[CONTRIBUTION FROM THE CHEMICAL LABORATORY, OHIO STATE UNIVERSITY.]

THE INFLUENCE OF TEMPERATURE ON THE ELECTROLYTIC PRECIPITATION OF COPPER FROM NITRIC ACID.[1]

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Received January 13, 1908.

While determining copper electrolytically with stationary electrodes, it was observed upon several occasions that after the copper appeared to be almost all precipitated it slowly re-dissolved and disappeared from view within a very few minutes. This took place without any change in the current conditions as registered on either the ammeter or voltmeter. Evidently the conditions for the determination were very close to the limits of the ability of the current to precipitate the metal. A slight variation of the conditions, therefore, in some one of the possible directions during the course of an experiment, was sufficient to permit the free nitric acid in the electrolyte to overcome the influence of the current and dissolve what metal had already been deposited.

Increasing temperature of the electrolyte caused by fluctuation of the gas pressure was blamed for the difficulty. It was soon found that higher temperatures than customary[2] existed in the electrolytes which caused trouble. The following work was then undertaken to ascertain just what were the safe limits of temperature for a variety of concentrations of nitric acid, using a fixed amount of current.

Platinum-iridium dishes approximating the customary form were used as cathodes. They were 9 cm. in diameter and 5 cm. deep and when they contained 100 cc. the cathode area was about 100 sq. cm. The anode was a platinum-iridium wire nearly 1.5 mm. in diameter (about No. 15, B. and S. gauge). It was bent in the form of a spiral 4 cm. in diameter, comprising three complete turns. In all, there were 26.5 cm. of the wire exposed to the electrolyte. The current was supplied by storage cells, and the current conditions given in the tables have been calculated to the "Normal Density" from the instrument readings, because the "Normal" cathode surface was not used. The American Instrument Company's Type 2 switchboard ammeter had a capacity of one ampere and the scale was divided into hundredths. The voltmeter had a capacity of 50 volts with scale divisions of half volts.

As a result of some preliminary experiments the distance between the electrodes was maintained at 2 cm. throughout the work. This made their actual separation at all points approximately uniform. The current strength was kept constantly at 0.08 amp. (per 100 sq. cm.). The total dilution was maintained at 125 cc. When nitric acid was added to the electrolyte the metallic deposits were in all cases brilliant and com-

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[1] Read at the Chicago meeting of the American Chemical Society.

[2] Edgar F. Smith's "Electrochemical Analysis," 3d Ed., 1902, p. 59.

pact except at the higher temperatures (above 70°). In these latter cases the deposits were not smooth and burnished but were made up of a collection of lustrous individual crystals of copper. When examined under the microscope these crystals were of octahedral aspect. The deposits from the solutions in which nitric acid was entirely absent, were of a different character. All deposits were, however, thoroughly adherent, and no tendency to sponginess was observed in any case. This good condition of the deposits enabled them to be weighed without the use of a drying oven. Washing with boiling water was dispensed with for the same reason.

They were washed thoroughly with distilled water, carrying off the excess with a siphon in the usual manner without breaking the circuit. When washed free from all electrolyte the dish was removed and rinsed with dilute, and then absolute alcohol. Finally absolute ether was used, and after the adhering ether had been all vaporized and the dish rubbed on the outside with a piece of chamois skin it was placed in a desiccator and weighed in from 15 to 30 minutes. The wash water, or at least the first portion of it, was always preserved and tested in the usual manner. When, however, this solution was neutralized with ammonium hydroxide and acetic acid added followed by potassium ferrocyanide the presence of a trace of copper was often observed.

Occasionally, during the progress of the work there was a discoloration of the anode. This discoloration was of a more or less milky appearance, but at times it resembled anodic deposits that have been obtained from the electrolysis of gold solutions.[1] At other times it was like burnished deposits of gold itself. This discoloration was probably of the nature of a deposit for it could be removed by the touch of a finger, or immersion in nitric acid. No increase in weight of the anode could be detected, however, even in several determinations run for upwards of 20 hours. When the deposit was removed by nitric acid no change in the weight of the anode greater than a tenth of a milligram could be detected except in a single isolated case of 0.3 mg. No further attention was therefore given to the matter at this time. The amount of copper considered as present in the solutions used in the work was the mean of several determinations which were run until the electrolyte gave no further tests for copper.

It was found that in the complete absence of nitric acid the copper from a solution of pure copper sulphate (containing 0.25 gram of metal) could be completely precipitated in 16 hours. The rate of precipitation of copper was therefore determined from this electrolyte, in the total absence of nitric acid, to point out the value of the addition of this acid.

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[1] This Journal, 28, 1353.

