HYDROBROMIC ACID.

Br present in gram.	V.	A. N.D.$_{80}$.	Time. Min.	Br found in gram.	Remarks.
0.0700	4	0.4 –0.01	35	0.0685	Solution turbid after electrol.
0.0700	4	0.4 –0.02	35	0.0683	Solution turbid after electrol.
0.0700	3	0.35–0.01	35	0.0698	Clear solution.
0.0700	3	0.35–0.002	50	0.0699	" "
0.0700	3	0.35–0.002	50	0.0697	" "
0.0700	3	0.35–0.003	50	0.0698	" "
0.0700	3	0.35–0.003	50	0.0696	" "
0.0700	3	0.35–0.001	50	0.0700	" "
0.0700	3	0.35–0.001	50	0.0696	" "

UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

ELECTROLYTIC SEPARATIONS.

BY IRVING H. BUCKMINSTER AND EDGAR F. SMITH.

Received July 23, 1910.

During the last three years there have been carried out in this laboratory certain metal separations in the electrolytic way, which may be of interest to those who are engaged in work of this character, so that it seems only proper that the results should be brought together in a single communication. The following paragraphs give in sufficient detail all the data necessary for those who may have occasion to repeat the separations. Thus, the separation of mercury from nickel was conducted in the presence of sulphuric acid. The anode consisted of a flat platinum spiral, which was rotated. The cathode was an ordinary platinum dish. With 0.1437 g. of mercury, and 0.2772 g. of nickel in the presence of 0.1 cc. of concentrated sulphuric acid, a current of N. D.$_{100}$ = 0.3 amp. and a pressure of 2.9 volts there was precipitated in the course of thirty-five minutes 0.1436 gram of mercury. Again, 0.2876 g. of mercury was separated from 0.1386 g. of nickel in the presence of 0.1 cc. of concentrated sulphuric acid, by the means of a current of N. D.$_{100}$ = 0.3 amp. and a voltage of 2.8 in a period of forty minutes. Six additional separations with conditions like those just indicated resulted similarly, so that we may regard this as a satisfactory procedure for the separation of mercury from nickel. The deposits of mercury were in every instance examined for nickel, but it was not found.

In the separation of bismuth from nickel 0.2772 g. of nickel and 0.2640 g. of bismuth, in the presence of 1 cc. of concentrated sulphuric acid, were exposed to the action of a current of N. D.$_{100}$ = 0.3 amp. and 2.2 volts for forty-five minutes. The deposit of bismuth weighed 0.2642 g. It was free from nickel. Six additional experiments resulted similarly. The deposits of bismuth, however, were not coherent, and the greatest care was required in washing them to avoid loss of the metal.

In separating copper from nickel, the metals were present as nitrates and there was added 1 cc. of nitric acid, specific gravity 1.4, while a current of N. D. $_{100}$ = 0.3 amp. and 2.4 volts was allowed to act upon 0.1481 g. of copper and 0.2772 g. of nickel. There was completely precipitated in forty minutes 0.1482 g. of copper. In the five additional experiments, conducted under practically the same conditions, the results were equally good, and the separation may, therefore, be considered successful. The deposit of copper was perfectly adherent and bright in color. At no time was nickel found in the copper.

In endeavoring to effect a separation in nitric acid of silver from nickel in practically the same manner as just described under copper from nickel, the silver deposits were not very adherent, but upon adding 5 cc. of ordinary alcohol to the electrolyte, containing 0.2191 g. of silver and 0.1386 g. of nickel, in the presence of 0.3 cc. of nitric acid, specific gravity 1.4, a current of N.D.$_{100}$ = 0.1 amp. and 1.1 volts, precipitated in 45 minutes 0.2192 g. of silver. Eight additional trials were conducted and with results that were very satisfactory. In the absence of alcohol, there was invariably a considerable anodic deposition.

Another interesting separation was that of mercury from nickel in a nitric acid electrolyte. The results which were observed in a number of experiments are represented in the single one which is here offered: 0.2477 g. of mercury as nitrate and 0.1386 g. of nickel as sulphate, in the presence of 3 cc. of nitric acid of specific gravity 1.4, were electrolyzed with a current of N. D.$_{100}$ = 0.3 amp. and 1 volt. In 30 minutes 0.2476 g. of mercury was precipitated. The deposits of mercury were, in all instances, bright and metallic, and in no case was the metal found contaminated with nickel.

Three trials leading to the separation of lead from nickel in nitric acid were carried out without the slightest difficulty. Lead was, of course, precipitated as dioxide upon a sand-blasted dish. In this instance the rotating cathode consisted of a perforated dish. The variation in the quantities of lead found ranged from 0.0001 to 0.0003 g.

