solution, after complete reduction by zinc, is oxidized in the presence of air, but at about the same rate as the original Mohr's salt in acid solution. The point of equilibrium is probably complete oxidation, but the reaction velocity in the absence of catalyzers is very small.

7. Oxidation of Fe^{++} readily occurs in alkaline solutions; 50 per cent. ± of the iron is oxidized upon passage of air for 3 hours.

8. All of these experiments were performed at room temperature. At a temperature slightly below the boiling point of the solution, upon passage of air for 3 hours, the Fe^{++} from the different sources was oxidized to an extent of about 2 per cent. in the acid solutions and about 5 per cent. in the neutral solutions.

Conclusion.—We conclude that Fe^{++} in acid and in neutral solutions, at room temperature, is so slowly oxidized, and this oxidation is so slightly affected by such substances as are apt to be present, that expulsion of air during reduction by zinc is unnecessary and the titration may be performed at leisure, in ordinary determinations of iron by titration with potassium permanganate.

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THE RAPID DETERMINATION OF SILVER AND CADMIUM BY MEANS OF THE GAUZE CATHODE AND STATIONARY ANODE.

BY RAYMOND C. BENNER AND WILLIAM H. ROSS.

Received April 17, 1911.

The use of the gauze cathode with stationary anode, which was found to be so efficient in the determination of nickel and cobalt,[1] has been extended to include the metals, silver and cadmium. The range of electrolytes from which these elements could be deposited on the gauze cathode in an adherent form, when strong currents were used, was found to be much less than in the case of the metals referred to.

Several of the electrolytes, which are applicable in case of the slow electrolytic methods, did not give good deposits on the gauze cathode with high currents, but the deposits obtained for each metal with potassium cyanide as an electrolyte were entirely satisfactory.

The electrodes used in these experiments were the same as those already described in the work on nickel and cobalt.[2]

Silver.—The first determinations of silver, using the gauze cathode, were made by Stoddard[3] with satisfactory results. The same experiments were repeated by Price and Humphreys.[4] They, however, reported rather unfavorably on the use of this method for the determination of silver,

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[1] THIS JOURNAL, **33**, 493.

[2] *Loc. cit.*

[3] THIS JOURNAL, **31**, 385.

[4] *J. Soc. Chem. Ind.*, **29**, 307.

as the results which they obtained were always a little too low. In view of these conflicting results further work on the deposition of this metal was considered advizable.

The standard silver nitrate solution used in the following experiments was prepared by dissolving 1.5045 grams of C. P. silver foil in nitric acid. The excess of acid was then expelled on the water bath. The solution of the residue was made up to one liter and portions of 10 cc. containing 0.1504 gram of silver were taken for analysis. The purity of the foil had been previously established by careful analysis. Solutions of other concentrations were prepared by weighing out smaller portions of the silver foil, which were then converted into nitrate in the same way and electrolyzed directly.

A large number of experiments were made with a view of finding suitable electrolytes from which to deposit silver, but with the exception of potassium cyanide, none gave satisfactory results. Fairly good deposits were obtained from a warm solution of potassium persulfate, but the results were low, due to anodic deposition, on account of the strong oxidizing action of the solution. Electrolytes consisting of varying concentrations of nitric and other acids, as well as all of the electrolytes used

Amount taken.	Amount found.	Error, mg.	Amperes.	Volts.	Volume of solution, cc.	Time.	KCN. Grams.	KOH. Grams.
0.1504	0.1506	+0.2	2	5	50	25	8	2
0.1504	0.1508	+0.4	1	4.5	50	35	8	2
0.1504	0.1502	—0.2	4	5	50	15	8	2
0.1504	0.1505	+0.1	3	5	50	25	8	2
0.1504	0.1501	—0.3	3	5	50	25	8	2
0.1504	0.1508	+0.4	3	5	50	25	8	2
0.1052	0.1055	+0.3	3	5	50	30	8	2
0.1052	0.1056	+0.4	3	5	50	30	8	2
0.3156	0.3160	+0.4	3	5	50	25	8	2
0.1052	0.1052	±0.0	3	5	50	20	6	3
0.1052	0.1052	±0.0	3	5	50	25	6	2
0.2307	0.2305	—0.2	3	5	75	25	6	2
0.2360	0.2354	—0.6	3	5	50	25	6	2
0.2021	0.2014	—0.7	3	5	50	30	6	2
0.3563	0.3561	—0.2	3	5	75	30	6	2
0.3281	0.3284	+0.3	3	5	50	25	6	2
0.3048	0.3047	—0.1	3	5	50	25	8	2
			Rate of precipitation.					
0.1504	0.0508		3	5	50	2	8	2
0.1504	0.0877		3	5	50	4	8	2
0.1504	0.1154		3	5	50	6	8	2
.1504	0.1312		3	5	50	8	8	2
0.1504	0.1462		3	5	50	12	8	2
0.1504	0.1474		3	5	50	15	8	2
0.1504	0.1506		3	5	50	20	8	2
0.1504	0.1504		3	5	50	25	8	2