$CuSO_4$. Cu in grams.	HNO_3. cc.	Total dilution. cc.	Current.		Temp. Centigrade.	Time. Hours.	Cu found. Gram.
			$N.D._{100}$ amp.	Volts.			
0.2503	0	125	0.08	3.3–2.6	25	1	0.1112
0.2503	0	125	0.08	3.3–2.5	25	3	0.2234
0.2503	0	125	0.08	3.3–3.3	25	6	0.2482
0.2503	0	125	0.08	3.3–2.8	25	13	0.2510

In the absence of nitric acid the copper did not appear as rapidly upon closing the circuit as it seemed to do in the presence of small amounts of this acid. In the above determinations the solutions appeared to take on an olive-green tint before the copper became visible. This was also observed when a solution containing only copper nitrate was electrolyzed, but not when free nitric acid had been added. Owing no doubt to the liberation of sulphuric acid, the conductivity of the electrolytes in the above determinations increased steadily, requiring continued increase in the resistance of the rheostat to maintain the current strength at 0.08 ampere per 100 sq. cm. The deposit was about as bright at the end of one hour as it would be from a nitric acid electrolyte. After about two hours, however, the copper began to come down on this bright deposit in a pulverulent form. It would come off as a powder, if touched, but never of its own accord, even upon thorough washing. It appeared velvety and had completely lost its metallic luster. In color it approached the so-called "cherry-red" of powdered hematite. This pulverulent copper was in all cases only a superficial coating, as was shown by treating it with dilute nitric acid, when it dissolved with ease, exposing the bright copper beneath.

The copper from this electrolyte was completely precipitated in 13 hours. The deposit, however, weighed high. This seems to be a common complaint against the sulphuric acid electrolyte, if the determinations are run too long.

The rate of precipitation of the metal was determined from a solution of copper nitrate to which no free acid had been added.

$Cu(NO_3)_2$. Cu in grams.	HNO_3. cc.	Total dilution. cc.	Current.		Temp. Centigrade.	Time. Hours.	Cu found. Gram.
			$N.D._{100}$ amp.	Volts.			
0.2505	0	125	0.08	2.9–2.5	25	1	0.1087
0.2505	0	125	0.08	2.8–2.6	25	3	0.2208
0.2505	0	125	0.08	2.9–2.6	25	6	0.2450
0.2505	0	125	0.08	2.8–3.7	25	12	0.2504

These deposits were not all like those from pure copper sulphate. They resembled the deposits obtained in the presence of free nitric acid, but were not so brilliant and had a slight tendency to be pulverulent at the center. A comparison of these two tables will show that while the copper may appear first from copper nitrate, yet slightly more is precipitated in a given time after one hour and beyond, from copper sulphate.

Using the copper sulphate solution the rate of precipitation of copper was determined at 25° in the presence of varying amounts of nitric acid (sp. gr. 1.42).

$CuSO_4$. Cu in grams.	HNO_3. cc.	Total dilution. cc.	Current.		Temp. Centigrade.	Time. Hours.	Cu found. Gram.
			$N.D._{100}$ amp.	Volts.			
0.2503	0.25	125	0.08	2.2–2.4	25	1	0.1024
0.2503	0.25	125	0.08	2.2–2.6	25	3	0.2217
0.2503	0.25	125	0.08	2.4–2.6	25	6	0.2445
0.2503	0.25	125	0.08	2.3–2.8	25	12	0.2499
0.2503	0.25	125	0.08	2.3–3.1	25	13	0.2504
0.2503	1.0	125	0.08	2.1–2.2	25	1	0.1060
0.2503	1.0	125	0.08	2.2–2.3	25	2	0.1897
0.2503	1.0	125	0.08	2.2–2.4	25	3	0.2223
0.2503	1.0	125	0.08	2.2	25	6	0.2439
0.2503	1.0	125	0.08	2.2–2.4	25	9	0.2489
0.2503	1.0	125	0.08	2.2	25	12	0.2501
0.2503	1.0	125	0.08	2.2	25	13	0.2503
0.2503	1.0	125	0.08	2.2–2.5	25	15	0.2504
0.2503	1.0	125	0.08	2.0–2.5	25	20	0.2505
0.2503	1.0	125	0.08	2.2–2.4	25	23	0.2503
0.2503	1.0	125	0.08	2.2–2.5	25	24	0.2502
0.2503	1.0	125	0.08	2.2–2.5	25	24	0.2506
0.2503	2.5	125	0.08	2.2–2.3	25	1	0.0916
0.2503	2.5	125	0.08	2.2–2.3	25	3	0.1972
0.2503	2.5	125	0.08	2.0–2.3	25	6	0.2418
0.2503	2.5	125	0.08	2.2	25	13	0.2501
0.2503	2.5	125	0.08	2.2–2.4	25	14	0.2501
0.2503	6.25	125	0.08	2.2–2.3	25	1	0.0512
0.2503	6.25	125	0.08	2.2–2.3	25	3	0.1245
0.2503	6.25	125	0.08	2.2	25	6	0.1585
0.2503	6.25	125	0.08	2.2–2.4	25	13	0.2394
0.2503	6.25	125	0.08	2.2	25	17	0.2414
0.2503	12.5	125	0.08	2.2	25	13	0.0003
0.2503	62.5	125	0.08	1.5	25	2	0.0000

