

the presence of a sexivalent molybdenum atom, and may be properly considered a hydroxybromide represented thus— $\text{Mo}(\text{OH})_3\text{Br}_3$ —a derivative of the unknown hexabromide.

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## THE ELECTROLYTIC SEPARATION OF MERCURY FROM BISMUTH.

BY EDGAR F. SMITH AND J. BIRD MOYER.

The question as to whether mercury can be completely precipitated by the current in the presence of nitric acid has been frequently discussed and answered in the affirmative. We observe, too, that in electrolytic literature it is this solution of mercury which has been generally recommended for the separation of the latter metal from various other metals associated with it. Thus, in the latest edition (the third) of Classen's *Quantitative Analyse durch Elektrolyse*, p. 147, the author, in describing the analysis of an alloy containing tin, lead, bismuth, and mercury, writes as follows:

“Aus der salpetersauren Lösung (the filtrate from the tin oxide) kann man nun zunächst das *Quecksilber* und einen Theil des Bleies als Superoxyd auf der positiven Elektrode fällen. Um die vollständige Abscheidung des Bleies zu bewirken unterwirft man die von Quecksilber befreite Lösung nochmals der Elektrolyse, indem man die Schale mit dem positiven Pol des Stromerzeugers verbindet, verdampft zur Bestimmung des *Wismuths* die bleifrei Lösung zur Trockne und verfährt nach S. 81,” etc., etc.

These instructions would most certainly lead one to infer that mercury can be separated in the electrolytic way from bismuth in the presence of nitric acid. Trials, qualitative it is true, were made by one of us (S) years ago; these indicated a co-precipitation of the metals from a nitric acid solution, and therefore we find in Smith's *Electrochemical Analysis*,<sup>1</sup> p. 97, the statement that “mercury cannot be separated in the electrolytic way from silver and bismuth.” The recent experience of Smith and Saltar<sup>2</sup> with

<sup>1</sup>P. Blakiston, Son & Co., Philadelphia, Pa.

<sup>2</sup>*J. Anal. Appl. Chem.*, 7, 128.

copper and bismuth confirms this last observation. That others may be convinced that these two metals—mercury and bismuth—cannot be separated electrolytically, when present in a nitric acid solution, we submit the results obtained lately.

We first experimented upon the solution of a mercury salt. It contained 0.1132 gram of metallic mercury in ten cc. of liquid.

*Experiment 1.*

To ten cc. mercury solution (=0.1132 gram of metallic mercury) were added five cc. of nitric acid (sp. gr. 1.2), and then diluted with water to 180 cc. A current of 0.6 cc. electrolytic gas per minute was permitted to act upon this solution. The deposit of mercury weighed 0.1132 gram.

*Experiment 2.*

The quantity of metallic mercury was the same as in experiment 1. The volume of nitric acid (sp. gr. 1.2) was three cc.; the total dilution equaled 180 cc., and the current liberated 0.3 cc. electrolytic gas per minute. The precipitated mercury weighed 0.1137 gram.

*Experiment 3.*

The conditions were the same as in the preceding experiment, except that the volume of acid added equaled ten cc. and the current gave 0.3 cc. electrolytic gas per minute. The deposit of mercury weighed 0.1131 gram.

*Experiment 4.*

In this instance the only departure from the conditions observed in the preceding experiment was that fifteen cc. of acid were added to the solution undergoing electrolysis. The deposited mercury weighed 0.1131 gm. In appearance it was more drop-like than any of the previous deposits.

*Experiment 5.*

The conditions of experiments 3 and 4 were retained, but the volume of acid was increased to twenty-five cc. The precipitated mercury weighed 0.1083 gm. The filtrate showed the presence of unprecipitated metal. A second trial proved just as unsuccessful, but upon raising the current to one cc. electrolytic gas per minute, in two later experiments, with conditions otherwise the

same as indicated above, the quantities of metal precipitated were

a .....	0.1130 gram.
b .....	0.1130 "

The precipitation was complete. We see, however, from the above that as the quantity of free acid is increased it is well to increase the strength of the acting current.

It will be understood that the current strength mentioned by us in this article was that with voltameter and the electrolyte in circuit.

The deposits of mercury were washed with warm water and alcohol. They were dried by holding the dish in the hand and blowing gently over the metal surface, and also by standing over sulphuric acid for a brief period.

The bismuth solution employed by us was of such strength that ten cc. of it contained 0.1432 gram of metallic bismuth. The conditions of complete precipitation of this metal from nitric acid solution have already been given by Smith and Saltar.<sup>1</sup> We can therefore advance to an account of our experience in attempting to separate these metals.

