

similarity of constituents seems to be a strongly modifying condition however.

Note.—Since sending the above article to press I am in receipt of a reprint of a paper entitled, "A Contribution to the Study of Liquid Mixtures of Constant Boiling-point," by Dr. Garnett Ryland,¹ in which are described his investigations of some of the same mixtures as are given in the above paper and paper I. They are benzene and chloroform, benzene and methyl alcohol, methyl alcohol and ether, methyl alcohol and acetone, and methyl alcohol and chloroform. His results are in the main the same as those obtained by myself, except in the case of methyl alcohol and acetone. He finds that this mixture can be separated by fractional distillation, while I find that the mixture has a minimum point about 0.8° C. below the boiling-point of the pure solvent.

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THE ELECTROLYSIS OF METALLIC PHOSPHATE SOLUTIONS.

BY HARRY M. FERNBERGER AND EDGAR F. SMITH.

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THE action of the current upon metallic phosphates, has received considerable attention in this laboratory. The frequent satisfactory repetition of these methods has only served to convince us that they deserve a permanent place in electrolytic literature, hence we take the present opportunity of again calling attention to them in their modified forms as to current density, voltage, etc., factors which were not especially emphasized in the earlier communications. Furthermore, other interesting behaviors of various metals in phosphate solutions, having come to light, we shall include them here. They are at least suggestive.

COPPER.

To a solution of copper sulphate, equivalent to 0.1239 gram of metal, were added twenty cc. of disodium hydrogen phosphate (sp. gr. 1.0358), and the precipitate produced was dissolved in five cc. of phosphoric acid (sp. gr. 1.347). The electrolytic

¹ Dissertation, Johns Hopkins University, 1898.

decomposition was then made with the following prevailing conditions :

N.D. ₁₀₀	0.035 to 0.068 ampere.
Voltage.....	2.2 to 2.6.
Dilution.....	225 cc.
Temperature.....	54 ^o -64 ^o .
Time.....	6 to 7 hours.

The deposit of copper weighed 0.1244 gram. It showed a deep red color. The metal could not be detected in the filtrate. A second trial gave 0.1243 gram of copper.

COPPER FROM IRON.

Sixty cc. of a disodium hydrogen phosphate solution (sp. gr. 1.0358) were added to twenty-five cc. of a copper sulphate solution (= 0.1239 gram of copper) and fifty cc. of a ferric ammonium sulphate solution (= 0.2002 gram of iron). The resulting precipitate was dissolved in ten cc. of phosphoric acid (sp. gr. 1.347). The conditions existing during the electrolysis were :

N.D. ₁₀₀	0.04 ampere.
Voltage.....	2.4.
Dilution.....	225 cc.
Temperature.....	53 ^o C.
Time.....	7 hours.

The copper deposit weighed 0.1237 gram. Its color was brown-red, and it showed a silky luster. Iron was not found in it. The filtrate contained no copper.

COPPER FROM ALUMINUM.

To a solution containing 0.1239 gram of copper and 0.1000 gram of aluminum, were added sixty cc. of disodium hydrogen phosphate (sp. gr. 1.0338) and five cc. of phosphoric acid (sp. gr. 1.347). The conditions were :

N.D. ₁₀₀	0.068 ampere.
Voltage.....	2.6.
Dilution.....	225 cc.
Temperature.....	77 ^o .
Time.....	6 hours.

The precipitated copper weighed 0.1240 gram. It was not contaminated with aluminum, nor did the filtrate show any signs of copper.

COPPER FROM CHROMIUM.

Sixty cc. of disodium hydrogen phosphate (sp. gr. 1.033) and 8 cc. of phosphoric acid (sp. gr. 1.347) were added to a solution containing 0.1239 gram of metallic copper and 0.1403 gram of chromium. The precipitation of metal then occurred with the following conditions :

N.D. ₁₀₀	0.062 ampere.
Voltage.....	2.5.
Dilution.....	225 cc.
Temperature.....	64°.
Time.....	6 hours.

