| Time of heating. minutes. | Mode of heating. | Loss each time. gram. | Total loss. gram. | Loss in per cent. |
|---|---|---|---|---|
| 6 | Bunsen burner, crucible slightly uncovered | 0.0039 | 0.0039 | 1.4 |
| 5 | Bunsen burner, crucible slightly uncovered | 0.0034 | 0.0073 | 2.7 |
| 5 | Bunsen burner, lid off, contents half melted | 0.0047 | 0.0120 | 4.4 |
| 10 | Small flame, bottom just red hot, crucible slightly covered | 0.0010 | 0.0130 | 4.9 |
| 15 | Same, but flame slightly reduced | 0.0003 | 0.0133 | 4.9 |

It follows from these experiments that the full flame of a Bunsen burner, if applied to 0.549 gram of sodium fluoride, will cause a loss of nearly 0.4 per cent. in six minutes, and if applied to 0.2714 gram will cause a loss of 1.4 per cent. in six minutes, while if the flame be reduced so that it will hardly redden the bottom of the covered platinum crucible there will be no very appreciable loss in fifteen minutes.

By observing these two precautions—subjecting sufficient material to analysis to yield not less than 0.6 gram sodium fluoride and applying as little heat as possible—the Reischle method gives excellent results, and the slight discrepancy between the results of the analysis in Experiment A V of the preceding paper, executed after the fact of the volatilization of sodium fluoride was ascertained, and the results of the analyses in experiments A III and A IV is readily accounted for.

In conclusion I wish to express to Prof. Norton my sincerest thanks for the many courtesies extended to me during these experiments. I feel likewise much indebted to Prof. Langenbeck for his kindness in having carried out the experiments on a larger scale as before recorded.

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# ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH AND HENRY E. SPENCER.

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## I. SILVER FROM COPPER.

THE literature relating to electrolysis contains two suggestions bearing upon the separation of these metals. The first is that of Classen, (Quantitative Analyse durch Elektrolyse, dritte Auflage, p. 124). In reality this is not an electrolytic method as the author proposes to first separate the metals by precipitating out the silver as oxalate, filtering off the same, dissolving it in potassium cyanide, and then decomposing this solution of the double cyanide of silver and potassium by means of the electric current. The double oxalate of copper and ammonium being soluble in water is filtered from off the insoluble silver oxalate, and the copper is then deposited from this solution by the current. No data obtained in the actual use of the method appear to have been published. The insolubility of silver oxalate in ammonium oxalate is not generally conceded (Rose, Analyt. Chemie, **1**, 342), so that it might well be expected, if this statement be true, that the deposit of copper would contain silver. Experiments were instituted to ascertain how accurate the method really was. The results of a few are given below. They are at the least quite instructive.

*Experiment 1.*—Ten cc. of a cold saturated solution of ammonium oxalate were added to a solution containing fifty cc. of copper sulphate (= 0.2284 gram of metallic copper) and ten cc. of silver nitrate (= 0.1000 gram of metallic silver). The precipitated silver oxalate was filtered and washed with ten cc. of an ammonium oxalate solution and later with pure water. The washings were colorless and the filtrate was perfectly clear, not the slightest turbidity being observed. The liquid, now 200 cc. in volume, was heated to 50° C., and electrolyzed with a current of 3.4 cc. of electrolytic gas per minute. This procedure was as nearly like that prescribed by Classen (Elektrolyse, pp. 78, 124) as it could be, since that chemist fails to give details, leaving the same to the student for adjustment. The precipitation of the copper was rapid and in every respect satisfactory. The deposit of copper weighed 0.2285 gram. Apparently the separation was complete and in no way lacking. However, upon dissolving the copper in dilute nitric acid, diluting with water and adding dilute hydrochloric acid a decided cloudiness was produced. This was found to be *due to silver chloride.*

*Experiment 2.*—In this trial the quantity of copper was reduced to 0.1142 gram. The silver present equaled 0.1 gram. Twenty-five cc. of ammonium oxalate were used for the precipitation and eleven more for the washing. In other respects the conditions were similar to those in Experiment 1. The copper deposit weighed 0.1140 gram, instead of 0.1142 gram as required by theory, *yet it contained a very decided amount of silver*, which was revealed upon examining the copper.

