the value 1.23 volts, a value very close to the one found in this paper. A comparison of the two methods will be interesting in order to determine which is better capable of giving the most accurate results.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI, NO. 68.]

SOME NOTES ON TRIVALENT COBALT AND NICKEL.

BY STANLEY R. BENEDICT.

Received December 20, 1905.

IN view of the recent work of Tubandt[1] and Barbiere and Calyolari,[2] describing the formation of trivalent compounds of nickel and cobalt by electrolysis, it has been thought advisable to publish the following paper, preliminary in nature, describing results obtained which indicate more or less conclusively the existence of certain compounds of cobalt and nickel hitherto unprepared. Because of the instability of these compounds, very few have as yet been isolated. In all the instances herein described, however, the reactions given by the solutions seem to the writer to demonstrate the existence of the supposed, or closely allied, compounds. Hence it may not be entirely out of place to publish these partially worked out laboratory notes.

In a previous paper[3] the writer described a method for the detection of nickel which depends upon the formation of cobaltioxalic acid, salts of which had previously been made by both Kehrmann[4] and Marshall,[5] though not in the same way as that described by the writer. It was also mentioned in that paper that by a process analogous to the one described, other new compounds had been made which would be described later. An outline of this work and its continuation follows.

Cobaltioxalic acid may be obtained in solution as follows: A solution of a cobalt salt is treated with a slight excess of sodium peroxide and heated to boiling. The black cobaltic hydroxide thus obtained is filtered off and washed on the filter with hot water a few times, and then with ice water until completely

---

[1] Z. anorg. Chem. 45, 73 (1905).

[2] Atti. Accad. Lincei Roma, 5, 14, 1, 464. Chem. Centralbl, 1905, 1, 464.

[3] This Journal, 26, 695 (1905).

[4] Ber. 19, 3101.

[5] J. Chem. Soc. 59, 760 (1891).

cooled to the temperature of this wash-water. A cold, saturated solution of oxalic acid is now poured repeatedly through the filter. A considerable portion of the cobaltic hydroxide dissolves, yielding a green solution which closely resembles solutions of nickelous salts in color. This solution may very readily be shown to contain trivalent cobalt by treatment with sodium hydroxide and warming, when a black precipitate of cobaltic hydroxide will be obtained.

It exhibits the following properties: Upon standing a few hours a spontaneous reduction takes place, the color changing from green to pink, accompanied by a precipitation of cobaltous oxalate. Heating to boiling causes a reduction, though by no means an instantaneous one, it often being necessary to continue the boiling several minutes to effect complete reduction. The reduction in the cold is only slightly accelerated by the presence of sulphurous acid or hydrogen sulphide. This indifference to reducing agents is surprisingly great, and is even more marked in presence of excess of sodium carbonate solution. Solutions made alkaline with sodium carbonate are not noticeably reduced by boiling (though they cannot be evaporated to dryness without reduction), and appear to be unaffected by ferrous salts and even by stannous chloride. The formula of this acid, deduced from its salt described below is, $H_6Co_2(C_2O_4)_6$.

The calcium salt of cobaltioxalic acid may be obtained pure as follows. The acid solution prepared as described above is treated with an excess of pure calcium carbonate and the solution agitated until a neutral or only faintly acid reaction (due to carbonic acid) is obtained. The solution is now filtered off from the excess of carbonate and calcium oxalate. The filtrate contains now (theoretically) only calcium cobaltioxalate, together with some carbonic acid. This solution should yield no precipitate with calcium chloride solution in the cold, but will deposit calcium oxalate upon boiling. It is evaporated to dryness in a vacuum desiccator at ordinary temperature and the salt thus obtained recrystallized from water. As thus prepared, the calcium salt is in the form of dark green needles, crystallizing with six molecules of water. A quantitative determination gave Ca 13.50, C_2O_4 60.20, and H_2O 12.08 per cent., showing conclusively that its composition corresponds exactly with the barium salt prepared by Kehrmann,[1] which he found to have the following formula $Ba_3Co_2(C_2O_4)_6.6H_2O$.

A solution of this calcium salt exhibits great stability regarding reducing agents, none of those tried, among which were hydrogen sulphide, ferrous sulphate, sulphurous acid, and stannous chloride, reducing it in the cold. If silver nitrate solution be added to a solution of calcium cobaltioxalate, a white precipitate slowly forms, the solution still retaining its green color, showing that the cobalt is still trivalent. The precipitate is found upon examination to be silver oxalate. The filtrate will give no precipitate upon boiling with calcium, showing that all the oxalate has been removed. The question naturally arises as to what form the cobalt is in after removal of the oxalate. It would appear to have to be either a simple or complex cobaltic nitrate. This point is to be further investigated.

