Correction for change of jacket temperature due to barometric change is negligible. Thus, 23 mm. change of barometer causes a change of 1° in the boiling point of toluene (384° absolute), or 1 part in 384 in the result.

When the final level of the mercury in the gage tube is very different from that measured in finding the constant of the apparatus, it is plain that the gas content of the test tube will be somewhat different. Correction for this is usually unnecessary, and was not made in the above examples.

As every portion of the enclosed chamber is kept at the constant high temperature, there is nothing to be feared from the diffusion of the vapor to colder parts of the apparatus, as in the case of the Lumsden or Victor Meyer apparatus. Thus, Lumsden remarks:[1] "The accuracy of the results depends very much on the rapidity with which the substance is vaporized, and this is the more important the smaller the molecular weight, since a vapor which diffuses rapidly may reach the colder part of the apparatus before a measurement of pressure can be made." Again, as no air is driven from a hotter to a colder place, no uncertain correction on this account has to be considered.[2]

Since the vapor is likely to be diffused throughout the whole of the test tube, and since the pressure read is less than one-sixth of an atmosphere, the partial pressure of the vapor cannot even locally much exceed one-sixth of an atmosphere. This low pressure lessens any tendency to association, as is seen in the acetic acid example given above. It is obvious that the test tube may be filled with an inert gas if desired.

Instead of a glass stopper, a one-holed rubber cork may be used at the lower temperatures. A glass rod, bent for the lowest centimeter of its length, passes through the hole, and by its timely rotation breaks the neck of the bulblet, which is inserted into a small blind hole beside it, and is pressed against the top of the gage tube. This form of "release" is perhaps easier to operate than that described above.

In the form described, this apparatus is not suitable for temperatures above 200°; but the examples given seem to show that it is both rapid and accurate for use at temperatures at which it is applicable.

RAPID DETERMINATIONS AND SEPARATIONS BY MEANS OF THE MERCURY CATHODE AND STATIONARY ANODE.

By R. C. Benner and M. L. Hartmann.

Received October 11, 1910.

The mercury cathode has been used for most metals which can be determined electrolytically. In the case of bismuth it is possible to make

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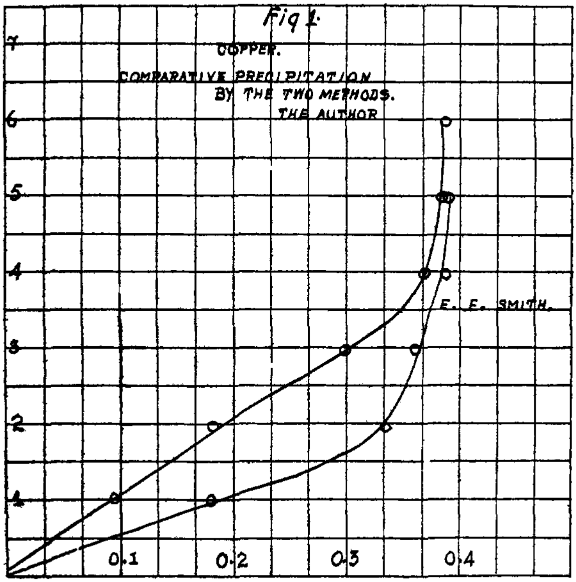
[1] *Loc. cit.*

[2] Cf. T. W. Richards, *Chem. News*, 59, 87.

the determination with greater ease by this method than with platinum electrodes. The determination of chromium, while impossible by ordinary electrolytic methods, can be thus accomplished.

The mercury cathode has been used with a stationary anode and low currents, as well as with the rotating anode and high currents, but not until recently has it been proven possible to use the stationary anode and high currents without some means of mechanical agitation.[1]

In order to determin what time could be saved by the use of the rotating anode, the rate of precipitation was determined without agitation under the same conditions as those used by Smith.[2] The curves in figures 1 and 2 show, that while the precipitation of copper and silver is more rapid when the rotating anode is used, the difference is not nearly as great as would be expected. This lack of rapidity is, moreover, much more than compensated for by the simplicity of the apparatus in case of the stationary anode.



