LXXIII.—CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF EDINBURGH.

No. IV. *Oxidation of Cobalt Salts by Electrolisis.*

By HUGH MARSHALL, D.Sc., F.R.S.E.

SEVERAL years ago I contributed a short note on cobalt ammonium alum to the Royal Society of Edinburgh (*Proc. Roy. Soc. Edin.*, **14**, 203). A full report of the work done in connection with the subject has, however, not yet been published. For a considerable time I was unable to carry the research further, and afterwards found some difficulty in repeating the experiments with satisfactory results. During the past year I have again taken up the subject with much greater success, and the results so far obtained are described in the present paper.

My attention was first called to the subject by a peculiar action noticed during the electrolytic separation of copper and cobalt by Claisen's method. The solution which was being analysed contained copper, cobalt, potassium, and hydrogen sulphates, and it was found that if too strong a current was employed to separate the copper, the colour of the solution, notwithstanding the rapid deposition of the metal, did not change to pink, as was expected, but became greyish-green. As this was apparently only slightly, if at all, altered by prolonged action of the current, some of the liquid was removed and tested for copper by means of sulphuretted hydrogen solution. This immediately changed the colour to pink, while the liquid became opalescent through separation of sulphur. There was, however, no copper present. This behaviour pointed to oxidation of the cobalt as the cause of the peculiar appearance, and it was found on testing the remainder of the solution with various reducing agents that these all brought about the change of colour from green to pink.

The next point to be settled was whether the amount of oxidation corresponded to any definite oxide or was only partial. For this purpose, two solutions were made up, one containing the sulphates before mentioned, the other being similar, except that it contained no cobalt. In each case there was a relatively large proportion of copper salt. These solutions were then electrolysed under similar conditions. The solution containing the cobalt behaved as in the case above mentioned. When it was evident that the copper was all precipitated, the current was stopped, and pure ferrous sulphate solution added to each in equal quantity. This changed the colour of the

cobalt solution to pink. The two were then titrated back with standard permanganate solution, when, as was expected, the cobalt solution required less than the other, corresponding to the oxidising action of the green compound formed. The amount of extra oxygen thus estimated was sufficient to raise barely one-sixth of the cobaltous salt present into cobaltic. The blank experiment, in which no cobalt was employed, was to get rid, as far as possible, of errors due to the formation of other oxidising agents. The result, whilst proving conclusively that oxidation had taken place, showed that it was only to a comparatively small extent.

From the conditions under which the action took place, it seemed most natural to conclude that the compound formed was a cobaltic salt, but the colour seemed to contradict this view. Solutions obtained by dissolving cobaltic hydrate in cold acids, and supposed to contain cobaltic salts, are brown. The supposition that a double salt might be formed did not seem quite satisfactory. The double sulphates of other similar metals—the alums—have not always the same colour as the simple sulphates which form them, as in the case of iron, but then they do not exist as such in solution in water. It therefore seemed necessary to isolate the substance in the pure state before it would be possible to decide conclusively as to its composition.

The part which the copper sulphate played seemed fairly evident. By its electrolysis we have a powerful oxidising agent—nascent SO_4 ions—liberated without at the same time setting free an equally active reducing agent, the copper being deposited directly as such on the cathode. Some of the SO_4 ions thus liberated would then act upon some of the cobaltous sulphate, converting it directly into cobaltic salt. Assuming the formation of the latter, the reaction might be represented by the equation

Of course this action is only very partial, large quantities of oxygen being also produced from decomposition of the water in the ordinary way.

The presence of the copper salt was, however, a considerable drawback, and it was sought to effect a similar result by a special form of apparatus. Two ways suggested themselves as suitable: 1st, the electrodes might be placed in separate vessels connected by a tube; or, 2nd, they might be separated from one another by a porous partition. In either case we should expect to see oxidation take place in the liquid surrounding the anode.

The second method was the one adopted. The solution to be oxidised was contained in a beaker, in the centre of which stood a porous battery jar containing dilute sulphuric acid. The anode consisted of

a spiral of stout platinum wire placed in the outer cell, while a sheet of copper in the inner one acted as cathode. The solution contained cobalt, potassium, and hydrogen sulphates, the former roughly in the proportion $2\text{CoSO}_4 : \text{K}_2\text{SO}_4$, whilst the latter was in large excess. The current was supplied by two large Bunsen's elements in series, that being the strength employed in the first experiments.

