opposit direction. The theoretical bearing of the results is discussed in the last two paragraphs of the preceding section. Taking also into consideration other accurate transference values for tri-ionic salts previously determined, it has been there shown that transference experiments make necessary one of two alternative conclusions: either the intermediate ion is not formed in any considerable proportion by the dissociation of tri-ionic salts up to moderate concentrations (0.1 to 0.2 normal), or else, if it is formed, its equivalent conductance has a definit value of such magnitude that the transference number is independent of its concentration.

BOSTON. September. 1910.

---

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

# THE CHARACTER OF SILVER DEPOSITS FROM VARIOUS ELECTROLYTES.

BY JOSIAH SIMPSON HUGHES[1] AND JAMES R. WITHROW.

Received September 27, 1910.

In some work previously undertaken by one of us it became of interest to know the conditions which would give silver deposits of various properties or characteristics. The discussion of this general subject by Bancroft[2] is of great assistance in indicating the variations of conditions which favor satisfactory deposition. The influence of each particular electrolyte on these conditions and the minor details of the deposit characteristics is a matter for experimentation. In this connection Snowdon[3] has gone thoroughly into the deposition of silver from nitric acid and potassium cyanide, using the rotating cathode. Other electrolytes have been used from time to time, especially in electroanalysis.

It was thought therefore that a repetition of some of the earlier work done on the electrolytic determination of silver would not only be helpful in the direction desired but would also be of interest from an analytical view point. The results included here give the outcome of some of these experiments, together with a summary of a series of trials made with new electrolytes.

The same dish cathodes were used that were employed in the work on copper.[4] The anode also was the same except that the diameter of the spiral was 5 cm. in the present case. The current was supplied by storage cells and was measured by Weston, Model 57, switchboard instruments. The ammeter had a range of one ampere and the scale was divided into hundredths. The voltmeter had a range of six volts and the scale was

---

[1] The major portion of this work is taken from Mr. Hughes' thesis for the M.A. degree, Ohio State University.

[2] *J. Physic. Chem.*, 9, 277.

[3] *Ibid.*, 9, 399.

[4] THIS JOURNAL, 30, 381.

divided into twentieths. All readings given herein are direct instrument readings and are not referred to the "normal density."

During electrolysis the anode was held 2 cm. above the bottom of the dish so that the distance from all parts of the cathode was nearly equal. The total dilution was always 125 cc., giving an estimated effective cathode area of 110 sq. cm. The time factor in the table is not of much importance, because in many cases the experiment ran all night and the silver was doubtless all out some time before the electrolysis was stopped. Sufficient silver nitrate solution was taken in each experiment to give the amount of silver indicated in the table as being present. Ammonium sulphide was used to test the end points. The following is a list of the liquid reagents used, together with their specific gravity in each case: Nitric acid, 1.42; ammonium hydroxide, 0.90; sulphuric acid, 1.84; perchloric acid, 1.12; and hydrofluosilicic acid, 1.06. Normal NaOH solution was used for this reagent. The deposits were washed and dried in the usual manner[1] before weighing. All data here given were obtained without agitating the electrolyte.

Since the early workers gave very few details of their work it is impossible to repeat it exactly. About all one can do in many cases is merely to use the same electrolyte and often the concentration of that is not known.

The first table gives the results obtained in the quantitative examination of electrolytes hitherto in use for various purposes.

The experiments with the nitric acid electrolyte showed that dense deposits cannot be obtained if the voltage is too high. When the voltage was kept lower, however, the deposits were good and of a crystallin nature. This is in agreement with the work of Küster and von Steinwehr[2] with this electrolyte. Although sponginess is entirely avoided when the voltage is kept below 1.4 volts, yet the silver is deposited so slowly that there is a tendency for the crystals to grow large and become easily detached. Dense adherent deposits can be obtained without much difficulty, however, if the rotating anode is used. With stationary electrodes it was impossible to set the voltage at 1.3 volts, for instance, and expect it to remain there, for with this electrolyte especially it soon begins to rise and thereby passes the point at which discoloration and sponginess appear on the cathode. If the voltage was kept below 1.35 the deposit was smooth and white, finally becoming visibly crystallin. If after such a deposit is well under way, the voltage is raised to 1.5–1.8 volts, the deposit almost instantly darkens and then becomes spongy. If now the voltage is again lowered to 1.3 volts, there is a flash of white as the whole turns this color without even apparently affecting the de-

---

[1] THIS JOURNAL, 30, 382.

