gas", except in so far as this gas is likely to give a hot and strongly oxidizing flame, when used in burners having an air supply, designed for a gas requiring more oxygen.

The behavior of platinum when heated under the last five conditions may be explained by the hypothesis that a volatile oxide of platinum is formed, stable at high and low temperatures, but unstable at intermediate temperatures, like the platinous chloride (Pt Cl_2) of Troost and Hautefeuille.¹

If, as is the case in the blast-flame, the compound is swept away or if, as in the porcelain furnace in the combustion tube and with the heated wire, there is no cooler part of the platinum, upon which the metallic product of the decomposition of the hypothetical oxide can settle, the platinum loses weight. If on the contrary the flame is a quiet one, as is the case when a crucible is heated in a Bunsen flame, and only a part of the metal is very strongly heated, the hypothetical oxide decomposes at once on emerging from the most strongly heated zone and the platinum is deposited on the cooler part of the crucible, producing the molecular change of the surface, without gain or loss of weight, noticed by Erdmann and Crookes.

It is hoped to continue this work in this laboratory, to examine the deposit, to test the behavior of purer platinum, to try to isolate the hypothetical oxide and to fix, if possible, the conditions under which commercial platinum may be heated to whiteness without loss.

LABORATORY OF ANALYTICAL CHEMISTRY, HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY, June, 1900.

THE PRECIPITATION OF THE SULPHIDES OF NICKEL AND COBALT IN AN ALKALINE TARTRATE SOLUTION, TOGETHER WITH AN INVESTIGATION INTO THE NATURE OF CERTAIN TARTRATES OF THESE METALS.

By O. F. TOWER. Received June 19, 1900. INTRODUCTION.

VILLIERS² recommended some time ago a method for the qualitative separation of nickel and cobalt based on the action of hydrogen sulphide on an alkaline solution of the tartrates

¹ Compt. rend., 84, 946 (1877).

² Ibid., 119, 1263, and 120, 46 (1894-95).

of these metals. This method as commonly carried out may be stated as follows: The solution of the sulphides of nickel and cobalt in aqua regia is evaporated to expel chlorine, and after suitable dilution sufficient tartaric acid is added to prevent precipitation by sodium hydroxide. This last reagent is then added until the solution is strongly alkaline, and hydrogen sulphide run in to saturation. Cobalt sulphide is precipitated, while nickel sulphide remains in solution, imparting to the solution a dark color. When nickel is present only in very small quantities the color is brown; with larger quantities it is a jet black.

The failure of this method to give good results in the hands of students, has led to a critical investigation of it, the results of which are given in the following pages. In order to be able to approach this subject intelligently this account will be preceded by an account of an investigation into the nature of some tartrate solutions of nickel and cobalt, together with a description of any such tartrates which it has been found possible to isolate.

All substances before being analyzed were dried in an air-bath at 120° .

Nickel and cobalt were always determined electrolytically following in most respects the method of Fresenius and Bergmann,' which may be outlined as follows: To the solution containing nickel or cobalt, which is free from chlorides, are added 100 cc. ammonia solution (sp. gr. 0.96) and 10 cc. of a solution of ammonium sulphate (305 grams to liter). A current from two storage battery cells (3.2 volts, 0.48 ampere) was passed through the solution for from four to five hours. This length of time was found to be sufficient to effect complete precipitation of the metal (quantities not exceeding 0.1100 gram), provided tartrates were absent. It was necessary, however, to determine these metals frequently in the presence of tartrates. In such cases the amount of metal deposited at the end of four or five hours was weighed, removed from the electrode, and the apparatus then reconnected and left running all night. The results were then very satisfactory.

Potassium was determined as sulphate. After removing the nickel either by precipitation as sulphide or by electrolysis, tar-

Ztschr. anal. Chem., 19, 314 (1880).

taric acid was destroyed by gentle ignition, and the potassium then converted into sulphate by heating with ammonium sulphate.

TARTRATES OF NICKEL.

The effect of tartaric acid in preventing the precipitation of the hydroxides of nickel and cobalt has been known since the time of Rose,¹ and since then has been frequently discussed. The literature on the preparation of well-defined tartrates of these metals is, however, rather meagre.

That nickel tartrate cannot be precipitated from solutions of nickel salts is well known. Werther² prepared it by saturating a boiling solution of tartaric acid with freshly precipitated nickel hydroxide. The substance was thrown down as a pale green powder practically insoluble in hot or cold water, but soluble in warm alkalies. This has been essentially confirmed. The precipitate is apparently amorphous, although Werther considered it crystalline. The filtrate is still colored green, showing that precipitation is incomplete, but what is precipitated is extremely insoluble in water. The substance washed and dried at 120° yielded 28.44 per cent. nickel. The theoretical percentage of nickel in NiC, H,O, is 28.39. This substance dissolves readily in alkalies, only when they are present in large excess. To effect solution, considerably more potassium hydroxide is required than a quantity equivalent to the nickel tartrate; that is, more than two molecules potassium hydroxide to one nickel tartrate, and the action is greatly accelerated by heating. The behavior of this nickel tartrate toward atmospheric moisture is worthy of remark. The precipitated powder dried at 50° still contains moisture. In this condition, however, it neither deliquesces nor effloresces, the moisture content remaining constant. On the other hand no definite hydrate seems to exist, for different samples on drying at 120° were found to contain different percentages of residual water. Furthermore, the water-free substance is not in the least hygroscopic. When exposed under a bell-jar to an atmosphere saturated with moisture, it does not gain in weight more than a milligram or two in several weeks. Nickel tartrate can be made

¹ Gilbert's Annalen, 73, 74, foot-note (1823).