The deposit of copper weighed 0.1243 gram. The filtrate did not show the presence of copper, nor could chromium be detected in the precipitated metal.

When the conditions given in the preceding separations are observed there need be no doubt as to the results.

COPPER FROM COBALT.

Sixty cc. of disodium hydrogen phosphate, and ten cc. of phosphoric acid were added to a liquid containing 0.1239 gram of metallic copper and 0.1000 gram of metallic cobalt. It was then electrolyzed with :

N.D. ₁₀₀	0.035 ampere.
Voltage.....	1.5.
Dilution.....	225 cc.
Temperature.....	62°.
Time.....	6 hours.

The precipitated copper weighed 0.1243 gram. It did not contain cobalt.

COPPER FROM ZINC.

Salts of these two metals, containing the same quantities of disodium hydrogen phosphate and phosphoric acid, were electrolyzed with:

N.D. ₁₀₀	0.035 ampere.
Voltage.....	2.5.
Dilution.....	225 cc.
Temperature.....	60°.
Time.....	5 hours.

The copper weighed 0.1244 gram, and was free from zinc.

COPPER FROM NICKEL.

A solution of copper sulphate (= 0.1239 gram of copper) and nickel nitrate (= 0.1366 gram of nickel) was mixed with seventy-five cc. of disodium hydrogen phosphate (sp. gr. 1.033) and ten cc. of phosphoric acid (sp. gr. 1.347). The conditions of electrolysis were :

N.D. ₁₀₀	0.072 ampere.
Voltage.....	2.45.
Dilution.....	225 cc.
Temperature.....	66° C.
Time.....	6 hours.

The precipitated copper weighed 0.1241 gram. The filtrate did not show the presence of this metal, and the deposit was free from nickel.

It was thought advisable to carry out the separation of copper in phosphate solution, not from a single metal alone, but from several, and note the most favorable conditions.

COPPER FROM IRON, COBALT, AND ZINC.

The solution contained 0.1239 gram of copper, 0.1007 gram of cobalt, 0.1000 gram of iron, thirty cc. of disodium hydrogen phosphate (sp. gr. 1.0358), and fifteen cc. of phosphoric acid (sp. gr. 1.347). The conditions of the electrolysis were :

N.D. ₁₀₀	0.04 to 0.05 ampere.
Voltage.....	2.3.
Dilution.....	225 cc.
Temperature.....	57°.
Time.....	6 hours.

The deposit of copper weighed 0.1240 gram. It was free from the other metals.

COPPER FROM MANGANESE.

A solution containing about equal amounts of the two metals together with sixty cc. of disodium hydrogen phosphate (sp. gr. 1.038) and ten cc. of phosphoric acid (sp. gr. 1.347), was electrolyzed with :

N.D. ₁₀₀	0.05 ampere.
Voltage.....	2.5.
Dilution.....	225 cc.
Temperature.....	56° C.
Time.....	6 hours.

The copper deposit weighed 0.1236 gram. The preceding determinations were all conducted with comparatively feeble currents.

Trials were made with stronger currents with several of the metals.

NICKEL.

Thirty cc. of disodium hydrogen phosphate were added to a nickel solution (\equiv 0.070 gram of nickel), and the resulting precipitate was then dissolved in just sufficient phosphoric acid (1.347 sp. gr.) for that purpose, with several drops in excess. The electrolysis was then made with:

N.D. ₁₀₀	0.50 ampere.
Voltage.....	7-8.
Dilution.....	225 cc.
Temperature.....	68° C.
Time.....	3½ hours.

The precipitate of nickel weighed 0.0703 gram. The filtrate was found free from that metal. A second nickel solution (\equiv 0.1360 gram of metal), forty-five cc. of disodium hydrogen phosphate (sp. gr. 1.038) and phosphoric acid (sp. gr. 1.347) sufficient to dissolve the precipitate, with a few drops in excess, was electrolyzed with:

N.D. ₁₀₀	0.53 ampere.
Voltage.....	7.
Dilution.....	225 cc.
Temperature.....	65°.
Time.....	3½ hours.

