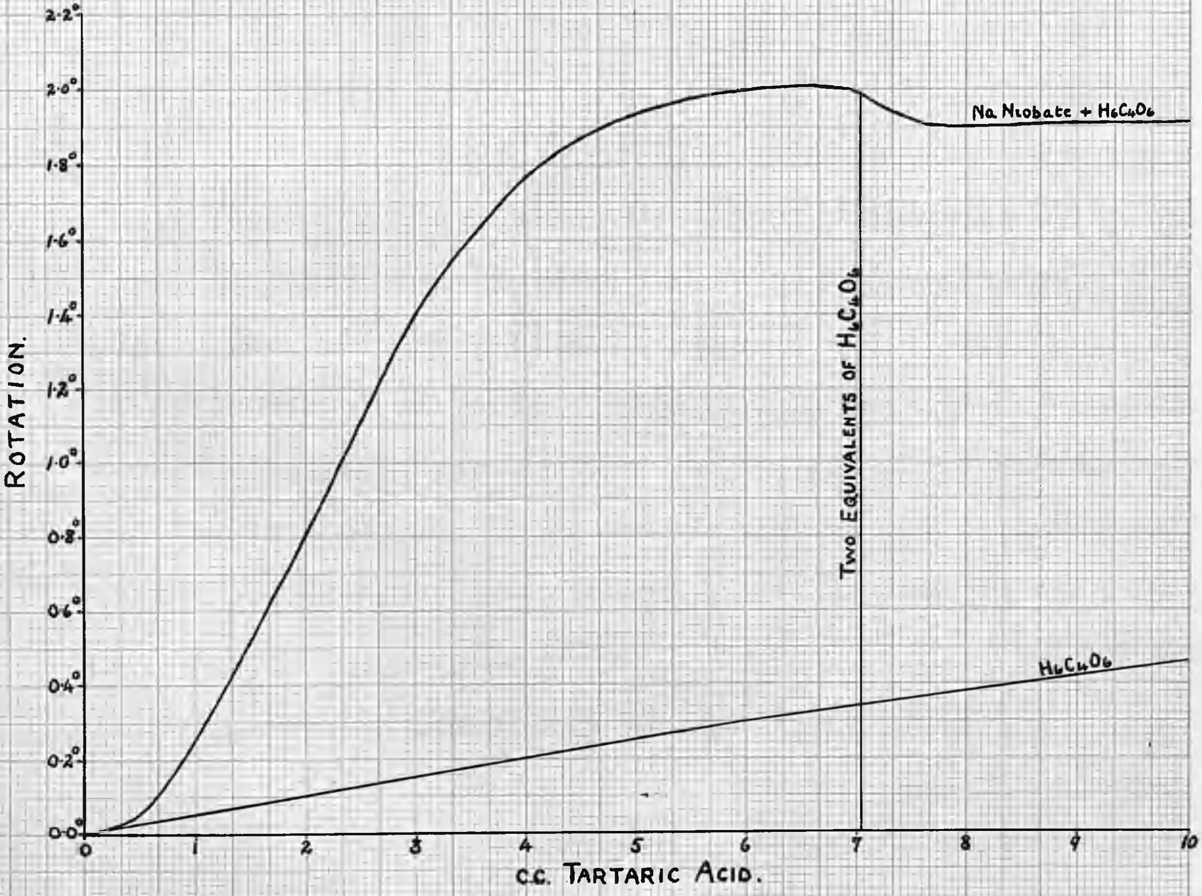
.8 gm. salt in 50 c.c. water. Titrated with N. Tartaric Acid.

| c.c. Acid. | Optical Rotation. | |
|---|---|---|
| | Na Niobate | Water. |
| 0.0 | 0.00° | 0.00° |
| 0.5 | 0.05° | |
| 1.0 | 0.25° | 0.05° |
| 1.5 | 0.52° | |
| 2.0 | 0.80° | 0.10° |
| 2.5 | 1.11° | |
| 3.0 | 1.40° | 0.15° |
| 3.5 | 1.60° | |
| 4.0 | 1.76° | 0.20° |
| 4.5 | 1.87° | |
| 5.0 | 1.93° | 0.25° |
| 5.5 | 1.98° | |
| 6.0 | 2.00° | 0.30° |
| 6.5 | 2.01° | |
| 7.0 | 1.99° | 0.34° |
| 7.5 | 1.92° | |
| 8.0 | 1.90° | 0.38° |
| 9.0 | 1.91° | 0.42° |
| 10.0 | 1.91° | 0.45° |