² J. prakt. Chem., 32, 400 (1844).

equally well by treating a hot solution of tartaric acid with nickel carbonate.

Fresenius' prepared a hydrated racemate of nickel from nickel acetate and racemic acid. It resembles nickel tartrate in some of its characteristics but was not further investigated.

If freshly precipitated nickel hydroxide is treated with cold dilute tartaric acid, the nickel hydroxide dissolves, imparting to the solution a green color, probably due to the formation of nickel tartrate. On warming this solution the light green powder mentioned above precipitates. To determine the molecular size of the substance in solution, a solution was prepared by treating an excess of nickel hydroxide with a known quantity of tartaric acid, and then finding the freezing-point of the resulting solution. The reaction between nickel hydroxide and tartaric acid is very slow, so that after five days' standing free tartaric acid was still present in sufficient quantity to redden blue litmus paper, 2 or 3 milligrams of the acid being uncombined. This was not sufficient to influence materially the results which follow. The apparatus employed for the freezing-point determinations was Beckmann's improved form,² and is particularly designed to exclude moisture from the solution during the process. This is accomplished by operating the stirrer by means of an electromagnet, thereby obviating the necessity of having a hole through the stopper for the stirring shaft. Since aqueous solutions were used in these experiments, the exclusion of moisture made very little difference, but this form of apparatus has other advantages. It is exceedingly convenient, requiring the operator's attention only for a few minutes at the time of freezing, and besides the regularity of stirring insures greater accuracy. Individual determinations of the freezing-point of the same substance did not vary more than 0.002°. Five cells of a storage battery were used to supply power for the electromagnet. Table I gives the results with solutions of nickel tartrate prepared as indicated above. The last four are with different concentrations of the same solution. The strength of such solutions was always determined by precipitating the nickel in an aliquot portion by electrolysis.

¹ Ann. Chem. (Liebig), 41, 23 (1842).

² Zischr. phys. Chem., 21, 239 (1896).

	TABLE I.	
Amount NiC ₄ H ₄ O ₆ in 100 cc. solution. Grams.	Depression.	Apparent Molecular weight.
1.8795	0.139°	260
1.7205	0.121 ⁰	273
0.8602	0.081°	202
0.4301	0.042 ⁰	193
0.2150	0.025°	163
M	Iolecular weight of $NiC_4H_4O_6 = :$	206.8.

In the case of the more concentrated solutions these results show the molecular weight calculated from the lowering of the freezing-point to be higher than that calculated from the formula. One would expect, however, the reverse, because of dissociation in aqueous solution. By the freezing-point method Kahlenberg has shown the apparent molecular weight of potassium tartrate in solutions of moderate strength to be about one-half that calculated from the formula, $K_2C_4H_4O_6^{1}$. These facts lead to the conclusion that nickel tartrate exists in fairly concentrated solutions largely in the form of double molecules.

Determinations of the electrical conductivity of these solutions show abnormal results also. In Table 2, *m* is the fraction of a gram-equivalent $(\frac{1}{2}NiC_4H_4O_6)$ in a liter; L is the equivalent conductivity expressed in reciprocal ohms.²

m

	1 A I	SLE 2.	
Tempe	rature 18°.	Temperat	ure 25°.
Nickel	tartrate.	Magnesium	tartrate.8
<i>m</i> .	L.	m.	L,
0.1664	8.29	0.03125	54.9
0.0832	9.34	0.0156	64.1
0.0416	10.8	0.0078	74.0
0.0208	18.7	0.0039	82.6
0.0104	26.5	0.0020	90.1
0.0052	36.8	0.0010	95.9
0.0026	48.8		
0.0013	63.6		

The values of the conductivity of nickel tartrate are exceptionally small, as will be seen by comparing them with the values for magnesium tartrate, which illustrate normal conduc-

1 Ztschr. phys. Chem., 17, 585 (1895).

² These units are those proposed by Kohlrausch, and fully described in "Leitvermogen der Elektrolyte," by Kohlrausch and Holborn.

8 Determinations by Walden, Ztschr. phys. Chem., 1, 537 (1887), recalculated by Kohlrausch and Holborn.

tivities of tartrates of this class. The different behavior of nickel tartrate can only be ascribed to a peculiar constitution of the salt itself. In seems reasonable to suppose that a substance COONiOOC

with the atoms arranged in this way CHOH CHOH might

COONiOOC well suffer less dissociation than a normal tartrate. Dissociation in concentrated solutions would probably be of the nature, $\stackrel{+,+}{\text{Ni}}$ and $C_4H_4O_6\text{Ni}C_4H_4O_6$. On dilution this anion itself would gradually be decomposed, so that the conductivity would not advance with the same regularity as it does in the case of simple binary electrolytes. In Table 2, the results with nickel tartrate show such behavior, as is seen by comparison with the value for magnesium tartrate. Such a formula as the above will also explain very satisfactorily the results obtained from the freezingpoint method. Measurements of the electromotive forces with solutions of this kind will not be given, until the facts relating to some other tartrates of nickel have been discussed.

