thanks to Dr. Hussein Off, third chemist in the Khedivial Laboratory for his aid; the devoted way in which he worked with me, often far into the small hours of the morning, has contributed greatly to the completion of my work.

ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH AND J. BIRD MOYER.

IN a former communication we demonstrated by a sufficient number of carefully made experiments that mercury and bismuth could not be separated electrolytically in a nitric acid solution. This was in line with the observations of Smith and Saltar,[1] who proved conclusively that copper and bismuth could not be separated under analogous conditions, and further that the statement in regard to the separation of bismuth and lead was incorrect. Pursuing our original intention of studying the electrolysis of metals in the presence of free nitric acid we offer the following additional experience in this field of investigation. We naturally expected little trouble, and indeed met with very little in our efforts to separate

Mercury from Lead.

1. Ten cc. of mercuric nitrate solution (= 0.1150 gram of metallic mercury), one cc. of lead nitrate solution (= 0.0126 gram of lead dioxide), and twenty-five cc. of nitric acid of sp. gr. 1.3, were diluted to 175 cc. and electrolyzed with a current liberating 1.3 cc. of electrolytic gas per minute. The precipitated mercury weighed 0.1151 gram, and the lead dioxide equaled 0.0123 gram. An examination of the mercury did not reveal any admixed lead.

2. In this experiment the quantities of lead and mercury were the same as in 1; the volume of nitric acid was increased to thirty cc. while the current registered 1.8 cc. of electrolytic gas per minute. The mercury deposit weighed 0.1150 gram and the dioxide of lead equaled 0.0126 gram.

In three other experiments in which the volumes of the added nitric acid (sp. gr. 1.3) equaled five cc., ten cc., and fifteen cc., respectively, the precipitated mercury contained metallic lead in varying but very considerable amounts.

[1] *J. Anal. Appl. Chem.*, 7, 128.

Mercury from Lead and Bismuth.

In our former communication we cited an outlined analysis of an alloy containing tin, mercury, lead, and bismuth by Classen in his *Quantitative Analyse durch Elektrolyse, dritte Auflage*, p. 147, and showed that if it were conducted as there directed the analyst would in the end have little bismuth to determine as it would have most certainly gone out in company with the mercury. Omitting tin, we subjected a nitric acid solution of the other three metals to the action of the current. The solution contained 0.1150 gram of mercury, lead equal to 0.0126 gram of dioxide, bismuth 0.0718 gram, and fifteen cc. of nitric acid (sp. gr. 1.3). The total dilution was 180 cc. The current liberated 1.7 cc. of electrolytic gas per minute. The deposited mercury weighed 0.1262 gram and the increase in weight of the anode was 0.0164 gram; bismuth was discovered at both poles. A second and a third experiment with increased volume of acid resulted similarly. We must, therefore, reject this course if a satisfactory separation is desired.

Silver from Lead.

The separation presented no particular difficulties when working with conditions analogous to those recorded in the two following experiments:

1. Ten cc. of silver nitrate solution (= 0.1028 gram of silver), one cc. of lead nitrate solution (=0.0144 gram lead dioxide), and fifteen cc. of nitric acid (sp. gr. 1.3), with total dilution of 200 cc. were acted upon by a current generating 1.8 cc. of electrolytic gas per minute. The deposit of silver weighed 0.1023 gram, and the lead dioxide 0.0145 gram.

2. The conditions were similar to those in 1. The precipitated silver weighed 0.1028 gram, and the lead dioxide 0.0145 gram.

Copper from Cadmium.

This separation was long since satisfactorily made by Smith. Classen met with similar results (*Berichte*, **17**, 2473). Those interested will find Smith's description of the method fully given in the *American Chemical Journal*, **2**, 41. The results

we append confirm those obtained by Smith in every particular.