# FIGURE 10

## SODIUM NIOBATE WITH TARTARIC ACID.

## OPTICAL ROTATIONS.



The observed rotation for the sodium niobate - tartaric acid solution at the titre corresponding to two equivalents of acid is almost six times as great as for the same titre of tartaric acid alone. This increase in rotation of tartaric acid in presence of sodium niobate shows a parallelism to the phenomena noted by Gernez for sodium tungstate - tartaric acid. It is probably analogous also to the large increase in optical rotation shown by tartaric acid in presence of boric acid.

These results, then, give definite evidence that complex formation takes place between sodium niobate and tartaric acid. They also show clearly that, in the complex formed, two molecules of tartaric acid are combined with one molecule of sodium meta-niobate. This conclusion is in accordance with the data obtained from the conductometric titration of sodium niobate with tartaric acid noted in Table 9 and Figure 8.

## Application of the Ostwald Basicity Rule.

The Ostwald basicity rule is simply an empirical relation discovered by Ostwald during his studies of the conductivities of solutions of the sodium salts of various acids. The relation is expressed by the equation -

$$\Lambda_{1024} - \Lambda_{32} = 10.8 \text{ b}$$

where $\Lambda_{1024}$ and $\Lambda_{32}$ are the equivalent conductivities of the salt at dilutions of 1024 and 32 litres respectively, and b is the basicity of the acid.

This empirical formula, then, may be used to determine the basicity of an acid. The values of $\Lambda_{1024}$ and $\Lambda_{32}$ are determined for the sodium salts and the difference of these two values divided by 10.8 gives an approximate value of the basicity.

It was decided to carry out conductivity measurements on solutions of sodium niobate with oxalic acid at dilutions of 32 - 1024 litres per gm-equivalent and to apply the Ostwald basicity rule to the results obtained. By this means it was hoped to establish the basicity of the complex nioboxalic acid and thus obtain some idea of the composition of nioboxalates.

0.3548 gm. sodium niobate and 0.0985 gm. oxalic acid were dissolved in water and the solution made up to 50 c.c. in a graduated flask. These amounts correspond to one gm-equivalent of each constituent in 32 litres of water. The equivalent conductivity of the solution was determined.
25 c.c. of this solution diluted to 50 c.c. in a graduated flask, and a repetition of the process, gave solutions containing one gm-equivalent per 64, 128, 256, 512, and 1024 litres. The equivalent conductivity of each of these

solutions was ascertained, the conductivities being found in the manner previously described. Two separate series of determinations were carried out and also parallel experiments, for comparison, using sodium tungstate in place of sodium niobate. The results of these determinations are noted below.

### Sodium Tungstate - Oxalic Acid.

| V. | 32 | 64 | 128 | 256 | 512 | 1024 | $\Lambda_{1024} - \Lambda_{32}.$ | |
|---|---|---|---|---|---|---|---|---|
| 1. | 83.0 | 90.4 | 95.7 | 99.3 | 106.5 | 114.8 | 31.8 | 31.6 |
| 2. | 83.6 | 90.6 | 96.6 | 99.5 | 106.2 | 115.0 | 31.4 | |
| G & K | 88.4 | 94.4 | 100.3 | 105.5 | 110.7 | 117.0 | | 28.6 |

### Sodium Niobate - Oxalic Acid.

| V. | 32 | 64 | 128 | 256 | 512 | 1024 | $\Lambda_{1024} - \Lambda_{32}.$ | |
|---|---|---|---|---|---|---|---|---|
| 1. | 71.4 | 81.0 | 91.1 | 97.4 | 102.6 | 108.1 | 36.7 | 36.4 |
| 2. | 71.1 | 80.4 | 89.4 | 95.2 | 102.6 | 107.2 | 36.1 | |
| Russ. | 97.2 | 106.9 | 114.6 | 122.0 | 131.9 | 146.6 | 47.4 | 52.4 |
| Russ. | 104.7 | 114.1 | 122.5 | 131.2 | 144.1 | 162.0 | 57.3 | |

The third set of figures shown for sodium tungstate - oxalic acid (marked G & K) were determined by Grossman and Kramer (Zeitsch. anorg. Chemie, 1904, 41, 43.). The figures were obtained from Gmelin's "Handbuch der anorganischen Chemie" - 8 Auflage, System-Nummer 54, Wolfram, pages 333 - 336, as also were the other results of Grossman and Kramer which are noted subsequently. The equivalent conductivities determined here are lower than those of Grossman and Kramer and give a slightly larger value for $\Lambda_{1024} - \Lambda_{32}$.