During the passage of the current, the colour gradually changed, becoming first purplish, but next morning it was dark-brown, not at all like the colour of the solutions previously obtained. The current was continued for some time, but little change seemed to occur, and there was no appearance of anything approaching a green colour.

The ratio of extra oxygen to cobalt in the solution was then determined, and this showed that fully a third of the cobalt might exist as cobaltic salt. The ratio would probably be too high, due to the presence of other oxidising agents. The solution behaved exactly like the brown solution obtained by dissolving cobaltic hydrate in sulphuric acid. It decomposed slowly on standing, rapidly if warmed. It was quickly reduced by easily oxidisable substances. Hydrogen peroxide decomposed it with rapid evolution of oxygen; hydrochloric acid with liberation of chlorine. When shaken with pure ether, a green coloration was produced, changing in course of time to pink. A similar effect was produced by very weak alcohol when added in small quantity. Caustic potash gave a black precipitate.

A new experiment was next tried with a modified apparatus. The beaker was replaced by a platinum basin which acted simultaneously as anode. A small porous cell was suspended centrally in this, a spiral of copper wire being employed as the cathode. The cell was filled with solution as before, but a stronger current was used, namely, three cells. The behaviour of the solution was the same as in the previous experiment. By next morning, however, a slight muddy deposit had formed round the side of the basin above the level of the liquid. It was mostly of a brown colour, but there was an edging coloured greenish-blue. On touching the basin, the deposit fell into the liquid and dissolved almost entirely. As the further action of the current produced no change in the appearance of the solution, the experiment was stopped.

Up till now it had been assumed that the potassium sulphate was a necessary constituent of the solution, but it was necessary to prove whether this was so or not. An experiment was therefore started in which simply an acid solution of cobaltous sulphate was electrolysed in the above-described manner. The current was allowed to act all night, and next morning the appearance was quite unchanged. Some ammonia solution was then added so as to form ammonium sulphate with part of the free acid. The current was then continued as before.

The colour now gradually changed, becoming first violet, and next morning the solution was a deep greenish-blue. On pouring off the liquid, some small, dark-blue crystals were found in the bottom of the vessel. These, when examined under the microscope, showed no distinct form, having apparently been largely redissolved. On examining the reaction of the solution, it was found to contain copper, evidently from a brass ring above the basin, which had been attacked by acid spirted on it. A fresh solution was therefore made up in the same manner as before and similarly treated. The behaviour was exactly as before, and in the course of two days a crop of crystals was obtained. These were removed and dried between filter paper. When examined under the microscope, they proved to be nearly all perfect octahedra, whilst a few showed faces of the dodecahedron and the cube. The total quantity weighed about 1 gram, and was all used for analysis. The ammonia determination was unfortunately spoiled. The percentages obtained agreed well for cobalt ammonium alum, considering that it is not possible to get the crystals quite pure and free from mother liquor.

	Found.	Calculated for alum.
Co	12.5	12.1
SO ₄	41.2	39.6

The experiment was continued after making up the liquid with more of the original solution, and after several days a quantity of substance amounting to 2 or 3 grams was obtained. The analysis of this gave the following results:—

	Found.	Calculated for alum.
Co	12.70	12.10
NH ₄	3.75	3.71
SO ₄	39.38	39.62
H ₂ O by diff.	44.17	44.57

In the next experiment, potassium sulphate was again employed in place of the ammonium salt, and as much as the solution would dissolve was used. The solution behaved precisely as with the ammonium sulphate, becoming deep greenish-blue. The only crystals which separated in the course of several days, however, were potassium sulphate. At last a few dark-blue crystals were noticed among the colourless ones. Some strong solution of cobaltous sulphate was then added and the liquid further electrolysed. In this way a blue deposit was at last obtained, which was freed as much as possible from mother liquor by pressing between filter paper. The soft cake thus obtained, although it necessarily still contained a considerable proportion of impurity, was analysed with the following results:—

Co	10.45
K.....	9.98
SO ₄	51.70
Difference	27.87

It was, therefore, concluded to be a mixture of the alum with potassium hydrogen sulphate.*

Several experiments were next tried with nickel sulphate in place of cobalt sulphate, but without result.