It is possible to precipitate:

(1) 0.2075 gram of iron in 10 minutes with three to four amperes when the rotating anode is used.

(2) 0.1000 gram in the same time with four amperes when the solution is rotated by means of the solenoid.

(3) 0.2007 gram in 20 minutes with the stationary anode and four

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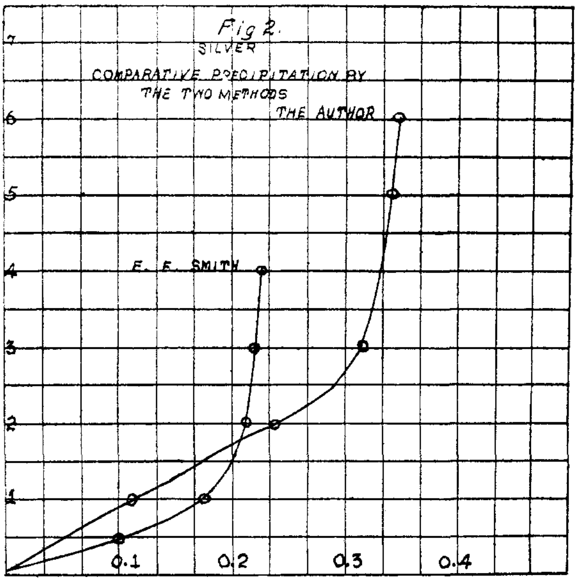
[1] Stoddard, THIS JOURNAL, 31, 385; Benner, *Ibid.*, 32, 1231.

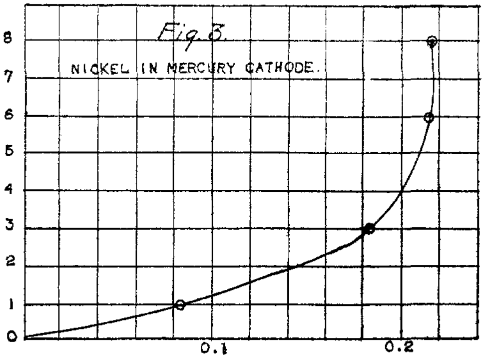
[2] "Electroanalysis," Phila., 1907.

amperes. Therefore, although there was no means at hand for making a direct comparison between this method and that in which the electrolyte was rotated by means of a solenoid,[1] it would seem that there is little, if anything, to be gained from magnetic rotation.



The following determinations and separations were carried out using the apparatus of our previous article.[2]

Nickel.—For the determination of nickel a solution of C. P. nickel sulphate was prepared and the nickel determined electrolytically.[3] It was found to contain 0.1089 gram of metallic nickel per 10 cc.:



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[1] Frary, *Z. Elektrochem.*, 1907, 308.

[2] This Journal, 32, 1231.

[3] Smith, *Ibid.*, 25, 884.

Nickel taken.	Found.	Error.	Amperes.	Volts.	Drops of acid.	Volume of solution.	Time.
0.1089	0.1096	+ 0.0007	3–4	7–8	8 H_2SO_4 1.84 sp. gr.	10	15
0.1089	0.1095	+ 0.0006	5–6	8–9	8 H_2SO_4	10	5
0.2178	0.2187	+ .0009	5–6	8–9	8 H_2SO_4	20	10
0.1089	0.1088	— 0.0001	5–6	8–9	2 H_2SO_4	10	10
0.1089	0.1084	— 0.0005	6–7	8–9	2 H_2SO_4	10	5
0.1089	0.1096	+ 0.0007	3–4	7–8	2 H_2SO_4 6 HNO_3	10	7
0.2178	0.2183	+ 0.0005	3–4	7–8	2 H_2SO_4 6 HNO_3	20	12
0.2178	0.2172	— 0.0006	3–4	7–8	2 H $_4$ 6 HNO_3	20	12
0.1089	0.1087	— 0.0002	4–5	9–10	5 HNO_3 2 H_2SO_4	10	10
0.1088	0.1086	— 0.0002	4–5	9–10	3 HNO_3 2 H_2SO_4	10	10
0.2178	0.2178	+ 0.0000	4–5	9–10	10 H_2SO_4	20	15
0.2178	0.2179	+ 0.0001	4–5	9–10	4 H_2SO_4	20	15
0..1089	0.1090	+ 0.0001	4–5	9–10	2 H_2SO_4	10	15
0.2178	0.2180	+ 0.0002	4–5	9–10	8 H_2SO_4	20	12

Rate of Precipitation of Nickel (Fig. 3).