Fabian¹ prepared potassium nickel tartrate by allowing cream of tartar to act on nickel carbonate at a temperature of about 50° . On evaporating the solution obtained over sulphuric acid a greenish substance was deposited, which effloresced on exposure to air and was soluble in water. After drying this substance at 110° and analyzing, he obtained the following results :

:	Found.	Theory for NiK ₂ C ₈ H ₈ O ₁₂ .
P	er cent.	Per cent.
NiO	16.8	17.3
K ₂ O	20.9	21.7

This work has been repeated with essentially the same results. Cream of tartar was allowed to stand in contact with an excess of nickel carbonate at about 40° for some time. The green solution was filtered off, and left to evaporate over sulphuric acid. No definite crystals were obtained, neither by evaporating rapidly in a partial vacuum nor slowly in the air with a string.

The residue was invariably of a scaly appearance possessing ¹ Ann. Chem. (Liebig), 103, 248 (1857).

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a very light green color. The results of the analysis of this substance are:

	Found. Per cent.	Theory for K ₂ NiC ₈ H ₈ O ₁₂ Per cent.
K	18.21	18.06
Ni	13.38	13.55

According to Fabian, on boiling a solution of this substance a gelatinous mass separates out, which cannot be washed completely free from alkali. This has been found to be true, the precipitate being rather flocculent and of a very light green color. If, however, a solution of potassium nickel tartrate is digested for some time at about 75°, a light green pulverulent precipitate can be obtained, which was supposed to be a basic tartrate of nickel. After washing it thoroughly and drying at 120°, analysis proved it to be identical with the insoluble nickel tartrate already described, a sample yielding 28.25 per cent. nickel. On long standing this decomposition takes place gradually at lower temperatures. It is, therefore, necessary to exercise care in the preparation of potassium nickel tartrate, for, if tartaric acid is digested for a long time with nickel carbonate, some of the potassium nickel tartrate formed is apt to decompose in this manner:

> Insoluble form $K_2 \operatorname{NiC}_8 H_8 O_{12} = \operatorname{NiC}_4 H_4 O_6 + K_2 C_4 H_4 O_6.$

When the solution is filtered, the potassium tartrate passes through with the potassium nickel tartrate, and remains mixed with it on evaporation. This is revealed by the percentage of potassium being too high and that of nickel too low to correspond to the formula $K_sNiC_sH_sO_{12}$.

Determinations of the molecular weight of this substance were made by means of the freezing-point method. For this purpose different solutions were employed,—some prepared as above described, some by dissolving the solid substance in water, and others by dissolving nickel hydroxide in the proper amount of tartaric acid and adding that quantity of potassium hydroxide just sufficient to form $K_2NiC_8H_8O_{12}$. The results follow : O. F. TOWER.

TABLE 3.

к	Amount $_{2}NiC_{8}H_{8}O_{12}$ in 100 cc. solution. Grams.	Depres- siou.	Apparent molecular weight.
Solution prepared direct from	(3.764	0.434	162
Nico and HKC H O	{ 1.88 2	0,255	140
MCO_3 and $MCC_4M_4O_6$	(0.941	0.170	105
Solid substance dissolved in	3.752	0.430	165
water	ίĭ.876	0.253	140
	3.295	0.419	153
Solution prepared from Ni(OH),	1.6475	0.246	128
$H_{2}C_{4}\hat{H}_{4}O_{6}$ and $KOH \dots$	0.8238	0,139	112
	0.4119	0.079	98
Molecular weight of I	K, NiC, H,O1.	= 433	

It is essential to know something about the dissociation of this substance before one can judge intelligently of its true molecular size. To throw light on this subject the electrical conductivity of a solution of potassium nickel tartrate was measured. The equivalent conductivity is given on the basis of one potassium atom $(\frac{1}{2}$ molecule $K_2 NiC_2 H_3 O_{12}$ in a liter).

	TABI	Æ 4.	
Temperature 18°. Potassium nickel tartrate.		Temper Sodium	ature 25°. tartrate.1
m,	L.	т.	L.
0.1522	74.6		
0.0761	84.3	· · · · · · ·	
0.0381	94.2	0.03125	87.1
0.0190	IOI	0.0156	93.2
0.0095	114	0.0078	98.2
0.0048	124	0.0039	102.1

The conductivity of the double tartrate is increasing with the dilution much faster than that of the sodium tartrate. This is undoubtedly due to the dissociation of potassium nickel tartrate mostly into \mathbf{K} ions and $Ni\mathbf{C}_s\mathbf{H}_sO_{12}$ ions in the more concentrated solutions. On dilution, however, the nickel also begins to dissociate from the complex anion, thus causing the rapid increase in the conductivity. For corresponding concentrations the conductivity of the double tartrate always exceeds that of the sodium tartrate.