1. Ten cc. of a copper sulphate solution (=0.1341 gram of copper), five cc. of cadmium nitrate solution (= 0.1 gram of cadmium), and five cc. of nitric acid (sp. gr. 1.2), with total dilution of 200 cc., were electrolyzed with a current that gave 0.6 cc. of electrolytic gas per minute. The precipitated copper weighed 0.1346 gram; it contained no cadmium.

2. With conditions similar to those in 1, the precipitated copper weighed 0.1341 gram. The current gave 0.6 cc. of electrolytic gas per minute.

Copper from Zinc.

The quantities of metal were equal; the volume of nitric acid was five cc. (sp. gr. 1.3), total dilution 200 cc., and the current gave one cc. of electrolytic gas per minute. The precipitated copper weighed 0.1345 gram instead of 0.1341.

Copper from Zinc, Cobalt, and Nickel.

The quantities of metal were equal; the volume of nitric acid (sp. gr. 1.3) was five cc., and the total dilution 200 cc. The current registered 0.4 cc. of electrolytic gas per minute. The precipitated copper weighed 0.1339 gram.

Copper from Iron and Zinc.

The metals were equal in quantity. The volume of nitric acid was five cc. (sp. gr. 1.3). The current gave 0.7 cc. of electrolytic gas per minute, while the dilution was the same as in the preceding separations. The metal deposit weighed 0.1340 gram.

The copper obtained in each of these separations was examined for the metals associated with it in solution, but they were not found present. We may say here that we claim nothing new in these separations of copper from zinc, nickel, cobalt, and iron. They have been performed by others, but we merely offer our results and the conditions under which they were obtained as guides for any who may have occasion to make such separations.

Bismuth from Cadmium.

1. Five cc. of bismuth nitrate solution (=0.0718 gram of metallic bismuth), five cc. of cadmium nitrate solution (= 0.1

gram of cadmium), and fifteen cc. of nitric acid (sp. gr. 1.1) were dilnted to 180 cc. and electrolyzed with a current liberating 1.6 cc. of electrolytic gas per minute. The precipitated bismuth weighed 0.0716 gram instead of 0.0718 gram.

2. The conditions in this experiment were analogous to those in 1, except that no additional acid was added to the nitric acid solution of the two metals. The precipitation bismuth weighed 0.0719 gram.

Bismuth from Zinc.

0.0718 gram of bismuth, 0.1 gram zinc in the presence of two cc. of nitric acid (sp. gr. 1.3), with total dilution of 200 cc., gave 0.0712 gram of bismuth to a current setting free 0.4 cc. of electrolytic gas per minute. The anode was slightly discolored; its increase in weight was 0.0003 gram.

In a second trial with 1 cc. of additional acid the precipitated bismuth weighed 0.0717 gram. We can therefore regard this separation as satisfactory.

Bismuth from Nickel.

1. 0.0718 gram of bismuth, 0.1 gram of nickel, in the presence of two cc. of nitric acid (sp. gr. 1.3), were diluted to 180 cc. with water. A current liberating 0.5 cc. of electrolytic gas per minute acted upon this solution. The precipitation of bismuth was complete; the metal deposit weighed 0.0724 gram.

2. In this trial the quantities of the metals equaled those given in 1; the total dilution was 200 cc.; the volume of nitric acid of sp. gr. 1.3 equaled three cc. and the current gave 0.2 cc. of electrolytic gas per minute. The precipitated bismuth weighed 0.0716 gram.

A third experiment with conditions exactly like those of 2 gave 0.0716 gram of bismuth. The latter contained no nickel, and there was no deposit upon the anode.

Bismuth from Cobalt.

The quantities of metal were 0.0718 gram of bismuth and 0.1 gram of cobalt; the nitric acid (sp. gr. 1.3) equaled three cc., and the current gave 0.2 cc. of electrolytic gas per minute. The deposit of metalic bismuth weighed 0.0714 gram and there was also a very slight discoloration of the anode.

Other trials showed that the separation was possible.