0.2178	0.0859		5	13–14	2 H_2SO_4	20	1
0.2178	0.1858		5	13–14	2 H_2SO_4	20	3
0.2178	0.2125		5	13–14	2 H_2SO_4	20	5
0.2178	0.2146		5	13–14	2 H_2SO_4	20	6
0.2178	0.2182		5	13–14	2 H_2SO_4	20	8

SEPARATION OF NICKEL FROM ALUMINIUM.

Nickel taken.	Found.	Error.	Amperes.	Volts.	Drops of acid.	Volume of solution.	Time.	Alumina.
0.1089	0.1088	— 0.0001	4–5	9–10	4 H_2SO4	20	10	0.0904
0.1089	0.1087	— 0.0002	4–5	9–10	4 H_2SO_4	20	10	0.0904
0.1089	0.1083	— 0.0004	4–5	9–10	10 H_2SO_4	20	10	0.0904
0.1089	0.1083	— 0.0004	4–5	9–10	10 H_2SO_4	20	10	0.0904

SEPARATION OF NICKEL FROM TITANIUM.

							Titanium dioxide.
0.1089	0.1080	— 0.0009	4–5	9–10	10 H_2SO_4	20	0.0435
0.1089	0.1088	— 0.0001	4–5	9–10	10 H_2SO_4	20	0.0435

SEPARATION OF NICKEL FROM THE RARE EARTHS.

							Oxide of the rare earths.
0.1089	0.1086	— 0.0003	4–5	9–10	2 H_2SO_4 3 HNO_3	20	0.2228
0.1089	0.1080	— 010009	4–5	9–10		20	0.2228

Reference to the table shows that with currents varying from three to six amperes, at seven to ten volts, it is possible to make accurate determinations of nickel, from a sulphate solution, either in the presence of from two to ten drops of sulphuric or four to six drops of nitric acid, when one or two drops of sulphuric acid are present, in 10 to 20 cc. of the electrolyte. The precipitation is sufficiently rapid for all practical purposes, as it is possible to precipitate 0.2178 gram of nickel from 20 cc. of solution in 8 minutes (Fig 3).

The determination of nickel in the presence of aluminium, titanium and the rare earths in a sulphuric acid solution, under the same conditions as were used for its determination alone, is as rapid and as accurate as when they are not present.

Cobalt.—A solution of cobalt sulphate was prepared from C. P. cobalt sulphate and made acid by the addition of a few drops of sulphuric acid. Ten cc. of the solution were found, by the electrolytic method,[1] to contain 0.1041 gram of metallic cobalt.

Cobalt taken.	Found.	Error.	Amperes.	Volts.	Drops of acid. H_2SO_4.	Volume.	Time.
0.1041	0.1037	— 0.0004	5–6	11–12	1	10	10
0.1041	0.1034	— 0.0007	5–6	11–12	1	10	10
0.2082	0.2090	+ 0.0008	3–4	6–7	1	20	20
0.1041	0.1044	+ 0.0003	3–4	6–7	1	20	20
0.1041	0.1042	+ 0.0001	3–4	6–7	1	10	8
0.1041	0.1041	+ 0.0000	4–5	7–8	1	10	10
0.1041	0.1036	— 0.0005	4–5	7–8	1	10	10
0.2082	0.2084	+ 0.0002	4–5	7–8	1	20	20
0.1041	0.1043	+ 0.0002	4–5	7–8	1	10	10
0.1041	0.1042	+ 0.0001	3–4	6–7	1	10	12
0.2082	0.2081	— 0.0001	3–4	6–7	1	20	..
0.2082	0.2085	+ 0.0003	3–4	6–7	1	20	..
Rate of Precipitation of Cobalt (Fig. 4).							
0.3516	0.1885		5	6–7	1	20	3
0.3516	0.3039		5	6–7	1	20	6
0.3516	0.3428		5	6–7	1	20	9
0.3516	0.3510		5	6–7	1	20	12
0.3516	0.3512		5	6–7	1	20	15