Kahlenberg,' in his article on complex tartrates of lead and

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The conductivity of sodium tartrate is given for comparison. The results are those of Bredig, Ztschr. phys. Chem., 13, 191 (1894), recalculated by Kohlrausch aud Holborn.
2 Ztschr. phys. Chem., 17, 577 (1895).

copper, found that these substances were probably dissociated sufficiently, so that the apparent molecular weight was about one half the true molecular weight. The solutions of potassium nickel tartrate used here were, however, a little more dilute than Kahlenberg's solutions ; besides the substances are somewhat different in nature. Table 3 shows the apparent molecular weight to be only a little more than $\frac{1}{3}$ of the molecular weight of K, NiC, H, O₁₂. This may be accounted for on two hypotheses; either the substance is in large part dissociated into \vec{K} , \vec{K} and Ni $\vec{C_sH_sO_1}$ ions as was indicated in connection with the conductivity measurements, or there exist separately in the solution potassium tartrate and nickel tartrate, the former dissociated, the latter, however, not. The evidence seems to favor the former of these hypotheses. For, if the second were correct, one would expect the deposit left on evaporation of the solution not to have a uniform composition. But the deposit on the side of the dish was of the same composition as that on the bottom. Furthermore, washing the deposit slightly with water had no effect on its composition. If the substance had been a mixture of potassium tartrate and nickel tartrate, this treatment would very likely dissolve more of the former salt than of the latter.

The fact that the addition of tartaric acid to solutions of nickel salts prevents the precipitation of nickel hydroxide is usually explained by the supposition that in such cases the nickel replaces the hydrogen atoms of the alcoholic hydroxyls of the tartaric acid, while the potassium takes the place of the two carboxyl hydrogen atoms. The formula of such a substance

COOK

ĊHO would be | >Ni. To see if any experimental basis can be CHO

COOK

found for this view, solutions of nickel tartrate, to which potassium hydroxide had been added, were investigated by the usual physico-chemical methods.

The freezing-point method was first employed in order to observe the effect on the size of the molecule of successive

additions of potassium hydroxide¹ to a solution of nickel tartrate.

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TABLE 5.
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Solu	ation containing :	1.8795 grams nicl	kel tartrate in 100 cc.
Expt. No.	KOH added to above solution. Gram.	Depression.	Remarks.
I	0.0000	0.139°	Reaction acid.
2	0.1226	0.180	Reaction alkaline.
3	0.3270	0.187	
4	0.5314	0.134	
5	0.7358	0.180	Solution jelly-like.
6	0.8175	0.156	
7	1.311	0.233	

In Experiment 7, the quantity of potassium hydroxide is just sufficient to form, with the nickel tartrate, $K_2NiC_4H_2O_6$. In the fourth the depression is a minimum, and here the amount of potassium hydroxide added is nearly one half that added in the seventh, or the ratio is about one molecule potassium hydroxide to one nickel tartrate. If the molecular weight is calculated from the depression, 0.134° , on the basis of NiKC₄H₅O₆ existing in solution, 299 is obtained. The molecular weight according to the above formula is in round numbers 245. This case is almost exactly parallel to the results obtained by Kahlenberg² with certain alkaline tartrate solutions of lead and copper. So undoubtedly the molecular size of the substance here is about twice that represented by the formula NiKC₄H₅O₆, and following Kahlenberg the molecular structure may be represented as

	COOK	KOOC				
follows :	CHOH CHOH CHOH	HOHC HOHC	Such	а	substance	would

hardly be expected to dissociate so as to yield nickel ions. The evidence for such a molecular structure would, therefore, be increased, if it could be shown that no nickel ions exist in the solution.

For this purpose measurements were made of the electromotive force generated by an element with nickel electrodes, one

2 Loc cit.

¹ Sodium hydroxide was also employed, but since the results are similar, only those with potassium hydroxide are given.

electrode being surrounded by a solution of a nickel salt of known concentration and the other surrounded by the solution in question. The electromotive force of such an element is expressed by the formula,

$$\pi=\frac{\mathrm{RT}}{n\mathrm{E}_0}\,\ln\frac{c_1}{c_2}\,,$$

where the letters indicate the usual quantities, c_1 and c_2 being the concentration of the nickel ions in the two solutions. Evaluating the equation for R = 8.311 electrical units, T = 291 (18° C.), *n*, the valence of nickel = 2, $E_0 = 96,540$ coulombs, and reducing to Briggs' system of logarithms, one obtains,

$$\pi = 0.02881 \log \frac{c_1}{c_2}$$

Measurements were made according to the Poggendorf-Ostwald method with a Lippmann capillary electrometer. The nickel solution of constant concentration was in every case a solution of nickel nitrate containing 0.1 gram-molecule in a liter. The electrodes were made by covering platinum electrodes with nickel by electrolysis. These electrodes were tested by connecting them with an electrometer, when they were dipping into the same solution of nickel nitrate. Under these conditions the electrometer reading should be zero. Few electrodes, however, could be found which would fulfil this condition. Those chosen showed potential differences of not more than 0.003 volt. Measurements were made first of the electromotive forces between the standard solution and solutions of nickel nitrate containing 0.05 and 0.01 gram-molecule in a liter, respectively, and afterwards with the solutions of nickel tartrate under consideration. In each case the electrodes were reversed and the potential difference measured again. The averages of the two readings so obtained are given in Table 6.

TABLE 6.

Temperature 18^c.