The third and fourth set of figures shown for sodium niobate - oxalic acid were obtained by Russ, (loc. cit.), who carried out a series of conductivity measurements on solutions of the nioboxalates which he had prepared. For his measurements he used bright electrodes since he found that platinised electrodes caused catalytic decomposition of the complex. In the larger dilutions, however, he had to use platinised electrodes because of the difficulty of establishing definite minima on the wire bridge while using bright electrodes. In the present determinations platinised electrodes were used and no such decomposition took place. With the type of apparatus used, however, the solution is only momentarily in contact with the electrodes.

Applying the Ostwald basicity rule to his results, Russ calculated that the difference $\Lambda_{1024} - \Lambda_{32}$ should be $3 \times 11 = 33$ for the formula which he assigned to his salts, i.e. $R_3NbO(C_2O_4)_3$. The actual difference obtained was 52.6 and from this value Russ concludes that nioboxalic acid is a six-basic acid and that the actual composition of the salts is $R_6Nb_2O_2(C_2O_4)_6$. According to Britton and Robinson (see page 94), Russ's conclusion cannot be correct although they consider that the salts might have the composition $Nb_2O_5.6RHC_2O_4$.

The equivalent conductivities determined here for sodium niobate - oxalic acid are much lower than those obtained by Russ and give a mean value for $\Lambda_{1024} - \Lambda_{32}$ of 36.4 as compared with Russ's value of 52.6. For a tribasic acid the value would be $3 \times 10.8 = 32.4$. The observed value approximates quite closely to this figure and it would appear that the complex acid formed is tribasic. That the observed difference is greater than the calculated difference is probably due to hydrolysis.

## Tartaric, Citric, and Malic Acids.

Similar determinations of the equivalent conductivities were carried out on solutions of sodium meta-niobate with tartaric, citric, and malic acids. Two series of determinations were made for each acid and the appropriate parallels were run, using sodium tungstate in place of sodium niobate. The solutions consisted of amounts of sodium niobate or tungstate and of tartaric, citric, or malic acid in 50 c.c. water corresponding to one gm-equivalent of each constituent per 32 litres. The subsequent dilutions were obtained as previously described.

The results are given overleaf.

## Tartaric Acid.

### Sodium Tungstate - Tartaric Acid.

| V. | 32 | 64 | 128 | 256 | 512 | 1024 | $\Lambda_{1024} - \Lambda_{32}$. | |
|---|---|---|---|---|---|---|---|---|
| 1. | 75.3 | 84.8 | 90.2 | 98.0 | 102.8 | 110.7 | 35.4) | 32.9 |
| 2. | 79.0 | 87.7 | 94.2 | 98.5 | 104.2 | 109.5 | 30.5) | |
| G & K | 79.2 | 88.3 | 94.8 | 99.6 | 104.4 | 109.2 | | 30.0 |

### Sodium Niobate - Tartaric Acid.

| V. | 32 | 64 | 128 | 256 | 512 | 1024 | $\Lambda_{1024} - \Lambda_{32}$. | |
|---|---|---|---|---|---|---|---|---|
| 1. | 55.4 | 62.5 | 70.1 | 76.3 | 84.1 | 91.5 | 36.1) | 36.6 |
| 2. | 55.1 | 62.3 | 70.4 | 77.0 | 85.3 | 92.3 | 37.2) | |

## Citric Acid.

### Sodium Tungstate - Citric Acid.

| V. | 32 | 64 | 128 | 256 | 512 | 1024 | $\Lambda_{1024} - \Lambda_{32}$. | |
|---|---|---|---|---|---|---|---|---|
| 1. | 75.5 | 83.4 | 89.6 | 92.9 | 97.9 | 101.6 | 26.1) | 26.4 |
| 2. | 79.0 | 84.7 | 90.6 | 95.4 | 99.7 | 105.6 | 26.6) | |
| G & K | 79.2 | 85.1 | 90.5 | 95.9 | 100.2 | 106.4 | | 27.2 |