From the results given above it will be seen that the rate of precipitation in presence of 0.25 cc. of nitric acid was slightly lower than when no free acid is present in the copper nitrate electrolyte and much lower than with pure copper sulphate. This gave a fairly good idea of the retarding effect of the presence of nitric acid. The effect, however, was not great, and the improvement in the character of the deposits more than compensated for it.

In the presence of 1 cc. of nitric acid a quarter gram of copper was precipitated in 12 to 13 hours. Running the determination for 15, 20, 23 or 24 hours had no effect on either the appearance or weight of the deposit. The results in presence of this amount of acid were almost identical with those from the 0.25 cc. nitric acid electrolyte.

When two per cent. (2.5 cc.) of nitric acid was present the precipitation of a quarter gram of copper required 13–14 hours. The retarding influence of the free nitric acid was now becoming more emphatic, and when five per cent. (6.25 cc.) of acid was used, the effect was pronounced. In this case the precipitation of the quarter gram of copper was still incomplete after 17 hours. As this was too long an interval for the precipitation of such a small amount of this metal, the work with these conditions was not carried farther. The result with ten per cent. nitric acid (12.5 cc.) came from a faint film (or line) of metal at the upper edge of the cathode surface exposed to the electrolyte, and probably should not be called a deposit from this strength of solution. Red oxides of nitrogen were evolved from the solution containing 50 per cent. nitric acid and no copper was deposited. This work showed that nitric acid retarded the precipitation of copper, but that as it had such a beneficial effect on the character of the deposits, the presence of a small amount was a most desirable addition. The following comparison of the amounts of copper precipitated in six hours from the electrolytes containing varying amounts of free nitric acid, illustrates very clearly the retarding effect of this acid, a fact already appreciated by those who have used this electrolyte.

Electrolyte.	Temperature centigrade.	Cu present. Gram.	Cu deposited in 6 hours. Gram.
$CuSO_4$ + 0 cc. HNO_3	25	0.2503	0.2482
$Cu(NO_3)_2$ + 0 cc. HNO_3	25	0.2505	0.2450
$CuSO_4$ + 0.25 cc. HNO_3	25	0.2503	0.2445
$CuSO_4$ + 1.00 cc. HNO_3	25	0.2503	0.2439
$CuSO_4$ + 2.50 cc. HNO_3	25	0.2503	0.2418
$CuSO_4$ + 6 25 cc. HNO_3	25	0.2503	0.1585

Having found just what the influence of nitric acid was on the precipitation of copper at ordinary temperature, the minimum amount of this acid was used in a number of experiments at higher temperatures.

$CuSO_4$. Cu in grams.	HNO_3. cc.	Total dil. cc.	Current.		Temp.	Time. Hours.	Cu found. Gram.
			$N.D._{100}$ amp.	Volts.			
0.2503	0.25	125	0.08	2.4–2.3	40°	1	0.0972
0.2503	0.25	125	0.08	2.3–2.4	40°	3	0.2261
0.2503	0.25	125	0.08	2.3–2.4	40°	6	0.2493
0.2503	0.25	125	0.08	2.3–2.5	40°	7	0.2500
0.2503	0.25	125	0.08	2.4–2.4	60°	1	0.0833
0.2503	0.25	125	0.08	2.3–2.2	60°	3	0.2288
0.2503	0.25	125	0.08	2.2–2.3	60°	6	0.2501
0.2503	0.25	125	0.08	2.1–2.1	70°	1	0.0683
0.2503	0.25	125	0.08	2.1–2.1	70°	3	0.2214
0.2503	0.25	125	0.08	2.1–2.2	70°	5	0.2488
0.2503	0.25	125	0.08	2.2–2.3	70°	6	0.2501
0.2503	0.25	125	0.08	2.1–2.1	80°	3	0.1823
0.2503	0.25	125	0.08	1.7	80°	6	0.2491
0.2506	0.25	125	0.08	2.1–2.2	90°	3	0.0821
0.2503	0.25	125	0.08	2.1–2.3	90°	6	0.2460
0.2503	0.25	125	0.08	.....	70°	6	0.0000
0.2506	0.25	125	0.08	2.4–2.2	25–70°	3	0.2258

From these results it seemed that even the slight elevation of temperature to 40° decreased the time by a considerable amount. A further elevation to 60° still decreased the time but to a much smaller extent, while 70° did not seem to improve the results at 60°. In fact the time reducing effect of increased temperature reached its limit at 60–70°, and from that point any elevation of temperature had a retarding effect on the precipitation. This is well illustrated by a comparison of the amounts of metal deposited in six hours at the various temperatures.