No.	Between 0.1 mol. Ni(NO3)2 and	ob ser ved. Volt.	calculated. Volt.
I	0.05 mol. $Ni(NO_3)_2$	0.010	0.0087
2	0.01 " " 10.0	0.032	0,0 28 8
3	0.0208 '' $(NiC_4H_4O_6)_2$	0.048	· · · · · ·
4	0.0761 " NiK ₂ C ₈ H ₈ O ₁₂	0.075	• • • • • •
5	0.0572 "KC ₄ H ₄ O ₆ NiONiO ₆ H ₄ C ₄ K ₂	0.210	· · · · · · ·
Ğ	0.0748 '' K,NiC,H,O,	0.236	

Where the concentration of the nickel ions was known the electromotive force has been calculated from the formula. The agreement is seen to be fairly good. Nos. 3 and 4 are measurements with the solutions already mentioned of nickel tartrate and potassium nickel tartrate, respectively. The potential differences show that the concentration of the nickel ions in these solutions is somewhat less than in a 0.01 mol. solution of nickel nitrate. Fewer nickel ions are present in the potassium nickel tartrate solution than in the solution of nickel tartrate, which was to be expected, for the same reason that the replaceable hydrogen atom of an acid salt is only very slightly dissociated.¹

To find the concentration of the nickel ions in solution 5, which is the one formed by adding to 100 cc. of a solution containing 18.795 grams of nickel tartrate, 0.5314 gram of potassium hydroxide,² 0.210 is substituted for π in the formula and c_1 is made equal to 0.1 \times 0.8, for 0.1 mol. nickel nitrate is about 80 per cent. dissociated. From this the value of c_2 is found to be 10^{-8.386}. This shows that, relatively speaking, no nickel ions are in the solution, which is corroborative evidence of the existence of the molecular structure ascribed to this substance on page 510.

Referring to Table 5, it will be noticed that the depression gradually increases with the addition of potassium hydroxide from the fourth experiment to the seventh, except in No. 5. In this case the contents of the tube were viscous having the consistency of thin jelly, which interfered materially with the determination. This gelatinous mass completely dissolved on addition of more potassium hydroxide. The appearance of this substance is peculiar. The green liquid simply solidifies to a transparent mass without any change in appearance. On reversing the tube containing the substance it is found to be solid or viscous according to the amount of water present, and this is the only evidence of a change. On standing for a length of time it gradually becomes opaque. Several years ago this phenomenon was observed by Professor Bradley, of Middletown, who called my attention to it at that time. He obtained it by adding first tartaric acid to a solution of nickel sulphate and then adding a solution of potassium hydroxide drop by drop

1 For the discussion of this, see Ostwald : Ztschr. phys. Chem., 9, 553 (1892).

2 See Table 5

until the mass gelatinized. As can be seen from Table 5, it is formed when about one molecule of nickel tartrate is treated with one molecule of potassium hydroxide. It was shown just before the solution gelatinized (experiment 4, Table 5), that from the depression of the freezing-point and other considerations the molecule probably is $KC_4H_4O_6NiONiO_6H_4C_4K$. It is, therefore, possible that this gelatinous mass is a hydrated form of that substance. Heating almost to the boiling-point completely dissolves it.¹

To return to the effect on the depression of the freezing-point of adding potassium hydroxide, as seen in Table 5 from Experiment 4 on. Leaving out of consideration No. 5, where the solution was viscous, the increase in the depression from 0.134° to 0.156° and in the last case to 0.233° is by no means sufficient to be equal to the entire effect of the potassium hydroxide added, if it existed as such in the solution. 0.4935 gram more of potassium hydroxide was added in Experiment No. 7 than in No. 6. This quantity of potassium hydroxide should give normally a depression of 0.121° ,² but the difference between 0.233° and 0.156° is only 0.077° . In No. 7 the proportion of potassium hydroxide to nickel tartrate is two molecules of the former to one of the latter, or in the proper ratio to form

KOOC

OCH

Ni < | , the molecular weight of which is 283. The apparent OCH

коос

¹ Since writing this, Prof. Bradley has kindly allowed me to look over an unpublished manuscript by himself and F. A. Johnston on "A Tartrate of Sodium and Nickel," which treats of the formation, conduct, and gives some results of the analysis of this gelatinous substance. It was prepared from nickel sulphate, tartaric acid, and sodium hydroxide. It was isolated by stirring it up in alcohol, filtering and then washing with an equal volume of alcohol and water. When so treated the gelatine frequently remains transparent for a long time. It was found difficult to dry it to constant weight over sulphuric acid, for it is exceedingly hygroscopic. Preliminary analysis of the substance after drying over sulphuric acid showed: water, 7.04 per cent.; sodium, 6.30 per cent.; nickel, 21.04 per cent. We obtain by calculation from the above formula plus 2 molecules of water, Na₂Ni₂C₄H₈O₁₃ + 2H₈O: water, 7.04 per cent.; sodium, 9.00 per cent.; nickel, 23.95 per cent. The most marked difference between these results and the results of the analysis is in the percentage of sodium. This may be accounted for from the fact that the gelatine is strongly alkaline and that washing removes some of this alkali, so that the residue may not have a constant composition. However, it is not asserted that the above formula represents the composition of the substance, for more analyses are needed in which the amount of tartaric acid is also determined, before the differences in the above results are explained and a suitable formula established. ² Calculated from the constant for potassium hydroxide reported by Raoult Anz