The determinations given in the table were carried out in solutions containing from 0.05 to 0.1 cc. of sulphuric acid and with currents varying from three to six amperes, at 6 to 12 volts. This gave complete precipitation of 0.1041 to 0.3516 of a gram of cobalt in from 10 to 15 minutes (Fig. 4). Results were good from weak sulphuric acid but not from strong acid solutions or those containing nitric acid.

Zinc.—A standard solution of zinc was prepared by dissolving a weighed amount of C. P. metallic zinc in sulphuric acid and diluting so that 10 cc. of the solution contained 0.2980 gram of metallic zinc and 0.3 cc. of sulphuric acid.

It was found that by carrying out the determination of zinc in a manner similar to the previous determinations of the other metals, it was possible to deposit zinc quantitatively either from solutions of the sulphate containing sulphuric acid or with nitric acid in the presence of a little sulphuric acid. The deposits were made with currents varying from three to six

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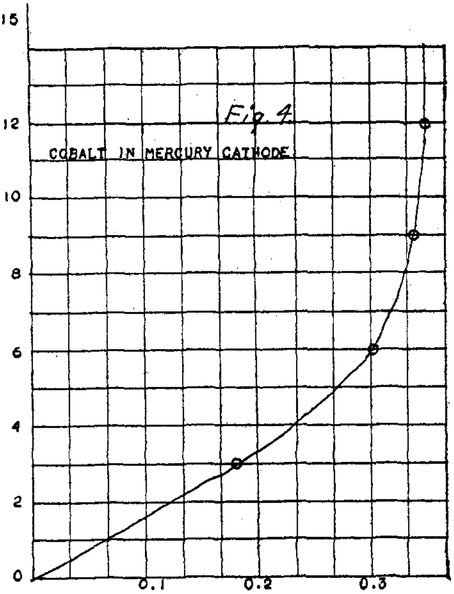
[1] THIS JOURNAL, 25, 884.



amperes and at from four to seven volts, in 10 to 20 cc. of solution, with results equal to those obtained with low currents and the mercury cathode or with the rotating anode and mercury cathode:

Zinc taken.	Found.	Error.	Amperes.	Volts.	Drops of acid.	Volume.	Time.
0.2980	0.2978	— 0.0002	5–6	6–7	6 H_2SO_4	10	20
0.2980	0.2974	— 0.0006	5–6	6–7	6 H_2SO_4	10	20
0.2980	0.2975	— 0.0005	5–6	6–7	6 H_2SO_4	10	20
0.2980	0.2988	+ 0.0008	5–6	6–7	6 H_2SO_4 3 HNO_3	10	20
0.2980	0.2980	± 0.0000	5–6	6–7	6 H_2SO_4 3 HNO_3	10	20
0.2980	0.2988	+ 0.0008	4–5	6–7	6 H_2SO_4	10	20
0.5960	0.5966	+ 0.0006	4–5	6–7	9 H_2SO_4	20	25
0.5960	0.5964	+ 0.0004	3–4	6–7	9 H_2SO_4	20	25
0.5960	0.5963	+ 0.0003	5–6	6–7	9 H_2SO_4 3 HNO_3	20	25

Most of the determinations made with acid as strong as the following were low:

0.2980	0.2975	— 0.0005	7–8	4–5	12 H_2SO_4	10	15
0.2980	0.2975	— 0.0005	7–8	4–5	6 HNO_3 6 H_2SO_4	10	15

Rate of Precipitation of Zinc (Fig. 5).