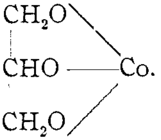
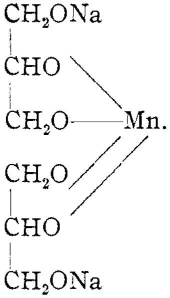
A more rapid method for the preparation of potassium cobaltioxalate than the one described by either Kehrmann[1] or Marshall,[2] is the following: To a neutral solution of cobalt nitrate an excess of solid potassium oxalate is added and the solution warmed. A heavy precipitate of cobalt oxalate forms at first but soon dissolves in the excess of potassium oxalate forming a deep red solution. A little sodium carbonate solution is now added (no precipitation takes place) then bromine water is added and the solution warmed to boiling. Practically all of the cobalt present is converted into the cobaltioxalate compound, coloring the solution a deep greenish black, which, upon considerable dilution, yields a solution nickel-green in color. The black solution is treated with excess of solid calcium hydroxide with constant stirring until all excess of oxalate has been removed. The solution is now filtered and the filtrate treated with a slight excess of alcohol. This precipitates the green potassium cobaltioxalate which may be filtered off and recrystallized from water. Kehrmann[1] gives a description of its properties.

If a solution of a cobalt salt be treated with some glycerol, then a little sodium hydroxide and next some bromine water be added and the solution boiled, a black solution is obtained which contains a trivalent compound of cobalt. This compound may be isolated by precipitating with a mixture of equal parts of

---

[1] Kehrmann: Loc. cit.

[2] Marshall: Loc. cit.

alcohol and ether, and washing off the excess of glycerol with alcohol. As thus obtained the compound is a black, amorphous substance, soluble in water to a black solution. No attempt has yet been made to crystallize this substance from its aqueous solution nor to analyze it. For this reason its formula can only be suggested. Certain indications point to the following compound of trivalent cobalt with glycerol, . These indications are (1) we are certain that we have not a simple cobaltic nitrate or hydroxide, (2) if we substitute manganese for the cobalt in the above reaction, a deep red solution is obtained, corresponding in its properties to a solution of a manganic-glycerol compound described by Schottlander,[1] who ascribed to it the formula . We can substitute tartrate for glycerol in the reaction described for cobalt above, obtaining in this case a black compound less stable and more difficult of isolation than the glycerol compound.

The impossibility of obtaining compounds containing trivalent nickel, other than the hydroxide, has been set forth in the textbooks as one of the few distinctions in the behavior of nickel and cobalt. Recently however, Tubandt[2] has prepared a compound of trivalent nickel by electrolysis. It will be shown below that we can readily obtain solutions of nickelic salts without recourse to electrolysis.

To prepare a solution of nickelic acetate the procedure is as follows: Freshly precipitated nickelic hydroxide is filtered off and washed upon the filter first with hot water, then with ice

[1] Ann. 155, 230 (1870).

[2] Tubandt: Loc. cit.

water until entirely cooled to the temperature of this wash-water. A 90 per cent. solution of acetic acid which has been previously cooled to just above its freezing-point is now poured upon the filter. The first portion of the filtrate will be green in color and contain practically no trivalent nickel. (This is probably due to the heat liberated by the reaction of the acid with the excess of alkali always present.) In a moment however the nickelic hydroxide will dissolve with little or no reduction, yielding a filtrate coal-black in appearance which gives the reactions we should expect of trivalent nickel. All reducing agents cause immediate reduction, the solution changing from black to green in color. Reduction takes place shortly upon standing and instantaneously upon warming. Sodium hydroxide solution gives an immediate precipitate of black nickelic hydroxide.

Strong solutions of tartaric or citric acid may be substituted for acetic acid in the above, the solutions thus prepared resembling that obtained with acetic, save that they are slightly less stable. They all liberate iodine from potassium iodide with instantaneous reduction, but have little, if any, similar action upon potassium bromide.