While engaged in these experiments, an abstract of a paper by Kehrmann (*Ber.*, 19, 3101b) appeared in this Journal, describing the preparation of a double cobaltic potassium oxalate which yielded a green solution. In Classen's handbook on quantitative electrolytic analysis, it is stated that during the deposition of cobalt from cobaltous double oxalate solutions the liquid becomes first green and ultimately colourless. It seemed highly probable that this colour was due to the oxidation of the cobalt, according to the equation

This cobaltic oxalate would then unite with the alkaline oxalate present to give the compound obtained by Kehrmann. To confirm this, a solution containing potassium cobaltous oxalate and oxalic acid was electrolysed in the apparatus, as used in the preparation of the alum, when a bright green solution was obtained. This was not reduced by sulphuretted hydrogen in the cold, but on standing some time it gradually changed to a solution of cobaltous salt. Owing to this decomposition and the great dilution, it was not possible to crystallise out the solid salt. There seemed no doubt, however, that a cobaltic compound was actually formed.

As already mentioned, the further study of the subject was not proceeded with for a considerable time, and when again taken up great difficulty was experienced in repeating the experiments, in so far as getting crystals of alum was concerned. The blue solutions could be prepared without much difficulty.

One point which early became evident was the necessity of some means of keeping the temperature of the solution constant, as decomposition sometimes occurred, due to heating caused by the passage of the current for a prolonged period. A coil of glass tube through which cold water circulated was first tried, but without satisfactory results. It appears preferable to cool directly the outside of the basin, as it is in the layer in contact with it that the oxidation takes place. For this purpose a special cooling apparatus was constructed. The

* In all probability it was a mixture of cobaltic sulphate with potassium persulphate.

arrangement will be understood from the following diagram, which roughly represents a section through the whole apparatus.

The platinum basin *a*, of about 200 c.c. capacity, is supported in a copper ring *b*. The latter is made of stiff sheet metal, in which a circular opening, considerably smaller than the basin, is cut. The inner edge of this ring is then cut in to a sufficient depth at short intervals, and the teeth thus formed bent downwards, till the basin can be pushed inside and still held firmly. This ring in turn rests on the edge of the cylindrical vessel *c*, which is also made of copper. It is provided with a trough *d*, to the bottom of which a short outflow tube *e* is attached. In the centre of the bottom of the vessel *c*, is the supply tube *f*. The short arm *g* has a binding screw *h* soldered to it. The whole is supported by the ring of an ordinary retort stand. The cathode consists of a stout platinum wire *i*. This is attached to the tubular binding screw *k*, which passes through an

india-rubber stopper held by an ordinary retort stand clamp. This ensures the insulation of the cathode. The porous cell *b* is supported by a small glass rod, which passes through two holes drilled in the sides, and also through a loop on the platinum wire *i*.

The whole cooling apparatus, except where electrical contact is necessary, is coated with black varnish, to preserve the metal from corrosion by acid liquid spirted on it from the basin. Cold water enters by *f*, rises round the basin, and flows over the edge into the trough, escaping at *e*. This continued flow of water keeps the points of contact between the basin and the ring, and between the ring and the vessel *c*, always clean, so that we have complete metallic connection between the basin and the binding screw *h*.

The apparatus acts very efficiently. Even with strong currents, the temperature of the liquid in the basin may be kept within 2—3° of that of the cold water, while that in the inner compartment may be 20—25° higher.

The small tube *m* was added so that the apparatus might be used as a steam bath in electrolytic analysis with warm solutions, as in the estimation of cobalt. The steam is introduced by the tube *f*, and the condensed water escapes at *m*. When used for cooling, the latter opening is of course closed.

The solutions first experimented on were prepared by saturating dilute sulphuric acid (1 acid to 8 water by vol.) with cobalt and potassium or ammonium sulphates. The inner cell was filled with dilute sulphuric acid. During the electrolysis, the liquid in the outer cell of course gets more and more strongly acid. The ordinary porous pots are gradually attacked by the acid, and some aluminium and ferric sulphates get into solution. For this reason it is advisable to use any one pot for only a limited period, and also to use those made from pure kaolin free from iron. The current as a rule varied from $1\frac{1}{2}$ to $2\frac{1}{2}$ ampères, and was supplied from a battery of accumulators, which made the work much less troublesome than when ordinary batteries had to be employed. The solution containing ammonium sulphate was first tried, as it had given the most satisfactory results previously. The liquid became distinctly blue in the space of an hour or two, and after fully two days a solid began to separate. This was finely crystalline, and when agitated gave the liquid a peculiar silky appearance. Examined under the microscope, it was seen to consist of small needles, with here and there a larger piece, somewhat resembling the partly dissolved alum crystals first obtained. When a considerable quantity had separated, forming a muddy deposit on the bottom of the basin, it was filtered off through a piece of very thin platinum foil, pierced with numerous fine holes. The foil was laid, just like a piece of filter paper, on the flat perforated plate of a

porcelain funnel. The paste thus obtained was then dried in thin layers on porous plates. When dry, it was scraped off, and formed a crystalline, powdery mass, of a fine, blue colour. The analysis gave no satisfactory result. The ratio of cobalt to ammonium was not a simple one, and the amount of sulphuric acid was much in excess of what was required for both metals. A slight excess was of course to be expected, owing to adhering mother liquor, of which the last traces can hardly be removed by the method of drying adopted.