[2] *Z. Elektrochemie*, 4, 451.

| | Ag present. | Electrolyte. | | Current. | | Temp. | | | |
|---|---|---|---|---|---|---|---|---|---|
| No. | Gram. | Reagent. | Amount. | Ampere. | Volts. | Centigrade. | Time. Hours. | Ag found. Gram. | Deposit characteristics. |
| 1 | 0.2505 | $HNO_3$ | 4 cc. | 0.07 | 1.5 | 25° | 12.0 | | Spongy |
| 2 | 0.0312 | $HNO_3$ | 3 cc. | 0.07 | 1.5 | 25° | 13.0 | 0.0315 | Spongy |
| 3 | 0.0312 | $HNO_3$ | 3 cc. | 0.07 | 1.5 | 25° | 10.0 | 0.0305 | Spongy |
| 4 | 0.2505 | $HNO_3$ | 4 cc. | 0.04–0.001 | 1.2–1.35 | 25° | 14.0 | 0.2503 | Crystallin |
| 5 | 0.2505 | $HNO_3$ | 4 cc. | 0.03–0.001 | 1.1–1.4 | 25° | | 0.2506 | Crystallin |
| 6 | 0.2505 | $NH_4OH$<br>$(NH_4)_2SO_4$ | 5 cc.<br>12 g. | 0.05 | 1.6–2.0 | 25° | | | Very spongy |
| 7 | 0.2505 | $NH_4OH$<br>$(NH_4)_2SO_4$ | 1 cc.<br>12 g. | 0.04 | 1.4–2.0 | 25° | | | Very spongy |
| 8 | 0.2505 | $NH_4OH$<br>$(NH_4)_2SO_4$ | 0.5 cc.<br>12 g. | 0.04 | 1.4–1.9 | 25° | | | Spongy. Anode deposit |
| 9 | 0.2505 | $NH_4OH$<br>$(NH_4)_2SO_4$ | 10 cc.<br>12 g. | 0.03–0.02 | 1.2–2.0 | 25° | | | Spongy |
| 10 | 0.2505 | $NH_4OH$<br>$(NH_4)_2SO_4$ | 25 cc.<br>12 g. | 0.04–0.001 | 1.0–1.3 | 25° | 14.0 | 0.2504 | Good, crystallin |
| 11 | 0.2505 | $NH_4OH$<br>$(NH_4)_2SO_4$ | 25 cc.<br>12 g. | 0.08–0.001 | 1.0–1.5 | 55°–65° | 7.5 | 0.2510 | Slightly dark |
| 12 | 0.2505 | $NH_4OH$<br>$(NH_4)_2SO_4$ | 2 cc.<br>10 g. | 0.05–0.001 | 1.0–1.4 | 65° | 7.5 | 0.2514 | Slightly dark |
| 13 | 0.2505 | $NH_4OH$<br>$(NH_4)_2SO_4$ | 2 cc.<br>10 g. | 0.03–0.001 | 1.0–1.8 | 25° | 15.0 | 0.2513 | Dark |
| 14 | 0.2505 | $NH_4OH$<br>$(NH_4)_2SO_4$ | 1 cc.<br>10 g. | 0.03–0.001 | 1.0 | 25° | | | Anode deposit |
| 15 | 0.2505 | $NH_4OH$<br>$(NH_4)_2SO_4$ | 2 cc.<br>10 g. | 0.03–0.001 | 1.0–1.9 | 60° | 8.0 | 0.2516 | Dark |
| 16 | 0.2505 | $NH_4OH$<br>$(NH_4)_2SO_4$ | 2 cc.<br>10 g. | 0.03–0.001 | 1.0–1.4 | 60° | | 0.2508 | Not so dark |
| 17 | 0.2505 | $NH_4OH$<br>$(NH_4)_2HPO_4$ | <br>10 g. | 0.07–0.002 | 1.0–1.7 | 60°–70° | 5.0 | 0.2502 | Crystallin |
| 18 | 0.2505 | $NH_4OH$<br>$(NH_4)_2HPO_4$ | 3 cc.<br>25 g. | 0.1 –0.001 | 1.2–1.8 | 25° | 16.0 | 0.2508 | Crystallin |
| 19 | 0.2505 | $NH_4OH$<br>$Na_4P_2O_7$ | 5 cc.<br>5 g. | 0.05–0.002 | 1.2–1.9 | 25° | 14.0 | 0.2509 | Crystallin |
| 20 | 0.2505 | $NH_4OH$<br>$Na_4P_2O_7$ | 10 cc.<br>5 g. | 0.05–0.001 | 1.2–1.9 | 25° | 14.0 | 0.2506 | Crystallin |
| 21 | 0.2505 | $HNO_3$<br>$NH_4C_2H_3O_2$ | 5 cc.<br>25 g. | 0.07–0.001 | 1.0–1.7 | 60° | 6.0 | 0.2506 | Good, crystallin |
| 22 | 0.2505 | KCN | 2 g. | 0.02–0.03 | 2.0–2.5 | 25° | 12.0 | 0.2506 | White |
| 23 | 0.2505 | KCN | 2 g. | 0.07 | 2.5–3.0 | 25° | 13.0 | 0.2515 | Brownish |
| 24 | 0.2505 | KCN | 2 g. | 0.07 | 2.5–3.0 | 60° | 7.0 | 0.2507 | White, good |
| 25 | 0.2505 | KCN | 2 g. | 0.07 | 2.5 | 25° | 15.0 | 0.2514 | Slightly dark |
| 26 | 0.2505 | KCN | 2 g. | 0.07 | 2.5 | 65°–70° | 4.0 | 0.2504 | White |