### Sodium Niobate - Citric Acid.

| V. | 32 | 64 | 128 | 256 | 512 | 1024 | $\Lambda_{1024} - \Lambda_{32}$. | |
|---|---|---|---|---|---|---|---|---|
| 1. | 54.9 | 62.4 | 70.8 | 77.3 | 86.0 | 94.1 | 39.2) | 39.8 |
| 2. | 53.8 | 62.0 | 70.7 | 78.5 | 87.4 | 94.3 | 40.5) | |

## Malic Acid.

### Sodium Tungstate - Malic Acid.

| V. | 32 | 64 | 128 | 256 | 512 | 1024 | $\Lambda_{1024} - \Lambda_{32.}$ | |
|---|---|---|---|---|---|---|---|---|
| 1. | 77.0 | 83.4 | 88.1 | 90.9 | 95.1 | 99.3 | 22.3) | ) 22.2 |
| 2. | 76.7 | 82.1 | 87.2 | 90.3 | 94.8 | 98.8 | 22.1) | |
| G & K | 85.9 | 90.3 | 95.5 | 99.4 | 103.0 | 106.9 | | 21.0 |

### Sodium Niobate - Malic Acid.

| V. | 32 | 64 | 128 | 256 | 512 | 1024 | $\Lambda_{1024} - \Lambda_{32.}$ | |
|---|---|---|---|---|---|---|---|---|
| 1. | 60.8 | 67.9 | 74.2 | 79.9 | 87.9 | 93.6 | 32.8) | ) 33.3 |
| 2. | 60.6 | 68.0 | 75.1 | 80.7 | 88.6 | 94.4 | 33.8) | |

The equivalent conductivities of sodium tungstate with tartaric and citric acids resemble closely those obtained by Grossman and Kramer and give approximately the same value for $\Lambda_{1024} - \Lambda_{32}$. With sodium tungstate and malic acid, however, the figures are lower than Grossman and Kramer's although the difference $\Lambda_{1024} - \Lambda_{32}$ is practically the same.

For sodium niobate the value of $\Lambda_{1024} - \Lambda_{32}$ is 36.6 with tartaric acid, 39.8 with citric acid, and 33.3 with malic acid. All of these are of the same order as the value calculated for a tri-basic acid, i.e. 32.4 . It would appear, therefore, that the complex niobtartaric, niobcitric, and niobmalic acids are similar to nioboxalic acid in that they are tri-basic.

## DISCUSSION.

### Sodium Niobate - Oxalic Acid.

The conductometric titrations of sodium niobate with oxalic acid show distinct evidence of the formation of a complex containing six molecules of oxalic acid per molecule of sodium meta-niobate. Also, the application of the Ostwald basicity rule to the equivalent conductivities at dilutions of 32 - 1024 litres per gm-equivalent shows that the complex formed is the sodium salt of a tri-basic nioboxalic acid. These facts can probably be correlated only in the following manner.

It is hardly probable that the fully hydrated niobium pentoxide or ortho-niobic acid will take part in the reaction between niobic acid and oxalic acid. It is much more likely to be a less hydrated oxide, probably the acid $H_3NbO_4$, thus :-

$$Nb_2O_5 + 5H_2O \longrightarrow 2Nb(OH)_5 \longrightarrow 2NbO(OH)_3 + 2H_2O.$$

The reaction between niobic acid and oxalic acid can be represented by the equation :-

$$2NbO(OH)_3 + 6H.C_2O_4.H \longrightarrow 2NbO(C_2O_4)_3H_3 + 6H_2O.$$

Applying this reaction to sodium niobate and oxalic acid, the following equation is obtained :-

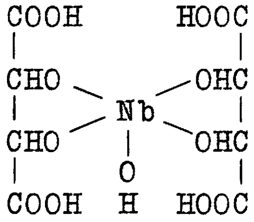
$$Na_2O.Nb_2O_5 + 6H.C_2O_4.H \longrightarrow 2NaH_2(NbO)(C_2O_4)_3 + 4H_2O.$$

It will be seen that the above reaction satisfies the facts obtained from the experimental work in that it gives a nioboxalic acid, $H_3NbO(C_2O_4)_3$, which is tri-basic, and also that six molecules of oxalic acid will react with one molecule of sodium meta-niobate to give two molecules of an acid sodium nioboxalate of composition $NaH_2(NbO)(C_2O_4)_3$.