Other products gave similar irregular results on analysis, showing that mixtures were obtained. Experiments were next tried in which potassium sulphate was employed. Here exactly the same thing occurred. The substance obtained had the same appearance and the same irregular composition as in the case of the ammonium compound. As a rule the proportion of alkaline metal was lower than in the alum, which seemed strange, as large quantities were present in the mother liquor. The explanation of this non-formation of alum was at length accidentally discovered. In an experiment with the potassium salt a white, crystalline powder separated first from the blue solution. This was supposed to be potassium sulphate, but was examined and found to be practically free from sulphate. Its properties and the subsequent analysis proved it to be potassium *persulphate*.* Taking this formation of persulphate into account, it seemed highly probable that the blue substance was really impure cobaltic sulphate, and an experiment with a saturated solution of cobaltous salt alone in dilute sulphuric acid was started. The solution became blue exactly as in the other cases, and ultimately deposited a similar solid. This was separated and dried as above described, and analysis showed that it was cobaltic sulphate, with a large quantity of water of crystallisation. The following numbers were obtained :—

	Found.	Calculated for $\text{Co}_2(\text{SO}_4)_3, 18\text{H}_2\text{O}.$
Co	16.0	16.07
SO_4	41.1	39.50
H_2O	43.7	44.43

The water was estimated directly by ignition with lead chromate. The sulphuric acid is in excess, as was to be expected, from the presence of free acid; consequently also part of the oxygen of the free acid is twice reckoned, coming in with the water. Some of the impure specimens first obtained were found to contain considerable quantities of aluminium sulphate from decomposition of the silicate in the porous pot. The quantity of water of crystallisation in the

* See succeeding paper, p. 771.

formula noted above was supposed to be probably the most correct. Aluminium sulphate crystallises with 18 mols. H_2O in the hydrate occurring naturally as "hair salt."

As already mentioned, the substance forms a blue, crystalline powder. When the paste is dried on porous plates, the surface has a silky appearance. If kept in a dry atmosphere, or if gently warmed, it loses water, and rapidly decomposes, becoming first of a brownish colour, which quickly gives place to pink. If kept in a moderately moist atmosphere, this does not take place nearly so readily; some which has been kept in a tightly stoppered tube for months does not show any signs of decomposition. Treated with water, it dissolves, but immediately begins to decompose, becoming of a dark, purplish colour, quickly changing to a greyish, neutral tint, and ultimately becoming pink. The oxygen liberated is evolved briskly during the process. The greyish tint seems to indicate that the colours of the cobaltous and cobaltic salts are nearly complementary. The salt dissolves very easily and without immediate decomposition in dilute sulphuric acid. Such a solution is greenish-blue, but gradually decomposes completely in the course of a day or two. It is, of course, very easily decomposed by all reducing agents. It gives a black precipitate when alkali is quickly added. The solid is also soluble in strong acetic and nitric acids. Strong sulphuric acid dissolves it, with formation of a deep reddish-brown solution. With hydrochloric acid, cobaltous salt and chlorine are formed.

The cause of failure in the first attempt to oxidise an acid solution of cobaltous sulphate alone is not very evident. The only probable explanation seems to be that the solution had got warm. Certain it is that next morning there was no appearance of change of colour.

Having succeeded in getting the simple cobaltic sulphate, there was no difficulty in getting the alums. A saturated solution of cobaltous sulphate was electrolysed till a large quantity of cobaltic salt had separated. The temperature was then allowed to rise to about 20° , and dilute acid added to dissolve the solid which still remained. The roughly calculated quantity of ammonium sulphate in fine powder was now added (only a small proportion of the cobalt passes to the inner cell) and a weak current passed till this was practically all dissolved. The clear liquid was then decanted and cooled by a freezing mixture. In this way a large crop of minute, octahedral crystals of the alum was obtained, and separated and dried like the sulphate. By more slowly cooling, larger crystals, recognisable with the naked eye, or easily with a hand lens, separated; they had a fine deep blue colour. That they were regular octahedra was shown by their behaviour in polarised light. It was hardly necessary to analyse them, but the cobalt, total water (including that from the hydrogen of the

ammonium), and sulphuric acid were estimated with the following results:—

	Found.	Calculated.
Co	12.05	12.09
SO ₄	40.1	39.62
H ₂ O (total)	52.6	52.00

In a similar way, the potassium compound was obtained. As would be expected, the alums behave towards water and acids like the cobaltic sulphate. They also decompose when they lose water. The crystals cannot be so completely freed from mother liquor by a porous plate, but may subsequently be pressed between filter paper, with which, however, they must not be left long in contact.