posit in any other way than color. Even the most delicate cauliflower-like effect of some spongy deposits is merely changed from dark (even black) to spotless white. This change is so closely connected with the change in voltage that it suggests its possible utilization in detecting the maximum allowable voltage for useful deposition from electrolytes which show the phenomenon. Nothing further could be done with it, however, at this time.

With the higher voltage much hydrogen is liberated at the cathode. This obviously reduces the cathode area and in this way greatly increases the effective current density. Conditions of this kind would naturally be expected to give rise to poor metallic deposits.

Once upon reducing the voltage in the manner described above, the deposit soon became a mass of needles a half millimeter or more in length.

Then when the voltage was raised to 1.6 volts bubbles of gas collected at once between the needles and did not visibly disengage themselves. This so reduced the cathode surface that only the termination of the needles was the effective cathode. This was shown by the fact that the terminations became like jet and stood out in marked contrast on the white background. Reducing the volts to 1.3 changed these terminations at once to their original white color.

In order to study the black deposit, often obtained, a heavy one was secured. The voltage was then reduced to 1.2 volts. This caused the usual flash of white metallic silver which covered everything that was black just before. The current was then reversed without disturbing anything in the dish. The double layer deposit (as it appeared to be) was now the anode and it almost completely corroded off without changing from the color of the later deposit of silver. That is, the layer of black which was laid down first on the cathode never became visible on what was now the anode. Although this is not definit proof, it seems to indicate that the white flash is a real bleaching or change in color of the black silver itself.

In the work with nitric acid there was often a tendency toward the formation of the well-known black, crystallized deposit on the anode.

Beautiful silvery deposits, difficult to distinguish from the dish, were often obtained at first from the ammonium sulphate-ammonium hydroxide electrolyte. Some of these deposits were like burnished silver but as the deposits became heavier they became more velvet-like and as the voltage ran above 1.4 volts they darkened. Rarely, however, did they develop sponginess as rapidly or to the same extent as those from nitric acid.

Number 9 started well but later became spongy. The 10th result and the beginning of number 9 show the favorable effect of lower voltage than was used at first. Experiments 11 to 16, inclusive, give in each case darkened deposits of varying intensity of shade. All of them were made with higher voltage. Some of them were run at elevated temperature but without any appreciable effect other than the usual corresponding shortening of the time necessary for complete precipitation. The weights of the deposits also in all cases with this electrolyte were high except when the pressure was kept below 1.4 volts. This is in agreement with the experience of Krutwig,[1] who proposed this electrolyte.

On a few occasions, when only a small amount of ammonium hydroxide was used with the ammonium sulphate electrolyte, the first layers of silver which came down were purple in color, changing in places to a deep blue color. This calls to mind at once the blue form of silver made by

---

[1] *Ber.*, **15**, 1262.

Carey Lea years ago. Snowdon[1] seems to have encountered this under other circumstances. The deposits here mentioned were not as uniform as Snowdon obtained when he used a colloidal addition agent. None of the deposits made at 1.5 volts were adherent. The simultaneous darkening of the deposits and excess weight might be explained by the assumption of the formation of silver sulphide at the cathode. The function of the ammonium hydroxide appears to be the prevention of anodic deposit formation. When the amount of this reagent was lessened there was an anodic deposit as was found in experiments 8 and 14.

When ammonium sulphate was employed in the absence of ammonium hydroxide there very quickly formed on the anode a heavy black deposit which shone at times like polished graphite. This deposit was at once dispelled upon the addition of a few drops of ammonium hydroxide.