#### *Experiment 1.*

Ten cc. of mercury solution ( $\equiv 0.1132$  gram of metallic mercury), five cc. of bismuth solution ( $\equiv 0.0716$  gram of metallic bismuth), and ten cc. of nitric acid of sp. gr. 1.2, were diluted to 200 cc. and electrolyzed with a current that gave 0.4 cc. of electrolytic gas per minute. The weight of precipitated metal was 0.1821 gram. The anode was also covered with bismuth peroxide. The precipitation of metals was complete, but the mercury contained bismuth.

#### *Experiment 2.*

Preserving the conditions of experiment 1, but increasing the volume of acid to fifteen cc., the weight of the metallic deposit was 0.1850 gram. The anode also showed bismuth. Thus, again, *this metal appeared at both poles.*

#### *Experiment 3.*

Here the volume of acid was increased to twenty-five cc. and

<sup>1</sup> *J. Anal. Appl. Chem.*, 7, 128.

the current lowered to 0.2 cc. electrolytic gas per minute. The precipitation of metals was incomplete, although bismuth was found at both poles. On repeating the experiment the precipitation was found to be incomplete.

*Experiment 4.*

The current was increased to 0.8 cc. electrolytic gas per minute. The precipitation was complete, but bismuth appeared at both poles.

*Experiment 5.*

In this experiment we observed the following conditions:

Ten cc. of mercury solution ( $=0.1132$  gram of metallic mercury), two cc. of bismuth solution ( $=0.0358$  gram of metallic bismuth), twenty-five cc. of nitric acid (sp. gr. 1.3), and total dilution of 180 cc., were electrolyzed with a current liberating 1.5 cc. of electrolytic gas per minute. The precipitated mercury weighed 0.1441 gram. The positive pole was covered with bismuth peroxide. The mercury contained metallic bismuth. The precipitation of metals was complete.

*Experiment 6.*

With conditions the same as those of experiment 5 the precipitated mercury weighed 0.1445 gram; the anode was covered with bismuth peroxide.

*Experiment 7.*

In this trial the only change that we made from the conditions of experiment 6 was to reduce the quantity of bismuth to 0.0179 gram. The precipitated mercury weighed 0.1290 gram. It showed bismuth. The anode was coated with bismuth peroxide. The precipitation of metals was complete.

*Experiment 8.*

With conditions similar to those of 7, except that the current registered 1.4 cc. of electrolytic gas per minute, the precipitated mercury weighed 0.1284 gram. The anode showed bismuth peroxide. We found that the metals were precipitated simultaneously. Indeed, at times, it seemed that the precipitation of the bismuth began before that of the mercury. This was true with the most varying conditions. Hence, we believe that the

conditions proposed by Classen (see quotation above) should be modified to accord with facts, as stated by us, and with his own personal observation, as recorded in the *Ber. d. chem. Ges.* (1886), **19**, 325:

“ Von *Wismuth* konnte das Quecksilber auf diese Weise nicht getrennt werden. Beide Metalle scheiden sich gleichzeitig aus der sauren Lösung aus.”

CHEMICAL LABORATORY OF  
THE UNIVERSITY OF PENNSYLVANIA.  
1893.

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## THE ELECTROLYTIC SEPARATION OF COPPER FROM ANTIMONY.

BY EDGAR F. SMITH AND D. L. WALLACE.

The separation of these two metals, in the electrolytic way, has long presented difficulties. These were first noticed by Wrightson (*Ztschr. anal. Chem.*, **15**, 297). Operating upon solutions containing 1.2075 per cent. of metallic copper and 0.280 per cent. to 0.800 per cent. of antimony, in the presence of twenty cc. of nitric acid of sp. gr. 1.21, and total dilution of 200 cc., he found that more or less antimony was precipitated together with the copper. Wrightson remarks, however, that in the presence of much less antimony (*e. g.*, in impure copper) it is possible to throw down the copper free from antimony. Classen corroborates this statement, and finds that the separation of copper and antimony may be made in a solution of the double oxalates (*Quantitative Analyse durch Elektrolyse*, dritte Auflage, p. 125), provided that the antimony content is very slight, and that the current is not permitted to act any longer than absolutely necessary for the complete deposition of the copper.

From the preceding statements it is manifest that a better, more certain, separation is desirable. In conjunction with Muhr (*J. Anal. Appl. Chem.*, **5**, 488) one of us (S) found that iron, cadmium, copper, nickel, and other metals could be completely precipitated from ammoniacal tartrate solutions. The iron carried down carbon with it; this was not the case with the other