0.2980	0.1690	4.5	5–6	6 H_2SO_4	10	1
0.2980	0.2097	4.5	5–6	6 H_2SO_4	10	2
0.2980	0.2458	4.5	5–6	6 H_2SO_4	10	3
0.2980	0.2843	4.5	5–6	6 H_2SO_4	10	4
0.2980	0.2976	4.5	5–6	6 H_2SO_4	10	5
0.2980	0.2985	4.5	5–6	6 H_2SO_4	10	10

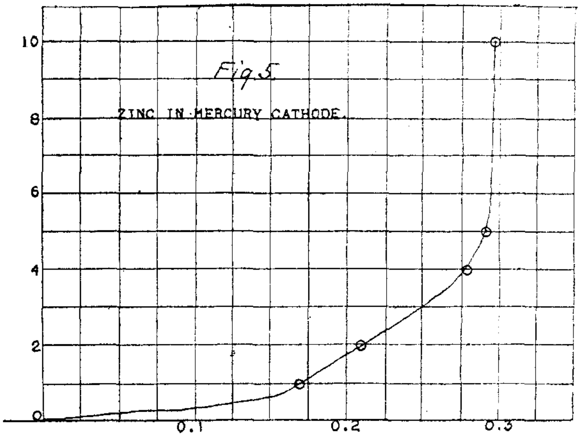
SEPARATION OF ZINC FOR TITANIUM.

Taken.	Found.	Error.	Amperes.	Volts.	Drops of acid.	Volume.	Time.	Titanium dioxide.
0.2980	0.2975	— 0.0005	4–5	7–8	13	20	15	0.0435
0.2980	0.2989	+ 0.0009	4–5	7–8	13	20	15	0.0435
0.5960	0.5954	— 0.0006	3–4	7–8	13	20	25	0.0435
0.5960	0.5961	+ 0.0001	3–4	7–8	13	30	25	0.0435
0.2980	0.2989	+ 0.0009	3–4	7–8	13	20	15	0.0435

SEPARATION OF ZINC FROM ALUMINIUM.

Taken.	Found.	Error.	Amperes.	Volts.	Drops of acid.	Volume.	Time.	Titanium dioxide.
0.2980	0.2986	+ 0.0006	3–4	7–8	8	20	20	0.0904
0.2980	0.2990	+ 0.0010	3–4	7–8	8	20	20	0.0904
0.5960	0.5969	+ 0.0009	3–4	7–8	7	20	25	0.0452
0.5960	0.5965	+ 0.0005	3–4	7–8	7	20	25	0.0452

Using the same conditions as in the determination of zinc, it is possible to separate zinc from aluminium and titanium without difficulty.



Iron.—The standard solution of iron was made by dissolving a weighed amount of ferrous ammonium sulphate in water and making acid with sulphuric acid to prevent the formation of basic iron sulphate. Ten cc. of this solution contained 0.1002 gram of metallic iron and 0.11 cc. of sulphuric acid. Iron was determined with the usual apparatus by means of currents varying from 3–4 amperes at 7–8 volts. Solutions containing either nitric or sulphuric acid were used with very satisfactory results. The rate of precipitation with the mercury cathode is slower than that for most metals, it being possible to deposit in twenty minutes only 0.2004 gram of iron, from 20 cc. of solution, with a current of four amperes (Fig. 6).

The separation of iron from aluminium, titanium, the rare earths of the cerium and yttrium groups as extracted from monazite, was tried under the same conditions used for the determination of iron, with satisfactory results.

Iron taken.	Found.	Error.	Amperes.	Volts.	Drops of acid.	Volume.	Time.
0.1002	0.1003	+ 0.0001	3-4	7-8	6 H_2SO_4	20	10
0.1002	0.1000	— 0.0002	3-4	7-8	6 H_2SO_4	20	15
0.2004	0.2008	+ 0.0004	3-4	7-8	6 H_2SO_4	20	25
0.2004	0.2004	± 0.0000	3-4	7-8	6 H_2SO_4	20	25
0.2004	0.2002	— 0.0002	3-4	7-8	6 H_2SO_4	20	25
0.2004	0.2002	— 0.0002	3-4	7-8	2 H_2SO_4 4 HNO_3	20	25
0.1002	0.1003	+ 0.0001	3-4	7-8	2 H_2SO_4 4 HNO_3	20	15
0.2004	0.2000	— 0.0004	3-4	7-8	2 H_2SO_4 4 HNO_3	20	20
0.2004	0.2002	— 0.0002	3-4	7-8	2 H_2SO_4 4 HNO_3	20	25

Rate of Precipitation (Fig. 6).