In experiment 17 sufficient ammonium hydroxide was added to dissolve the precipitate first formed. When the ammoniacal phosphate and pyrophosphate electrolytes were used the deposits were crystallin in every case. Here also, however, too high voltage causes sponginess.

The potassium cyanide used in the experiments with this electrolyte was the commercial grade. Most of the deposits from this electrolyte were white and good. The quantitative results seem to be best when an elevated temperature is used. The dark effect which appeared in the electrolyte around the anode seemed to migrate to the cathode. There was always a slight black residue left after dissolving the silver deposit in nitric acid. This substance resembled carbon and disappeared when the dish was heated but was not identified.

The final table shows in a compact way the general results obtained when using other electrolytes than those mentioned in the literature. The experiments are all qualitative and were made to determin the character of the resulting deposits. The fluosilicic acid electrolyte is not new, although given in the final table. It has been used by Jarvis and Kern in their study of the effect of addition agents on the density and coherence of silver deposits.[2] This article is only accessible to us through abstract.[3] The abstract gives no information, however, concerning the nature of the deposits obtained from this particular electrolyte. We only examined the electrolyte qualitatively and hence put it with the other qualitative results.

The deposits from sulphuric acid and glycerol were so coarsely crystallin as to be non-adherent. The sodium and ammonium hydroxide mixture gave a fairly adherent deposit. The deposit in experiment 8 was not so coarse as in the preceding experiments. The fluosilicic

---

[1] *J. Physic. Chem.*, **9**, 397.

[2] *School Mines Quart.*, **30**, 100.

[3] *Chem. Abs.*, **3**, 1495.

acid seems to be the most satisfactory of any of the last electrolytes tried. At 50° there was no oxide on the anode, and the deposit did not become spongy at as low a voltage as in the other cases.

| | Electrolyte. | | Current. | | | | |
|---|---|---|---|---|---|---|---|
| No. | Reagent. | Amount. | Ampere. | Volts. | Temp. Centigrade. | Anode deposit. | Cathode deposit. |
| 1 | $H_2SO_4$ | 1-10 cc. | | | 25° | Oxide each time | Coarse, crystallin |
| 2 | $H_2SO_4$<br>Glycerol | 10 cc.<br>1 cc. | 0.05 | 1.3 | 25° | None | Coarse, crystallin |
| 3 | Same | Same | 0.07 | 1.5 | 25° | None | Spongy |
| 4 | $NH_4CNS$ | 5 g. | 0.05 | 1.1 | 25° | Sulphur | Black |
| 5 | NaOH<br>$NH_4OH$ | 2 cc.<br>4 cc. | 0.04 | 1.1 | 25° | None | Coarse, crystallin |
| 6 | Same | Same | 0.08 | 1.6 | 25° | None | Spongy |
| 7 | $NH_4OH$<br>$HClO_4$ | 4 cc.<br>3 cc. | 0.05 | 1.2 | 25° | Oxide | |
| 8 | Same | 4 cc.<br>4 cc. | 0.04 | 1.1 | 25° | None | Crystallin |
| 9 | Same | 4 cc.<br>4 cc. | 0.08 | 1.7 | 25° | None | Spongy |
| 10 | $K_2F_2$ | 1-5 g. | | | 25° | Oxide each time | Coarse, crystallin |
| 11 | $H_2SiF_6$ | 5 cc. | 0.08 | 1.3 | 25° | Oxide | Coarse, crystallin |
| 12 | $H_2SiF_6$ | 5 cc. | 0.1 | 1.4 | 50° | | Good |
| 13 | $H_2SiF_6$ | 5 cc. | 0.2 | 1.7 | 50° | | Spongy |

## Summary.

1. The general characteristics are described of the silver deposits from a variety of electrolytes.

2. With all the electrolytes tried except cyanide there is a point at about 1.4 volts beyond which, with the conditions here used, spongy deposits will result. With cyanide this point is much higher.

3. Satisfactory conditions have been tabulated for the quantitative precipitation of silver from several electrolytes.

4. Several other electrolytes have been tried which seem worthy of further investigation.

COLUMBUS, OHIO.

---

# RATE OF HYDRATION OF PYROPHOSPHORIC ACID. A CORRECTION.

By G. A. Abbott.

Through the kindness of Dr. J. M. Bell, of the University of North Carolina, my attention has recently been called to the fact that the experimental data given in Table IV of my article on the Rate of Hydration of Pyrophosphoric Acid[1] are not consistent with the statement in the text that the specific conductance of a mixture of the pyro and ortho acids is a linear function of its composition. Through a regrettable error

---

[1] This Journal, 31, 766 (1909).