Cobaltic Ammonium Oxalate.

The experiments on the oxidation of cobaltous oxalate were also recommenced. As this salt is more soluble in ammonium than in potassium oxalate solution, the former was used. A small quantity was tried with a mixture of the two oxalates, with which a still stronger solution can be obtained. By fractional crystallisation of the oxidised solution, a solid compound was obtained which contained cobaltic, ammonium, and potassium oxalates, and agreed with the potassium compound described by Kehrmann. A much larger quantity of the pure ammonium compound was prepared. A hot saturated solution of cobaltous and ammonium oxalates was cooled and electrolysed, a considerable quantity of both the oxalates being added in a solid state. The inner cell was filled with oxalic acid solution, but, as a saturated solution of this acid is not very strong, the liquid in the inner cell soon becomes alkaline from free ammonia. To avoid this, a slow current of solution was kept flowing through the inner cell. With the oxalate it is quite unnecessary to cool the liquid. In this way a considerable quantity of dark-green solution was obtained. Alcohol was then added with the intention of fractionally precipitating the salts, and in this way the greater part of the ammonium oxalate and the cobaltous double salt were separated, but even a large quantity of alcohol did not precipitate the cobaltic compound. The solution was then left to concentrate spontaneously, during which operation a certain amount of decomposition took place. When a very strong solution had been obtained in this way, the evaporation was continued in a vacuum. Further quantities of impurities separated and ultimately a large mass of nearly black crystals was obtained and purified by recrystallisation. Analysis showed it to be the ammonium salt corresponding to the potassium salt obtained by

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Kehrmann. The oxalic acid and the water were determined by combustion.

	Found.	Calculated for $\text{Co}_2(\text{NH}_4)_6(\text{C}_2\text{O}_4)_6, 6\text{H}_2\text{O}$.
Co	13.80	13.61
NH_4	12.69	12.54
C_2O_4	61.20	61.31
H_2O (total)	38.76	37.62

The crystals are nearly black prisms which dissolve very readily in water, giving a dark-green solution. In thin films the salt exhibits dichroism—blue and green—as observed by Kehrmann in the case of the potassium salt. The solution was much more stable than was expected. It was only slowly decomposed on boiling, depositing cobaltous salt. Sulphurous acid, sulphuretted hydrogen, and even stannous chloride did not reduce it in the cold. Caustic alkalis gave a black precipitate on warming, but not immediately in the cold. With strong hydrochloric acid, the solution remained green, but changed to blue on warming, anhydrous cobaltous chloride being formed. The crystals effloresced when kept in a dry atmosphere (in a desiccator) at the ordinary temperature, yielding a bulky, green powder. A quantity which had been over sulphuric acid in a vacuum for several days was found to contain just about half as much water as the crystallised salt. The compound was found to be slowly decomposed by light, thus resembling the corresponding ferric salt. Some of the green powder which was left for several weeks in a tube was found to be bleached on the side towards the light, cobaltous salt and ammonium oxalate being formed, while the parts protected from the light remained bright-green.

Cobaltic Nitrate.

When a strong solution of cobaltous nitrate is electrolysed in a divided cell, it becomes of a deep indigo-blue, but soon returns to its original state when the current is stopped. Attempts to obtain a solid compound have not yet been successful, but the experiments are still being carried on.

In the last number of the *Berichte* (24, 2324), which has just been received, there is a paper, by Kehrmann and Pickersgill, "On the Cause of the Colour observed during the Electrolysis of Cobalt Oxalate Solution," in which they also prove that a cobaltic double oxalate is formed in this process. They have succeeded in isolating the potassium salt, and show that it is identical with that previously prepared by Kehrmann from cobaltic hydrate and potassium hydrogen

oxalate. They did not use a divided cell, the operation being carried out practically as in the quantitative electrolytic deposition of cobalt.

University of Edinburgh,
August, 1891.