² Calculated from the constant for potassium hydroxide reported by Raoult, Ann. chim. phys. (5), 28, 137 (1883).

molecular weight calculated from the depression, 0.233 is 185, which is a little more than half that calculated from the formula. Since such a substance would probably be dissociated in aqueous solution about as much as potassium tartrate,¹ it is very likely that a substance of the above formula does really exist in the solution. Nickel ions would not be expected to be present in any quantity in a solution of such a substance. The potential difference found between this solution and 0.1 mol. nickel nitrate is 0.256 volt (No. 6, Table 6). This shows that the concentration of the nickel ions is even less than in the preceding solution (No. 5), where the concentration of these ions was found to be $10^{-8.386}$. What has, therefore, probably taken place on the addition of potassium hydroxide from solution 4 to solution 7, Table 5, is that, although the potassium hydroxide is continually being removed from the field of action as such, the molecular structure of the substance in solution is undergoing a change; that is, the complex molecule, $KC_4H_4O_6NiONiO_8H_4C_4K_4$, is breaking up into the smaller molecule, K, NiC, H, O,; the number of molecules is, consequently, on the whole increased, and the depression of the freezing-point becomes greater.

TARTRATES OF COBALT.

Very little literature of a definite nature could be found on this subject. A tartrate of cobalt and a double tartrate of potassium and cobalt are mentioned in the following dictionaries of chemistry: Fehling's, Vol. 9 (1864); Watts', Vol. 5 (1868); Wurtz's, Vol. 3 (1878). Nearly all the early journals and such periodicals as Berzelius' *Jahresbericht*, Liebig and Kopp's *Jahresbericht*, the *Pharmaceutisches Centralblatt*, &c., were thoroughly searched, but no reference was found to the original articles describing these salts. Such works as Ladenburg's Dictionary, edition 1894, and Beilstein's, third edition, mention no such substances. It is, therefore, to be inferred that the original article contained nothing very definite. Fresenius² prepared certain racemates of cobalt, but gives no analyses.

Cobalt tartrate can be made in the same manner as nickel tartrate, by saturating hot tartaric acid with cobalt hydroxide

¹ See Kahlenberg, loc. cit.

² Ann. Chem. (Liebig), 41, 22 (1842).

or carbonate. It is thown down as a pale pink powder practically insoluble in hot or cold water, and possessing in general the other properties of nickel tartrate. A sample of this dried at 120° gave 28.32 per cent. cobalt (theory, 28.49 per cent.).

When cobalt hydroxide is treated in the cold with tartaric acid it dissolves to a certain extent a pink solution resulting, which, on standing, deposits reddish pink crystalline scales of cobalt tartrate. This crystalline substance differs from the cobalt tartrate just described by being somewhat soluble in water. It is impossible to obtain as concentrated solutions of cobalt tartrate as of nickel tartrate, for the reason just mentioned, that some of the salt crystallizes out. With, however, as strong a solution as could be obtained the following determinations were made of the depression of the freezing-point.

TABLE 7.

Amount CoC, H.O.

in 100 cc. solution. Gram.	Depression.	Apparent molecular weight.
0.6505	o.o59 [്]	207
0.3252	0.036	170
0.1626	0,021	146
Molecular	weight of CoC ₄ H ₄ O ₄	= 207.1.

These results run about the same as those obtained with solutions of nickel tartrate of similar concentration. The apparent molecular weight, 207, is very nearly equal to the molecular weight calculated from the formula; therefore, for the reasons already mentioned, the true molecular weight of cobalt tartrate is probably twice 207.1, which means its structure would be represented by twice the above formula or $(CoC_4H_4O_6)_2$. Table 8 gives the results of the determination of the electrical conductivity of solutions of this substance. The units are on the basis of equivalent ($\frac{1}{2}$ CoC₄H₄O₆) in a liter as before.

TABLE 8

Temperature 15	Tem	pera	ture	18°.
----------------	-----	------	------	------

<i>m</i> .	L.
0.0628	15.9
0.0314	22 . I
0.0157	28.7
0.0079	37.6
0.0039	47.1
0.0020	58.4
0.0010	69.9
0.0005	82.1

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These results are entirely analogous to the conductivity of nickel tartrate (Table 2). They are abnormally small and show that cobalt tartrate is only slightly dissociated, which affords additional evidence that the molecule is polymerized.

Cream tartar acts vigorously on cobalt carbonate in the presence of water, the resulting solution being colored a deep pink. When this solution is evaporated over sulphuric acid, reddish pink crystalline scales are deposited, very similar in appearance to the deposit from a solution of cobalt tartrate. When almost to dryness the solution assumes a pasty nature, and can be completely dried only with considerable difficulty. No salt of the formula, K,CoC,H,O,,, could be isolated. The crystalline deposit just mentioned yielded on drying 24.53 per cent. cobalt,' and a small quantity of potassium was also found. The deposit, therefore, consists largely of cobalt tartrate, but a small amount of potassium tartrate is mixed with it. Watts' "Dictionary," and the others above cited, say that potassiocobaltous tartrate forms large rhomboidal prisms. No such crystals could be obtained by any of the methods used here. Determinations of the freezing-point of solutions prepared from cream tartar and cobalt carbonate yielded essentially the same results as similar solutions prepared from nickel carbonate. Such results might well be in harmony with the separate existence in the solution of potassium tartrate and cobalt tartrate, so no definite knowledge of the nature of the molecules in solution could be obtained by this method. Heating this solution causes the precipitation of a light pink powder. After washing this and drying at 120°, 28.38 per cent. cobalt was found which showed it to be cobalt tartrate. This substance possesses all the properties and is apparently identical with the cobalt tartrate previously mentioned.² It is to be noted that the conduct of this solution on heating is somewhat different from that prepared from nickel carbonate and cream tartar, for a flocculent precipitate resulted on heating this latter to boiling.