It may be of interest to show what results were obtained when mixtures of the preceding metals were electrolyzed.

Bismuth from Zinc, Cobalt, and Nickel.

1. 0.0718 gram of bismuth, 0.1 gram of zinc, 0.1 gram of cobalt and 0.1 gram of nickel were mixed with two cc. of nitric acid (sp. gr. 1.3), diluted to 200 cc., and acted upon by a current liberating 0.8 cc. of electrolytic gas per minute. The precipitated bismuth weighed 0.0739 gram, and upon examination showed the presence of both nickel and cobalt. The anode was covered with a blue coating.

A second, third, and fourth trial, with conditions almost identical with those in the preceding example, showed the presence of 0.0729 gram, 0.0738 gram, and 0.0739 gram of bismuth, which in each instance was contaminated with cobalt and nickel.

Bismuth from Cobalt and Nickel.

Zinc was omitted, and by employing the remaining three metals in the amounts given in the preceding experiment, using three cc. of nitric acid of sp. gr. 1.3, and acting upon the mixture after dilution to 200 cc. with a current liberating 0.3 cc. of electrolytic gas per minute, the bismuth that was precipitated weighed 0.0736 gram. It contained nickel.

Bimuth from Cobalt and Zinc.

0.0718 gram of bismuth and 0.1 gram each of cobalt and zinc were mixed with two cc. of nitric acid of sp. gr. 1.3, diluted to 180 cc. with water, and electrolyzed with a current giving 0.6 cc. of electrolytic gas per minute. The bismuth weighed 0.0747 gram; it contained cobalt, and the anode was covered with a film of oxide.

Bismuth from Cobalt, Nickel, and Zinc.

Using the same quantities of metals as given in the preceding experiments we increased the volume of added acid to five cc. The deposit of bismuth weighed 0.0728 gram and contained both cobalt and nickel.

Upon making a trial with the following conditions we were successful in effecting the separation with all the metals present: 0.0718 gram bismuth, 0.1 gram zinc, 0.1 gram cobalt, 0.1 gram

nickel, eight cc. of nitric acid of sp. gr. 1.3, total dilution 200 cc., and a current that gave 0.4 cc. of electrolytic gas per minute. The deposit of bismuth weighed 0.0718 gram. It did not show the presence of any other metal upon examination. In this separation there was no discoloration of the anode. Subsequent experiments were equally successful in the separation, although in several of them the anode was slightly discolored; its weight, however, was not increased more than 0.0004 gram.

We may add that the bismuth was deposited upon platinum dishes weighing from sixty to seventy grams. The metal deposit was, in all those trials that approached success, adherent and regular in appearance. It was washed with warm water, alcohol, and ether. The strength of current indicated in all the experiments given in this communication were with voltameter and electrolyte in circuit.

While the separation of bismuth from the various metals mentioned is possible if the conditions we have worked out are preserved, we cannot fail to observe that the solution in nitric acid is not nearly so satisfactory as that in which the metals exist as sulphates together with free sulphuric acid. With this last solution Smith and Knerr[1] obtained very excellent results.

CHEMICAL LABORATORY OF
THE UNIVERSITY OF PENNSYLVANIA,
APRIL 27, 1893.

THE WORLD'S CONGRESS AUXILIARY OF THE WORLD'S COLUMBIAN EXPOSITION.

[DEPARTMENT OF SCIENCE AND PHILOSOPHY. GENERAL DIVISION OF CHEMISTRY].

THE committees in charge of the congress have selected Monday, August 21, as the date of the opening of the congress of chemists to be held in connection with the Columbian Exposition, in Chicago.

The chairman of the committee appointed for co-operation in this congress by the American Association for the Advancement of Science, Chemical Section, is Prof. Ira Remsen, Johns Hopkins University, Baltimore, Md. The chairman of the committee appointed by the American Chemical Society is Dr. Wm.

[1] *Am. Chem. J.*, 8, 206.