From the many separations of zinc from nickel which were carried out in the presence of an alkaline tartrate electrolyte, one may be given. With a current of N. D.$_{100}$ = 0.3 amp. and 2.4 volts, in the presence of 1 g. of Rochelle salt and caustic potash sufficient to precipitate and redissolve the hydroxides, 0.1430 g. of zinc and 0.1386 g. of nickel as sulphates were acted upon for a period of 45 minutes. 0.1433 g. of zinc was found.

In an electrolyte containing free phosphoric acid, the separation of copper from nickel is quite satisfactory. In the same electrolyte, an attempt to separate cadmium from nickel was unsuccessful. The cadmium was deposited very slowly, and almost invariably contained nickel. The separation of mercury from nickel in a phosphoric acid electrolyte is also quite good.

In attempting to separate nickel from aluminium in the well-known ammonia and ammonium sulphate electrolyte, aluminium hydroxide invariably attached itself to the nickel deposit and was not fully removed by water. However, upon adding a little dilute sodium hydroxide the aluminium hydroxide at once disappeared, and the nickel was then washed with pure water. Proceeding in this way, three experiments gave most satisfactory results. Upon attempting to separate nickel from iron in a similar electrolyte, it was discovered that the ferric hydroxide was apt to contaminate the deposit of nickel. In this electrolyte nickel may be successfully separated from magnesium and the alkaline earth metals, although, of course, in the case of the latter, some other ammonium salt than the sulphate should be used. Indeed, in separating nickel from barium, as well as from strontium and calcium, the electrolyte was introduced into a small beaker, a gauze cathode being bent so that there was a clearance of about 5 mm. between it and the anode, and about the same distance between it and the beaker. The weight of the anode was 15 g. and the cathodes were about 5 g. each. By this contrivance, the separations, ten in all, were conducted very satisfactorily, and with results that were extremely concordant.

In attempting to separate nickel from chromium in the presence of ammonium hydroxide and ammonium sulphate no deposit was observed after two hours, although a current of 0.8 of an ampere with a pressure of 2.5 volts was employed. At first chromium hydroxide, of course, separated and was soon oxidized. This peculiar retention of the nickel led to trials with cobalt in a similar electrolyte. Indeed, it was soon discovered that in an ammonium hydroxide and ammonium sulphate electrolyte containing cobalt, an electrolyte which under ordinary circumstances answers splendidly for cobalt as it does for nickel, upon the addition of potassium chromate there was absolutely no deposition of metallic cobalt. This did not take place even after several hours' passage of the current; and strangely enough, when the electrolyte was removed from the platinum dish its pink color suggested the presence of cobaltammine. When hydrochloric acid was added to the solution, and the latter warmed gently, quite an abundance of purpureocobaltic chloride separated out. As this happened in a number of trials, it was concluded to make this method of preparing a cobaltammine the subject of a special study, which is now in progress and the results of which will be reported in a later communication. Upon the addition of potassium chromate to an ammonium hydroxide and ammonium sulphate electrolyte containing copper, the deposition of metallic copper was also completely prevented. This curious behavior led us to add the same reagent, potassium chromate, to a solution of silver nitrate containing ammonium hydroxide and ammonium sulphate. Upon the passage of a current of 0.6 of an ampere with a pressure of 2.5 volts, the silver was precipitated in an adherent and weighable form upon the cathode. This difference in behavior of silver and copper in an electrolyte, such as has just been described, led to an attempt to separate these two metals. The five experiments instituted resulted most satisfactorily. The deposits of silver were perfectly coherent and light gray in color and were readily washed. This separation, however, would not be used in place of other older and just as reliable methods.

A problem of considerable interest to electro-analysts has been the separation of silver from gold. A reference to early papers communicated from this laboratory will show that on several occasions a marked difference of deportment in various electrolytes justified the hope that this separation had been realized. Upon testing out the new methods, however, they were found to be inadequate. The remarkable behavior of the metals copper, silver, nickel and cobalt when exposed to the action of the current in the presence of potassium chromate led Mr. J. T. Lay, of this laboratory, to let the current act upon a solution of gold chloride, containing ammonium sulphate and ammonium hydroxide, with a considerable quantity of potassium chromate. To our amazement, gold was not precipitated, although the current was increased to 3 amperes with a pressure of 5.6 volts.

Again, the thought came that now a separation of silver from gold in this new electrolyte might be obtained. While fairly good separations were reached, it was impossible to remove the last traces of silver without carrying down some gold, so that our hopes were cast to the ground. When for a moment one considers the new electrolyte, and the peculiar behavior of the metals, it seems altogether likely that complexes of the most varied nature must exist in the electrolyte.