The nickel precipitate weighed 0.1360 gram. These deposits of nickel were dull gray in color, resembling the appearance to some extent of the platinum dish. They were very adherent, and were readily handled and washed. Notwithstanding the precipitation of the metal was complete, the attempts to separate it in this way from manganese and chromium were fruitless. On examining the deposit from the nickel and manganese solution it was found to contain phosphorus.

The use of stronger currents with zinc salts failed to give satisfactory results. A qualitative test made with cobalt seemed to indicate that this metal could be deposited with conditions similar to those used with nickel. A solution, containing both

iron and manganese, was also acted upon with a current similar to that employed with nickel and cobalt but neither of the metals was deposited. We were equally unsuccessful in depositing uranium from an acid phosphate solution.

MERCURY.

Twenty-five cc. of a mercuric chloride solution (= 0.1159 gram of metal), thirty cc. of disodium hydrogen phosphate (sp. gr. 1.038) and five cc. of phosphoric acid (sp. gr. 1.347), were electrolyzed with :

N.D. ₁₀₀	0.04 ampere.
Voltage.....	1.6.
Dilution.....	175 cc.
Temperature.....	50° C.
Time.....	4 hours.

The precipitated mercury weighed 0.1162 gram. It was silvery white in color and drop-like in appearance.

MERCURY FROM ZINC.

Twenty-five cc. of a mercuric chloride solution (= 0.1159 gram of metal), twenty-five cc. of zinc sulphate (= 0.1010 gram of zinc), sixty cc. of disodium hydrogen phosphate (sp. gr. = 1.038) and ten cc. of phosphoric acid (sp. gr. = 1.347), were electrolyzed with :

N.D. ₁₀₀	0.01 ampere.
Voltage.....	1.5.
Dilution.....	175 cc.
Temperature.....	60° C.
Time.....	4-5 hours.

The deposit of mercury weighed 0.1163 gram. It was free from zinc. The filtrate did not show any mercury.

The separation of mercury from cadmium did not succeed. As uranium was not precipitated under similar conditions we hoped for a separation of this metal from mercury and also from copper.

MERCURY FROM URANIUM.

A solution containing 0.1159 gram of mercury, 0.1018 gram of uranium, sixty cc. of disodium hydrogen phosphate (sp. gr. 1.038), and ten cc. of phosphoric acid (sp. gr. 1.347), was electrolyzed with :

N.D. ₁₀₀	0.017 amperes.
Voltage.....	2.45.
Dilution.....	175 cc.
Temperature.....	61° C.
Time.....	5½ hours.

The deposit weighed 0.2370 gram. It was heavier, therefore, than the combined weights of the mercury and uranium. A second trial was made after increasing the volume of phosphoric acid to fifteen cc. The deposit weighed 0.2012 gram. It had a dull lead color. It was strongly ignited to expel the mercury. The scaly residue was boiled with dilute nitric acid and the solution tested with ammonium molybdate. Large amounts of phosphorus were indicated. This would prove that the original deposits of metallic mercury so influenced the uranium salts that they were coprecipitated with that metal. Whatever the composition of the deposit may be it is certainly very variable. It is quite probable that a hydrous uranium phosphate is deposited with the mercury. The filtrates were all free from uranium.

On trying to effect the separation of copper from uranium in acid phosphate solution we experienced the same difficulty as with mercury and uranium. The precipitate consisted of copper, uranium, and phosphorus. The filtrate showed no signs of either copper or uranium. The separation of mercury and manganese was far from satisfactory. The same must be said of nickel and cobalt. They were partially precipitated with the mercury and carried down phosphorus with them. A qualitative test was made to separate uranium in the presence of mercury and phosphoric acid, electrolytically from iron. The deposit contained no iron when a current of $N.D._{100} = 0.006$ ampere was employed. This separation will receive further study in the immediate future.

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OBSERVATIONS UPON TUNGSTEN.

By EDGAR F. SMITH.

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THIS communication presents fragmentary data upon tungsten collected during a period of years and amply verified by repeated reviews. As tungsten in its various combinations has been an object of great interest to the writer, particularly