When potassium hydroxide is added to a solution of cobalt tartrate the conduct is very similar to that when it is added to a solution of nickel tartrate. It differs, however, in this respect,

² That prepared by treating hot tartaric acid with cobalt hydroxide.

¹ The theoretical percentage of cobalt according to formula $K_2CoC_6H_6O_{12}$, is 13.61.

that when the quantities of potassium hydroxide and cobalt tartrate are in the proportion of one molecule of the former to one of the latter, instead of obtaining a gelatinous mass, a *flocculent* precipitate results, which readily dissolves on further addition of potassium hydroxide. The range of the existence of this precipitate is considerable; that is, it begins to form when the amounts of the two substances are in about the ratio of one-half molecule of potassium hydroxide to one of cobalt tartrate, and does not entirely disappear until the potassium hydroxide is present in about the ratio of 11 molecules to 1 of the cobalt tartrate. This seriously interfered with following the effect on the freezing-point of successive additions of potassium hydroxide to cobalt tartrate. There is no difficulty, however, in determining the freezing-point of the solution when the potassium hydroxide is present in the ratio of two molecules of it to one of the tartrate; the results thus obtained are given in Table 9.

TABLE 9.		
Amount CoC ₄ H ₄ O ₆ in 100 cc. solution. Gram.	Amount KOH added. Gram.	Depression.
0.6505	0.0000	0.061°
0.6505	0.4530	0,106

If the molecular weight is calculated from the depression 0.106°, it gives 159, while according to the formula, K, CoC, H, O., the molecular weight is 283.3. Owing to the dissociation which such a salt would suffer in aqueous solution, it is very probable that it exists here in the solution, and that it is due to its formation that cobalt hydroxide cannot be precipitated by alkalies from a solution of a cobalt salt to which tartaric acid has been added. The precipitate above referred to, formed when the amount of potassium hydroxide added to the cobalt tartrate is in the ratio of one molecule of the former to one of the latter, was filtered off and washed until the wash-water was no longer alkaline. It was then dried and the cobalt in it determined. In one sample the percentage of cobalt was 42.78 and in another 38.04. The precipitate has, therefore, no definite composition, but undoubtedly contains some cobalt hydroxide, for no conceivable tartrate of cobalt has as great a percentage of cobalt as was found.

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SOLUBLE NICKEL SULPHIDE.

It is evident that when investigating the effect of an alkaline tartrate solution in preventing the precipitation of nickel sulphide by hydrogen sulphide, it is desirable to exclude the presence of other chemical substances. Tartaric acid and sodium hydroxide were, consequently, not added to a solution of a nickel salt, as for instance the chloride, for this would produce some sodium chloride, whose influence on the precipitation with hydrogen sulphide would then be entirely unknown. Solutions of pure nickel tartrate were prepared as has already been indicated, and to this the alkali and hydrogen sulphide were then added. If it was desired to note the effect of any neutral salt, as sodium chloride, on the precipitation, such salt was added separately. All the nickel tartrate used was made from nickel nitrate, which was a preparation of Schuchardt's and was marked "purissimum." According to Villiers,' sodium hydroxide is more effective in holding nickel sulphide in solution than potassium hydroxide. Solutions of nickel tartrate were treated with one equivalent of sodium hydroxide,² with two equivalents of sodium hydroxide, with three equivalents, and so on. Hydrogen sulphide was run into these solutions to saturation and the solutions filtered. In the first solution nickel sulphide was precipitated and the filtrate was only slightly colored, in the second the filtrate was a decided brown, in the third it was black, but to be certain that no nickel sulphide is precipitated it is necessary to have at least five equivalents of sodium hydroxide to one of nickel tartrate. This black filtrate oxidizes with remarkable rapidity, which is shown by the continual separation of sulphur. It is apparently the sodium sulphide present, which thus suffers oxidation, but what is peculiar, is that the oxidation is more rapid than ever takes place in a solution of sodium sulphide alone. The more dilute the solution, the less marked is the oxidation. If this black alkaline solution of nickel sulphide is allowed to stand for an indefinite length of time, the nickel sulphide gradually precipitates, so that in from five to ten days the supernatant liquid has usually become clear.

¹ Compt. rend., 119, 1263 (1894).

² By an equivalent of sodium hydroxide is meant that quantity which bears a ratio to the nickel tartrate used of 2 molecules NaOH to 1 molecule $NiC_4H_4O_6$.

This settling can be greatly accelerated by the presence of a neutral salt, as sodium chloride or potassium sulphate, the time necessary for settling varying with the amount of such salt added. The presence of a large quantity of these salts before the introduction of hydrogen sulphide causes a large portion of the nickel sulphide to be precipitated.