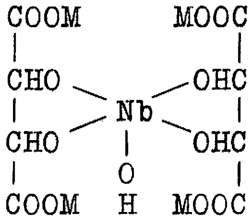
## Sodium Niobate - Tartaric Acid.

The experimental evidence from the optical rotations of sodium niobate with tartaric acid, supported by that from the conductometric titrations, points to the formation of a complex niobtartrate containing two molecules of tartaric acid per molecule of sodium meta-niobate. Application of the Ostwald basicity rule to the equivalent conductivities at dilutions of 32 - 1024 litres per gm-equivalent shows that the complex is the sodium salt of a tri-basic niobtartaric acid.

It is considered that the reaction is more complex in this case than in the case of oxalic acid, because of the presence of the alcoholic hydroxyl groups in the tartaric acid. It seems fairly definite from the evidence brought forward by Edmister and Albritton (see page 85) that the linkage resembles that of, say, boric acid with tartaric acid and takes place through the hydrogen of the hydroxyl groups and not of the carboxyl groups. Edmister and Albritton, as has been stated, assigned to niobtartaric acid and its salts the following formulae :-



and



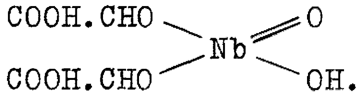
Niobtartaric Acid.

Alkali salt where M represents the alkali metal.

According to this formula for the alkali niobtartrate, the complex acid is tetra-basic. Edmister and Albritton have not, however, taken into account the remaining hydroxyl group attached to the niobium, and it seems more probable that the formula postulated by them demands the consideration of niobtartaric acid as a five-basic acid. Also, one molecule of sodium meta-niobate would require four molecules of tartaric acid to promote the complex suggested by Edmister and Albritton, whereas the experimental evidence obtained here shows clearly that only two molecules of tartaric acid are combined.

The following suggestion is therefore put forward :-

That the combination of tartaric acid with niobic acid takes place through the alcoholic hydroxyl groups, as was suggested by Edmister and Albritton, but that only one molecule of tartaric acid combines with an atom of niobium, the suggested formula for the complex acid being :-



Applying this to the reaction of tartaric acid with sodium niobate, we get the equation :-

$$Na_2O.Nb_2O_5 + 2H.C_4H_4O_6.H \longrightarrow 2NaH_2(NbO_2)(C_4H_2O_6) + 2H_2O.$$

It will be seen that this suggestion satisfies the experimental data in that it gives a tri-basic niobtartaric acid, $H_3(NbO_2)(C_4H_2O_6)$, and also that two molecules of tartaric acid will react with one molecule of sodium meta-niobate to give two molecules of an acid sodium niobtartrate, $NaH_2(NbO_2)(C_4H_2O_6)$.

As regards the niobcitric and niobmalic acids, the only thing that can be said is that they are tri-basic. Since these acids contain but one alcoholic hydroxyl group, their reactions with niobic acid will not be similar to that of tartaric acid nor is it probable that they will be similar to oxalic acid because of the presence of that hydroxyl group. Further experimental data will, therefore, have to be available before any suggestion can be made as to their composition.

An examination of the literature and the results of the present work have given rise to the opinion that some sort of hydrolytic equilibrium is set up between niobic acid and tartaric or oxalic acids, or their sodium salts. It seems possible to adjust this equilibrium so that a definite complex acid, or salt of a complex acid, may be crystallised from the solution. It is difficult, however, to draw a definite line between actual complex formation and the peptization effects of those organic acids on niobic acid. The complex ferri- and chrom-tartrates, for example, do not give optically clear solutions and always contain some hydroxide in the hydrosol form, although it is known that they do form actual complexes. The salts obtained from such solutions are, of course, contaminated with hydroxide and cannot be regarded as individual substances. It seems probable that similar conditions will exist in many of the niobtartrate and nioboxalate solutions, although these solutions may be optically clear.

To quote Britton and Robinson (loc. cit.) - "The true explanation will not be forthcoming until we have a greater knowledge of solutions that are intermediate between true and obviously colloidal solutions".

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I wish to express my sincere thanks to Professor Henderson and to Dr. Mair for their constant interest and invaluable assistance during the course of this work. I also wish to thank Mr.J.L.Cameron of the Organic Chemistry Dept. for carrying out micro-combustions for nitrogen on the guanidine niobates.

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