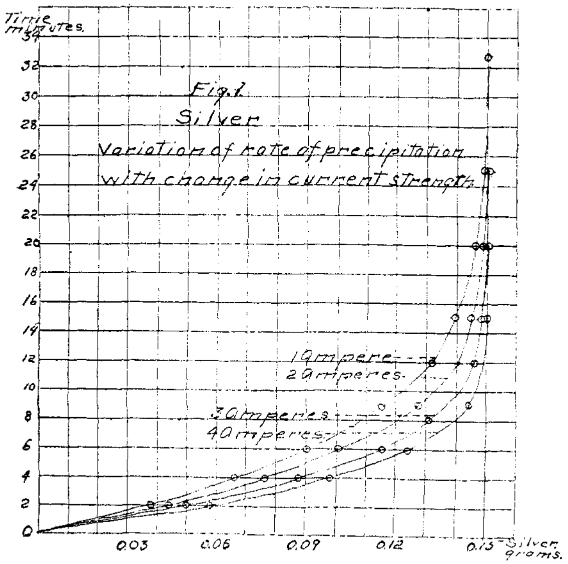
in connection with the deposition of nickel and cobalt, gave unsatisfactory results.

When carried out under the proper conditions, the deposits obtained from a solution of potassium cyanide were white in color and perfectly adherent. This electrolyte was very convenient to use, as the resistance of the solution was low and the conductivity did not change during the deposition of the metal. Consequently there was no tendency for the solution to boil over, even when currents as high as 5 amperes were used. When the cyanide only was used as an electrolyte, the solution became colored red as the electrolysis proceeded. This was prevented to a greater or less extent, when pure cyanide was used, by the addition of potassium hydroxide. The amount of hydroxide used (up to two grams in 50 cc. of solution) had but little effect on the rate of deposition. Larger amounts delayed the precipitation somewhat. The conditions under which the best deposits were obtained are given in the above table.

Careful qualitative tests were made at intervals, which showed that the precipitation of the silver was complete in the time given.

Before breaking the current at the end of the electrolysis the solutions were usually replaced with water, as otherwise the results obtained were usually a little low (about 0.4 mg. on an average).

When other conditions were the same the character of the deposit varied very decidedly with the amount of silver deposited. As the amount of silver increased, the deposit showed a greater tendency to sponginess. In order to get good results not more than 0.3 gram of silver should be deposited at one time on a cathode the size of the smaller ones used. When depositing amounts of silver weighing 0.15 gram, or less, from the concentrations of potassium cyanide given in the table, the strength of the current was found to have comparatively little effect on the character of the deposit and perfectly adherent deposits were obtained, even with currents of 5 amperes.



Increasing the potassium cyanide decreases the rate of precipitation to a marked extent but the amount of silver which can be deposited in an adherent form may be correspondingly increased. For quantities of silver weighing less than 0.3 gram, 8 grams of potassium cyanide in 60 cc. of solution proved most satisfactory.

The effect of varying the strength of current on the rate of deposition may be seen from the curves in Fig. 1. For each ampere increase between 1 and 5 amperes, the time required to deposit 0.1504 gram of silver was decreased by about 5 minutes. This made the time for complete deposition of this amount of silver about twice as long with 1 as with 4 amperes.

The size of the cathode had a more important bearing on the character of the deposit than was noted for nickel and cobalt. The differences obtained by using cathodes of different sizes and by varying the amount of silver deposited may be seen in Figs. 2 to 4: Fig. 2, a microphotograph of a small section of the gauze cathode, weighing 6 grams, magnified 20 times, on which 0.1504 gram of silver was deposited, with a current of 3 amperes, from an electrolyte consisting of 8 grams of potassium cyanide in 60 cc. of water; Fig. 3, the same electrode upon which 0.4512 gram was deposited under the same conditions; and Fig. 4, the same amount of silver as shown in Fig. 3, deposited on the large cathode, weighing 16 grams, with the same electrolyte and current as were used to give the deposit shown in Fig. 1. The deposits shown in Figs. 2 to 4 were quantitative, and all appeared equally good to the naked eye.