A few attempts were made with the copper salt in the presence of ammonium hydroxide, ammonium sulphate and potassium chromate to determine the electromotive force of the combination, with the result that very few free copper ions were found, all of which would indicate that in such a solution there are probably complexes, the exact nature of which it is not possible for us at the present moment to give. These are receiving proper consideration.

The determination of zinc in a potassium cyanide electrolyte has been discussed at various times, and there has always been a difference of opinion as to the conditions under which success could be obtained. Our experience has shown that if to a zinc salt solution there be added sufficient caustic potash to completely precipitate the zinc as hydroxide, with enough of cyanide to just redissolve the precipitate, in the presence of 20 cc. of ammonium hydroxide of specific gravity 0.96, a current of 2 amperes with a pressure of 5 volts will precipitate 0.1487 gram of zinc in from 15 to 30 minutes. Six successful experiments confirmed this result. The deposition of the zinc was made upon a silver-coated platinum dish. The total dilution did not exceed 100 cc. With these conditions, substituting nickel and cobalt for zinc, there was no deposition of either metal, so that it was hoped that by observing the preceding conditions it might be possible to separate zinc from nickel and cobalt in such an electrolyte. All of the results proved the contrary. It is a well-known fact that lead and manganese, when deposited from solutions containing nitric acid by the current, appear in the form of peroxides at the anode. If, however, the volume of nitric acid be increased to from 15 to 30 cc. acid, specific gravity 1.46, it was found that with quantities of metal like the following, namely 0.0982 gram of lead and 0.0555 gram of manganese, and a current of 8.5 amperes with a pressure of 4.5 volts, in 20 minutes there was deposited 0.0980 gram and 0.0979 gram of lead. Eight experiments of this character were made. The deposits of lead dioxide were all that could be desired. Upon testing, however, each of these eight deposits, traces of manganese were found. Perhaps these were due to occlusion. The deposits were made upon a dish anode and the cathode made to revolve 250 times per minute. It should be added that even with twice the quantity of lead given in the preceding paragraph, the separation was apparently as exact as with the small amount, but traces of manganese were found in this larger quantity of lead.

The metal bismuth may be deposited in a perfectly adherent form, and, at the same time, separated from tungsten and from molybdenum, if conditions similar to those shown in the following examples be observed: 0.1926 gram of bismuth as nitrate, 0.1862 gram of tungsten as sodium tungstate, 3 grams of tartaric acid, 0.5 of a gram of sodium hydroxide, and a current of 0.2 ampere with a pressure of 3 volts. The anode was rotated and the bismuth was precipitated upon the platinum cathode. Its quantity was 0.1928 gram. The time of precipitation did not exceed 30 minutes. The quantity of molybdenum used in a number of successful trials was 0.1 of a gram.

A separation that has generally been regarded as difficult in the electrolytic way is that of silver from bismuth. In our study of this problem more than eighty-three determinations were made. We submit two results, showing the conditions which proved most favorable: *Experiment 1.*—To a solution containing 0.0637 gram of silver as nitrate and 0.0875 gram of bismuth as nitrate was added 0.15 of a gram of ferric alum and 0.15 of a gram of chrome alum. The dilution of the electrolyte was 100 cc. Upon adding 6 cc. of nitric acid, specific gravity 1.47, and electrolyzing with a current of 0.15 of an ampere and a pressure of 1.2

volts, there was precipitated in 30 minutes 0.0634 gram of silver. *Experiment 2.*—To a solution containing 0.1274 gram of silver as nitrate and 0.0875 gram of bismuth were added 0.1 of a gram of ferric alum and 0.2 of a gram of chrome alum. The solution was again diluted to 100 cc., and after the addition of 7 cc. of nitric acid of specific gravity 1.4, a current of 0.15 of an ampere and pressure of 1.3 volts precipitated in forty minutes 0.1274 gram of silver. It was noticed that when the pressure exceeded 1.5 volts, some bismuth peroxide appeared at the anode, and that traces of metallic bismuth were found in the silver deposit. It was noticed, also, that alum alone was not sufficient to retain the bismuth in solution. The temperature of the electrolyte varied from 25° to 30°.