The behavior of this black solution of nickel sulphide seemed to indicate that it is not a true solution, but colloidal in nature. To decide this several tests were applied. With a high-power microscope it was impossible to detect solid particles of any sort. The following test employed by Muthmann¹ was applied : It consists in treating the solution in question with a solution of gumarabic, shaking well, and then adding alcohol to precipitate the gum. If the substance is a colloid, it is precipitated with the gum and colors it. Before applying this test it is necessary to assure one's self that alcohol will not produce a precipitate in the original solution. In this case if the alcohol did not exceed 50 per cent. of the total liquid, nothing was precipitated, so care was exercised not to add more than this amount. The gum when precipitated was colored black, and on standing a few hours the supernatant liquid became clear. The alcohol was then poured off, and the residue treated with water, which dissolved it up again, the solution being colored black as before. This is the typical behavior of a colloidal substance. Tyndall's experiment applied by Picton² to solutions of antimony and arsenic sulphides was tried with this solution. The method employed was essentially this: The liquid in question was placed in a small bottle and the bottle so supported that the rays from an arc light could be focused directly on its bottom. The light, which diffused from the side of the bottle, was examined through a nicol. Α colloidal solution of arsenic sulphide was first examined to see that the apparatus gave proper results. The light was polarized, which is in harmony with the results of Picton and the later ones of Stoekl and Vanino.3 The solution of nickel sulphide was then examined. On account of its dark color, it was necessary to use a very dilute solution so that the light would not be com-

¹ Ber. d. chem. Ges., 20, 983 (1887).

^{2 1.} Chem. Soc., 61, 143 (1892).

⁴ Ztschr. phys. Chem., 30, 111 (1899).

pletely absorbed. With such a dilute solution no difficulty was experienced in getting it into the bottle, before the separation of any sulphur due to oxidation could take place. The light diffused from this solution was completely polarized. Some distilled water from which the solutions were made, was then placed in the bottle and examined in the same manner. No polarization could be detected. I am greatly indebted to Mr. H. W. Woodward of the physical department of this university for very efficient aid in these optical investigations. Independent observations by him in each one of the foregoing cases confirmed mine in every particular. All these tests, therefore, seem to show that nickel sulphide exists in an alkaline tartrate solution in the colloidal state; that is, as solid particles in an extremely finely divided condition, too small to be seen with any microscope but not so small but that they reflect light.

COBALT SULPHIDE.

Cobalt sulphide was produced in a manner exactly similar to that used in preparing soluble nickel sulphide. A solution of cobalt tartrate was made alkaline with a quantity of sodium hydroxide sufficient to hold nickel sulphide in solution, and then hydrogen sulphide run in to saturation. The cobalt tartrate was prepared from chemically pure cobalt chloride of Kahlbaum's, marked "nickel frei." After the hydrogen sulphide had been run into the alkaline solution, it was filtered. According to Villiers, the cobalt sulphide is entirely precipitated, but in nearly every case the filtrate was colored brown. Villiers points out that by this method one can detect the presence of nickel in most preparations of cobalt supposedly free from nickel. It was, therefore, expected that the brown coloration just referred to was due to the presence of a trace of nickel. This brown filtrate was refiltered two or three times, then shaken with sodium chloride, and allowed to stand over night. In the morning a slight black sediment had deposited and the supernatant liquid was perfectly clear. The deposit was filtered off, washed and dissolved in aqua regia. After removing the excess of acid, acetic acid and potassium nitrite were added, and the mixture left twenty-four hours, at the end of which time a well-defined

yellow precipitate had appeared. This shows conclusively that the brown color of the alkaline solution was due to cobalt sulphide in solution and not nickel, for not a trace of nickel could be found in the filtrate from the nitrite precipitate. This experiment was repeated several times and nearly every time some cobalt sulphide went into solution. The presence of a moderate quantity of a neutral salt, will, however, insure complete precipitation of the cobalt sulphide.

CONCLUSION.

The difficulties attendant on the separation of nickel and cobalt by the method of Villiers are the following: The oxidation of the solution to which the hydrogen sulphide has been added results in the separation of so much sulphur, that if nickel is present and cobalt is not, the black solution will color the sulphur, making it very difficult to distinguish from precipitated cobalt sulphide. Furthermore, according to the process used in this separation, sodium chloride is present in the solution, and although this aids in the complete precipitation of cobalt sulphide, it may cause some nickel sulphide to be precipitated, which in the absence of cobalt sulphide might readily be mistaken for it.

The nickel sulphide in solution in an alkaline tartrate medium is in the colloidal state.

Of the different tartrates of nickel and cobalt investigated, the most interesting are the solutions of the tartrates of these metals prepared from their hydroxides and cold tartaric acid. The results of determinations of the lowering of the freezing-point and of the electrical conductivity are very exceptional for salts of this sort, and seem to point to the existence of a polymerized molecular structure.

The evidence seems to be pretty conclusive, that the cause of the non-precipitation of the hydroxides of nickel and cobalt from solutions of their tartrates, or at least that any precipitate that may form dissolves in excess of the reagent, is due to the formation of a compound in which these metals replace the hydrogen atoms of the alcoholic hydroxyl groups of tartaric acid.

WESTERN RESERVE UNIVERSITY, CLEVELAND, OHIO, June, 1900.