Cadmium.—The rapid determination of cadmium by means of the gauze cathode and stationary anode has been made the subject of two previous studies.[1] Stoddard added just enough potassium cyanide to dissolve the precipitate formed, and deposited from 50 cc. of solution with a current of 5 amperes. Price and Humphreys used the same amount of potassium cyanide, depositing under the same conditions as used by Stoddard. In each case the results were satisfactory and obtained in a much shorter time than with other forms of stationary electrodes. As the same electrolyte was used in both cases it seemed advizable to repeat the work under varying conditions and try other electrolytes as well.

A standard solution was prepared by dissolving C. P. cadmium sulfate in water. The strength of this solution was determined by evaporating 10 cc. to dryness and weighing as the sulfate. This gave 0.1807 gram as a mean of 3 closely agreeing determinations. By the electrolytic method, using small currents and allowing the electrolysis to run over night, the mean of 5 determinations amounted to 0.1811 gram. The average of both methods of analysis gave 0.1809 gram as the cadmium content of 10 cc. of the solution.

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[1] Stoddard, THIS JOURNAL, 31, 385; Price and Humphreys, *J. Soc. Chem. Ind.*, 29, 307.

Fig. 2. × 20.

Fig. 3. × 20.

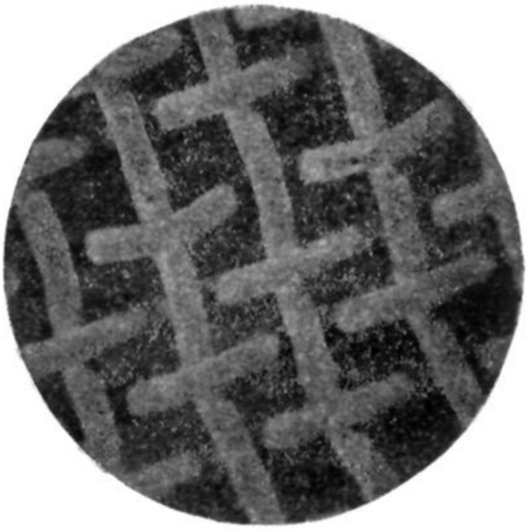

Fig. 4. × 20.

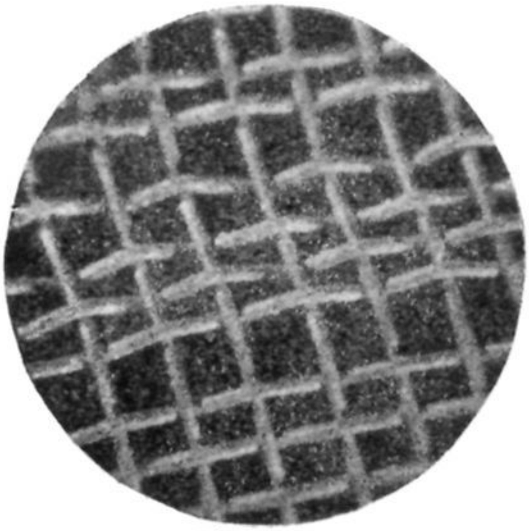

Fig. 5. × 20.

Fig. 6. × 20.

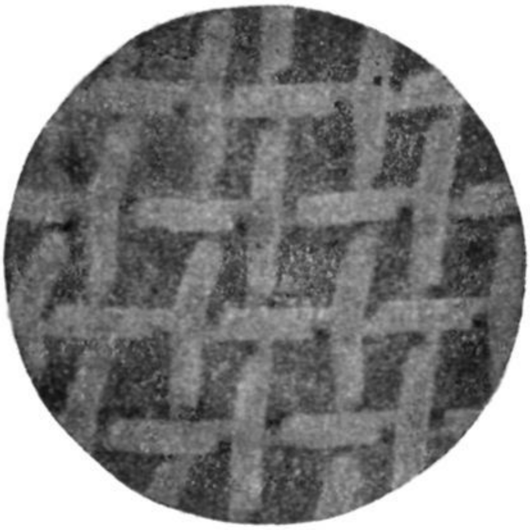

Fig. 7. × 20.

The varying conditions under which it was possible to obtain good results with potassium cyanide electrolyte will be seen from the following table:

Amount taken.	Amount found.	Error, mg.	Amperes.	Volts.	Volume of solution. cc.	Time.	KCN. Grams.	KOH. Grams.
0.1809	0.1801	−0.8	4	5–6	60	30	5	1*
0.1809	0.1807	−0.2	4	5–6	60	30	5	1*
0.1809	0.1810	+0.1	4	5–6	60	30	5	1*
0.1809	0.1807	−0.2	3–4	5–7	60	30	5	1*
0.1809	0.1813	+0.4	3–4	5–7	60	30	2	1*
0.1809	0.1809	±0.0	4–5	6–7	60	30	5	2*
0.1809	0.1806	−0.3	4–5	8–11	60	30	KCN, enough to dissolve ppt. formed.	KOH, to alkalinity.
0.1809	0.1801	−0.8	4–5	8–11	60	30		
0.1809	0.1815	+0.6	4–5	8–11	60	30		"
0.1809	0.1807	−0.2	4–5	8–11	60	30	"	"
0.1809	0.1814	+0.5	4–5	8–11	60	30	"	"
0.3618	0.3623	+0.5	3–4	8–9	75	50	"	"
0.3618	0.3618	±0.0	3–4	8–9	75	50	"	"
0.3618	0.3616	−0.3	3–4	8–9	75	70	"	"
0.3618	0.3619	+0.1	3–4	8–9	75	70	"	"
				Rate of Precipitation.				
0.1809	0.0916		4	10–12	60	3	"	"
0.1809	0.1300		4	10–12	60	5	"	"
0.1809	0.1601		4	10–12	60	7	"	"
0.1809	0.1779		4	10–12	60	11	"	"
0.1809	0.1790		4	10–12	60	15	"	"
0.1809	0.1815		4	10–12	60	25	"	"

In cases where cadmium was precipitated from solutions containing no potassium hydroxide, the solution became colored by the decomposition of the cyanide. This was likely to make the results high but was prevented by the addition of a little potassium hydroxide as in the case of silver. As cadmium is somewhat soluble in potassium cyanide solutions, it was found necessary to wash before the current was broken in cases where strong solutions were used. The deposits were at all times uniformly bright and adherent. When examined under the microscope it was seen that an occasional deposit showed a tendency to sponginess but, notwithstanding this, good quantitative results could always be obtained.

Varying the concentrations of the cyanide had much less effect on the character of the deposit obtained than was noted for silver, as may be seen in the microphotographs: Fig. 5, a section of the smaller cathode upon which 0.1815 gram of cadmium had been deposited with a current of 5 amperes from 75 cc. of an electrolyte made by adding just enough potassium hydroxide to the cadmium sulfate solution to make it alkaline and then enough potassium cyanide to dissolve the precipi-

* Washed before breaking the current.

tate formed; Fig. 6, the same electrode on which 0.1508 gram of cadmium was deposited from an electrolyte containing 2 grams of potassium hydroxide and 6 grams of potassium cyanide in 75 cc. of solution with a current of 5 amperes; and Fig. 7, a section of the larger electrode upon which 0.1812 gram of cadmium had been deposited under the same conditions as the deposit shown in Fig. 5.

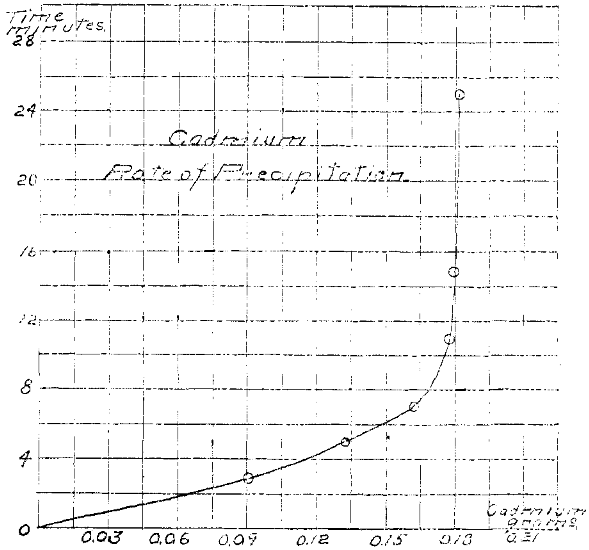

Fig. 8.

In addition to the experiments with potassium cyanide many others were made with other electrolytes, with the same negative results, as mentioned in the case of silver.

The anodes were weighed at the end of a number of consecutive electrolyses of both silver and cadmium in which the cyanide electrolyte was used to determin to what extent they decreased in weight. This appeared to be very slight, amounting to 0.1–0.2 mg. on an average for an electrolysis running from 20 to 30 minutes. The cathodes decreased in weight at about the same rate.

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A MODIFIED COLORIMETER AND SOME TESTS OF ITS ACCURACY.

BY EDWARD DEMILLE CAMPBELL AND WILLIAM B. HURLEY.

Received May 18, 1911.

In a colorimeter for general use, simplicity in construction and operation, and accuracy in reading are the principal features to be sought.

In the colorimeter described below the means of observing the colors is in principle the same as that employed in the colorimeter described by W. G. Smeaton in THIS JOURNAL, 28, 1433, although the construction has been simplified by using two half-mirrors permanently fixed at an angle of 45° instead of mirrors adjusted by springs.

The tubes for holding the solutions to be compared are those of one of the well-known colorimeters in which the unknown solution is placed