*Experiment 3.*—The details here were analogous to those in Experiment 1. The precipitated copper weighed 0.2283 gram, *but after solution gave 0.0012 gram silver chloride equal to 0.0009 gram metallic silver.*

*Experiment 4.*—This was similar to experiment 2. The precipitate of copper weighed 0.1134 gram. It was 0.0008 gram low, but notwithstanding it showed on examination the presence of 0.0009 gram of silver.

Many more trials were made with varying amounts of copper, silver, and ammonium oxalate, but in every instance silver showed itself upon examining the precipitated copper. The inevitable conclusion is then that, however insoluble silver oxalate may be in the absence of other metals when copper is present with it, weighable amounts do pass into solution. Care was taken not to electrolyze solutions that were not absolutely clear. At times great difficulty was experienced in getting a clear filtrate from the silver oxalate. All cloudy filtrates were rejected. The results given above demonstrate that the suggestion of Classen (*loc. cit.*) with reference to the separation of silver and copper is not entitled to any consideration on the part of those who are engaged in electrolytic studies.

From an article published in the *Ztschr. angew. Chemie*, 696 (1892), by Rüdorff, it would seem that this chemist also failed, in using Classen's method, to obtain satisfactory results. The experiments in this communication are, therefore offered as a confirmation of Rüdorff's observations so far as concerns the separation of silver and copper.

The second suggestion in regard to the electrolytic separation of these two metals was offered by Smith and Frankel (*J. Frank. Inst.*, 1889; Smith's Electrochemical Analysis, p. 100). They electrolyzed a solution containing the double cyanides in the presence of an excess of alkaline cyanide. Numerous repetitions of their method, made in this laboratory, confirm their observation. Rüdorff (*loc. cit.*) also found it satisfactory. The time-factor can, as will be noticed below, be much reduced by merely electrolyzing the solution at a temperature ranging from 65° to 70° C. The method in consequence is rendered more serviceable. Results obtained in this way follow:

*Experiment 1.*—A solution under electrolysis contained 0.1 gram of metallic silver and 0.1140 gram of metallic copper. The quantity of potassium cyanide present equaled 1.8 grams. The temperature of the liquid was maintained at 65° C., throughout the entire decomposition. The current was $N.D_{100}=0.07$ ampere. The total dilution of the solution equaled 200 cc. The time required for the complete precipitation of the silver was about three hours. The deposit weighed 0.0996 gram; it did not contain copper.

*Experiment 2.*—In this trial the conditions were similar to those in Experiment 1. The silver deposit weighed 0.1 gram. It contained no copper.

A silver dime was dissolved and the solution diluted to a definite volume. Twenty-five cc. of this solution contained 0.1081 gram of metallic silver. One gram of potassium cyanide was added to the solution and the whole then diluted to 200 cc. The temperature of the liquid during the electrolysis was 60° C. The time of precipitation occupied three hours. The silver deposit weighed 0.1080 gram; it was free from copper.

Fifty cc. of the coin solution (=0.2162 gram of metallic silver) were mixed with two grams of potassium cyanide, diluted with water to 225 cc., heated to 65° C., and electrolyzed with a current of $N.D_{100}=0.07$ ampere. The precipitated silver weighed 0.2153 gram.

The method of Smith and Frankel, as thus modified is applicable where results are desired in a comparatively short time-period.