Since these experiments were made, Dr. W. N. Chapin, of this laboratory, has repeated the work, with the following satisfactory results:

Silver.	Bismuth. Gram.	Ferric alum. Gram.	Chrome alum. Gram.	HNO_3. cc.	Volts.	Amperes.	Temperature. Degrees.	Time. Min.	Silver weighed.	Tests.
0.0994	0.1	0.09	0.2	3	1.3	0.15	30	105	0.0990	No Bis.
0.0994	0.1	0.09	0.2	3	1.3	0.15	30	105	0.0990	" "
0.0994	0.1	0.09	0.2	3	1.3	0.15	30	75	0.0996	" "
0.0994	0.1	0.09	0.2	3	1.3	0.15	30	70	0.0996	" "
0.0994	0.1	0.09	0.2	3	1.3	0.15	30	90	0.0992	" "

He has also found that the separation may be effected without the introduction of either of the alums. The conditions which he discovered to be wholly satisfactory were these: Silver 0.1 to 0.2 of a gram, bismuth 0.1 to 0.2 of a gram, 3 cc. of nitric acid in a total volume of 75 cc., temperature 60°, pressure 3 volts and current N. D.$_{100}$ = 0.15 to 0.20 ampere. A dish anode was employed and placed 3 mm. from the dish cathode. The anode made 250 revolutions per minute. It is expedient to maintain the voltage constant and allow the electrolysis to proceed until the amperage falls to 0.002. By observing these conditions Dr. Chapin succeeded in making the separation in 25 minutes. The deposit of silver was perfectly free from bismuth. The electrolyte contained no silver.

Since mercury and silver are deposited under very similar conditions, it seemed probable that the preceding method would serve in the separation of mercury from bismuth. The experiments performed by Dr. Chapin prove this to be correct. The conditions observed by him were these: Total volume of electrolyte 75 cc., to which were added 10 drops of nitric acid. The pressure was 1.3 volts, the temperature of the electrolyte 50° The dish anode was employed and rotated at the rate of 250 revolutions per minute. The current was allowed to fall to 0.002 amperes, using 0.1206 gram of mercury. The amounts obtained in two experiments with the above conditions were 0.1206 gram and 0.1208 gram. The amounts of bismuth were respectively 0.1000 and 0.2000 gram. Nitric acid exceeding the amount indicated above tends to prevent the last traces of mercury from separating.

Reference to the literature upon the separation of uranium in the electrolytic way from such metals as zinc, nickel and cobalt will disclose the fact that when using a platinum cathode with rotating anode, the uranium will be fully precipitated, but there seems to be a tendency on the part of the other metals to become enclosed in the deposit of uranium hydroxide. With this knowledge before us, it was thought worth the while to ascertain whether by employing a mercury cathode, the separations could not be made satisfactory. To this end there were made up stock solutions of zinc sulphate and uranium sulphate. Portions of these, representing 0.2071 gram of zinc and 0.1352 gram of uranium, were introduced into the mercury cup. 0.5 cc. of concentrated sulphuric acid was added, and with a current of 3.5 amperes and a pressure of 5 volts, zinc was completely precipitated in periods of time varying from 15 minutes to 60 minutes. The anode made 200 revolutions per minute. Twelve determinations were carried out with perfect success in every instance.

Cobalt and nickel sulphates were used in similar separations of these metals from uranium. The conditions were in the case of cobalt: 0.2036 gram of cobalt and 0.0322 gram of uranium, with 0.5 cc. of concentrated sulphuric acid; dilution 20 cc., current 5.6 amperes, pressure 7 volts, time 35 minutes; anode rotating 200 times per minute. The cobalt precipitated weighed 0.2034 gram. Eight determinations were made. In the case of nickel, the following conditions prevailed: 0.4290 gram of nickel and 0.0664 gram of uranium, with 0.5 cc. of concentrated sulphuric acid, and a current of 1.6 amperes, with a pressure of 5 volts. The anode performed 250 revolutions per minute. In 60 minutes there was precipitated 0.4288 gram of nickel. Eleven experiments confirmed the results of the preceding trial.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

SOME DERIVATIVES OF 2-ACETYL-NAPHTHOL-1.[1]

BY HENRY A. TORREY AND E. J. CARDARELLI.

Received August 27, 1910.

The 2-acetylnaphthol-1 used in this work was prepared and converted into its 4-nitro and 4-amino derivatives according to the method of Friedländer.[2] The free base, which had an orange-red color similar to that observed by him, was treated with thioacetic acid, when the monoacetyl compound obtained melted at 212°, whereas Friedländer's acetyl de-

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[1] This research was suggested by the late Professor H. A. Torrey, and the greater part of the work was done under his direction, but the remainder of the work and the writing of the paper were deprived of the advantage of his supervision by his untimely death. C. L. JACKSON.

[2] *Ber.*, **28**, 1946 (1895).