Electrolyte.	Temperature.	Cu present. Gram.	Cu deposited in 6 hours. Gram.
$CuSO_4$+0.25 cc. HNO_3	25°	0.2503	0.2445
$CuSO_4$+0.25 cc. HNO_3	40°	0.2503	0.2493
$CuSO_4$+0.25 cc. HNO_3	60°	0.2503	0.2501
$CuSO_4$+0.25 cc. HNO_3	70°	0.2503	0.2501
$CuSO_4$+0.25 cc. HNO_3	80°	0.2513	0.2491
$CuSO_4$+0.25 cc. HNO_3	90°	0.2503	0.2460

Upon one occasion where the current strength had fallen to 0.05 ampere and the copper appeared almost all precipitated, the electrolyte was heated with the result that about half of the dish was cleaned of its deposit in spite of the fact that the current increased at the same time to 0.15 ampere. That the increased solvent power of nitric acid, with elevated temperature, greatly overbalances the current's increased power of precipitation is further shown in the case of the five per cent. nitric acid electrolyte. At 70° no copper is precipitated, whereas 0.1588 gram is precipitated in the same time at 25°.

In the case of the last determination in the table the temperature was maintained at 25° for two hours and forty-five minutes. It was then raised to 70° during the next ten minutes and held there for the remaining five minutes of the three-hour period. The result indicates the accelerating influence of increase of temperature, it being much higher than for the same period of time at either 25° or 70°. This influence of temperature on electrolysis is completely masked at first in all cases where the electrolyte is heated to the desired temperature before turning on the current. From the table it will be seen that the amount of copper precipitated in one hour is less and less as the temperature increases. After this first hour, however, the beneficial effect of increased temperature is to be seen in every case until the temperature at which the solvent action of the nitric acid begins to persistently diminish the electrolytic deposition.

Conclusions.

1. Even the smallest amounts of nitric acid have a tendency to retard the electrolytic precipitation of copper, under the conditions here used.
2. The presence of nitric acid is, nevertheless, desirable because of its beneficial effect on the character of the deposit.

3. While in general increased temperature means d precipitation, yet with the low current strength an used, the reverse is the case above 70°, no doubt o e rapidly increasing solvent action of the acid.

COLUMBUS,
August 7, 1907.

THE GRAVIMETRIC DETERMINATION OF TELLURIUM.

BY VICTOR LENHER AND A. W. HOMBERGER.

Received January 17, 1908.

Of all the methods proposed for the precipitation of tellurium perhaps the one which is most used is a modification of the original method of Berzelius. He used sulphurous acid as a precipitating agent.

The method of procedure as commonly carried out consists in adding to the hydrochloric acid solution of tellurium a strong aqueous solution of sulphur dioxide and allowing this mixture to remain in a warm place for a few days in order to effect a complete precipitation. It has been shown by Schroetter,[1] Brauner,[2] Norris and Fay,[3] Crane,[4] Frerichs,[5] and others that the precipitation by means of sulphur dioxide is far from satisfactory. Brauner has pointed out that part of the precipitated tellurium undergoes oxidation in the liquid, becoming converted into the tetrachloride, in which form it remains in solution. Crane has suggested that the main cause of the incomplete precipitation by means of sulphur dioxide is the very rapid increase in the ratio of the acids to the unprecipitated tellurium in solution, two-thirds of this being due to the hydrochloric acid set free, and one-third to the sulphuric acid formed. He thought if these could be removed the reduction would be complete. The hydrochloric acid could be eliminated by evaporation, but the continuous increase in sulphuric acid would soon interrupt the reaction. This might, however, be kept under control by the addition of sodium or potassium hydroxide.

Whitehead has suggested a remedy in the use of acid sodium sulphite. He advises a moderately concentrated solution of the sulphite and that the quantity added to the tellurium solution be sufficient only to just neutralize the acids present and that formed during the reaction. When the solution is thoroughly agitated and then allowed to stand in a warm place, the precipitate will form and settle evenly. He states that "while acid sodium sulphite does not completely remove all of the tellurium from the solution in the cold, that if not used in great excess and the

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[1] Chem. News, 87, 17.

[2] J. Chem. Soc., 55, 392.

[3] Am. Chem. J., 20, 278.

[4] *Ibid.*, 23, 408.

[5] J. für pr. Chem., 66, 261.