### 2. MERCURY FROM COPPER.

These metals were also fully separated from each other by the electrolytic decomposition of their double cyanide solution (Smith and Frankel, *Am. Chem. J.*, **11**, 264, 104; Smith and McCauley, *J. Anal. Appl. Chem.*, **5**, 489, and *Ber. d. chem. Ges.*, **24**, 2936; also Freudenberg, *Ztschr. phys. Chem.*, **12**, 113). No difficulty attends the separation, and possibly the only objection that could be offered to the method is, that considerable time is required for its completion. As in the case of silver and copper it is only necessary to apply a gentle heat to the solution undergoing electrolysis and the time-factor will be greatly reduced. For example:

*Experiment 1.*—A solution of 200 cc. volume, containing 0.2167 gram of metallic mercury, 0.2156 gram of metallic copper, and two grams of potassium cyanide was heated to 65° C. and electrolyzed with a current of $N.D_{100} = 0.08$ ampere. The precipitation was finished in three and one-half hours. The deposit of mercury was adherent and weighed 0.2168 gram. It contained no copper.

*Experiment 2.*—Here the conditions were nearly like those in (1). The current of $N.D_{100} = 0.06$ ampere acted for a period of four hours. The precipitated mercury weighed 0.2169 gram, but it did not contain copper.

*Experiment 3.*—The temperature of the solution was 70° C. The current of $N.D_{100} = 0.08$ ampere acted through four hours. The mercury weighed 0.2170 gram. It contained no copper.

*Experiment 4.*—In this trial the quantity of each metal was half the amount given in the preceding experiments. But one gram of potassium cyanide was present. The current of $N.D_{100} = 0.08$ ampere acted three hours upon the solution heated to 70° C. The precipitated mercury weighed 0.1083 gram. Copper was not found in it.

### 3. SILVER FROM CADMIUM.

These metals have usually been separated electrolytically when present in nitric acid solution. As both are precipitated by rather feeble currents form solutions containing them as double cyanides, it did not occur to the writers until recently that they could also be separated from each other in a solution of this nature. The two experiments which follow show that such is indeed the case. The separation cannot be made in a cold solution. The silver will always be contaminated with cadmium. The most favorable conditions are noted in the examples here given.

*Experiment 1.*—A solution of 200 cc. volume contained 0.1000 gram of metallic silver, a like quantity of metallic cadmium, and three grams of potassium cyanide. It was heated to 65° and then electrolyzed for three and one-half hours with a current of $N.D_{100} = 0.04$ ampere. The precipitated silver weighed 0.1004 gram. No cadmium was found in it. The poles were separated two inches from each other.

*Experiment 2.*—Operating with conditions just like those in experiment 1, the deposit of silver weighed 0.0999 gram.

UNIVERSITY OF PENNSYLVANIA,
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# THE ACTION OF PHOSPHORUS PENTACHLORIDE UPON MOLYBDENUM TRIOXIDE.

BY EDGAR F. SMITH AND GEORGE W. SARGENT.

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THE action of phosphorus pentachloride upon the trioxides of tungsten and of molybdenum has been the subject of investigation by Schiff,[1] Teclu,[2] and Piutti.[3] Schiff announced that with tungstic acid and the pentachloride the products were in the main phosphorus oxychloride and a brown colored tungsten oxychloride. Teclu, upon repeating Schiff's experiments, obtained phosphorus oxychloride and the *hexachloride of tungsten*. This was the result when working with one part of $WO_3$ and three parts of phosphorus pentachloride. The mixture was heated in sealed tubes. Piutti substituted molybdenum trioxide and hoped to get a corresponding molybdenum *hexachloride*. This he did not realize; instead, he obtained a compound which gave results on analysis that led to the formula $MoCl_5.POCl_3$. Along with the dark-green colored crystals of this compound there was a reddish-brown liquid. The tube, after being opened, and as soon as the liquid was removed, was connected with a Woulff bottle to which a drying tube was attached. The other end of the sealed tube was opened and connected with a carbon dioxide generator. The tube was next surrounded with water at 80°, and a current of carbon dioxide conducted through it, when the green colored crystals sublimed. They were carefully collected and gave the results from which was deduced the formula given above. We have repeated the experiment of Piutti under

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[1] *Annalen der Chemie*, 102, 115.

[2] *Annalen der Chemie*, 187, 255.

[3] *G. ch. italiana*, 9, 538.