Attention is called to the slight differences in the mode of procedure given above and that usually employed for obtaining a solution of cobaltic acetate in acetic acid. In the latter case the reaction is carried on in a test-tube at ordinary temperatures, under which conditions a considerable amount of trivalent cobalt is obtained in solution, but this procedure will yield absolutely no trivalent nickel compound. Hence it has been stated that such a compound cannot be obtained. Yet if we substitute a filter for a test-tube and use cold solutions, the desired product is readily obtained. It is a fact that the trivalent hydroxides of both cobalt and nickel dissolve from a filter with less reduction than they do in a test-tube. If an attempt is made to prepare the cobaltioxalic acid described earlier in this paper by shaking cobaltic hydroxide with oxalic acid, in a test-tube, it will be found that little or none at all will be formed, whereas if cobaltic hydroxide be treated on a filter with oxalic acid, a considerable amount of the compound is readily obtained. Unless we suppose that the oxygen in the air and pores of the filter aids in preventing reduction, this fact appears very difficult of explanation.

If for the cold acetic acid solution used in obtaining a solution of nickelic acetate as described above, we substitute a nearly saturated solution of bisulphate of potassium, a very interesting result is obtained. (*Note.*—The bisulphate solution should not be cooled much, or too much of the salt is deposited.) The first portion of the filtrate is (as with the acetic acid) green in color. In a later portion this color is less apparent until soon a filtrate is obtained which is practically colorless. Yet this filtrate contains a large amount of nickel, as can readily be shown by adding sodium hydroxide solution to it. As more of the bisulphate solution filters through (pouring more upon the filter if necessary), the filtrate again becomes colored, but now the color is pink instead of green. The pink color is faint at first, but gradually increases in depth until in most instances a distinctly reddish pink solution is obtained. This solution upon standing deposits a green, crystalline salt and becomes more deeply colored. There is little or no doubt that from the time the filtrate comes through colorless it contains trivalent nickel, apparently nickelic sulphate, the amount increasing with the depth of color. The color of the solution alone would be ample evidence that the nickel is present in other than its usual condition, while the presence of a powerful oxidizing agent is shown by the fact that the pink solution will liberate both iodine and bromine instantaneously from their salts with a simultaneous change of color from pink to green. Chlorine is also liberated from chlorides, though this takes place much more slowly. It is certain that we must have here either a simple or a complex nickelic sulphate.

Although this solution of nickelic sulphate reacts as such a powerful oxidizing agent, it undergoes spontaneous reduction much more slowly than does the acetate compound. If kept cold, this pink solution retains its color for days. Sulphurous acid, ferrous sulphate, and practically all other reducing agents, reduce it instantly in the cold. Upon heating to boiling, a spontaneous reduction takes place. Sodium hydroxide solution precipitates green nickelous hydroxide. This apparent exception to the reaction we should expect of a nickelic salt is readily accounted for when we remember the large amount of heat liberated by the reaction between a strong solution of a bisulphate and sodium hydroxide. This heat would, of course, cause the spontaneous reduction of the nickelic compound before it could be precipitated as the hydroxide. Organic solvents added in the hope of precipitating the nickelic compound, caused its immediate reduction.

The color of the nickelic sulphate solution is interesting. It resembles in this respect almost exactly a somewhat dilute solution of a cobaltous salt. When it is remembered that trivalent cobalt in the form of cobaltioxalate yields nickel-green solutions, it will be seen that in compounds of both these metals we have an exact reversal of color according to the degree of oxidation.

The red or pink color of the solution of nickelic sulphate very readily explains the color changes found in the filtrate obtained during its formation. At first all is nickelous nickel, hence the green color; as nickelic sulphate is formed its pink shade neutralizes the green more and more, giving finally a solution looking like a mixture of nickel and cobalt. As more nickelic and less nickelous compound is formed, the color of course changes to pink. That there is always a certain amount of nickelous salt present is evidenced by the fact above mentioned that upon standing, an increase in the depth of pink color takes place, accompanied by the deposition of a green crystalline salt, which upon examination proves to be a neutral double sulphate of nickel and potassium. After a day or two this deposition of the nickelous double sulphate practically ceases and a brick-red, apparently amorphous powder is deposited, while the solution slowly loses its color.

This red powder is insoluble in water, but dissolves readily in sulphurous acid, yielding a green solution. It certainly contains trivalent nickel, being either the simple sulphate or possibly an alum. The amount so far obtained has been too small to analyze. Work is being continued upon this compound and it is hoped that an analysis of it can be reported before long.

Treatment of cobaltic hydroxide with potassium bisulphate solution will not yield a cobaltic sulphate. A reduction invariably occurs, seeming to indicate that cobaltic sulphate is less stable than the corresponding nickel salt.