Iron taken.	Found.	Error.	Amperes.	Volts.	Drops of acid.	Volume.	Time.
0.2004	0.0302		4	7-9	6 H_2SO_4	20	1
0.2004	0.0795		4	7-9	6 H_2SO_4	20	2
0.2004	0.0998		4	7-9	6 H_2SO_4	20	3
0.2004	0.1522		4	7-9	6 H_2SO_4	20	5
0.2004	0.1918		4	7-9	6 H_2SO_4	20	10
0.2004	0.1957		4	7-9	6 H_2SO_4	20	15
0.2004	0.2007		4	7-9	6 H_2SO_4	20	20

Separation of Iron from Aluminium.

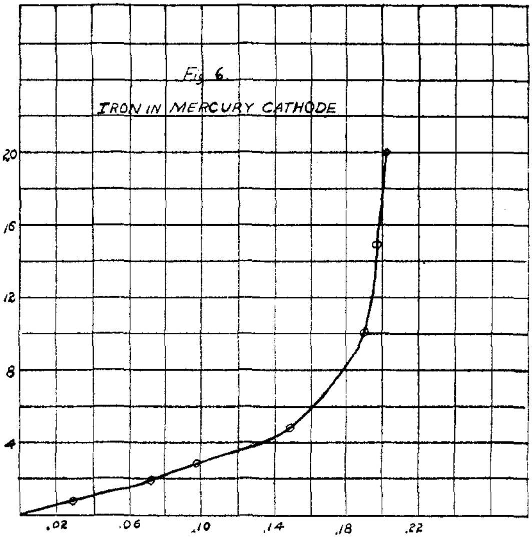
Iron taken.	Found.	Error.	Amperes.	Volts.	Drops of acid.	Volume.	Time.	Alumina.
0.1002	0.1005	+ 0.0003	4	7-9	8 H_2SO_4	20	15	0.0452
0.1002	0.1001	— 0.0001	4	7-9	8 H_2SO_4	20	15	0.0452
0.1002	0.1004	+ 0.0002	4	7-9	8 H_2SO_4	20	15	0.0452
0.1002	0.1000	— 0.0002	4	7-9	8 H_2SO_4	20	15	0.0452
0.1002	0.0995	— 0.0007	4	7-9	4 H_2SO_4 4 HNO_3	20	15	0.0452
0.1002	0.1002	± 0.0000	4	7-9	4 H_2SO_4 4 HNO_3	20	15	0.0452
0.1002	0.1001	— 0.0001	4	7-9	4 H_2SO_4 4 HNO_3	20	15	0.0452

Separation of Iron from Titanium.

Iron taken.	Found.	Error.	Amperes.	Volts.	Drops of acid.	Volume.	Time.	Titanium dioxide.
0.1002	0.1000	— 0.0002	4	6-7	10 H_2SO_4	20	25	0.0435
0.1002	0.0994	— 0.0008	4	6-7	10 H_2SO_4	20	25	0.0435
0.1002	0.1002	± 0.0000	3-4	6-7	10 H_2SO_4	20	25	0.0435
0.1002	0.1000	— 0.0002	3-4	6-7	10 H_2SO_4	20	15	0.0435
0.1002	0.1009	+ 0.0007	3-4	6-7	10 H_2SO_4	20	15	0.0435
0.1002	0.1002	± 0.0000	3-4	6-7	10 H_2SO_4	20	15	0.0435

Separation of Iron from the Rare Earths.

Iron taken.	Found.	Error.	Amperes.	Volts.	Drops of acid.	Volume.	Time.	Oxide of rare earths.
0.1002	0.1007	+ 0.0005	3-4	6-7	3 HNO_3	20	15	0.2228
0.1002	0.1003	+ 0.0001	3-4	6-7	2 H_2SO_4	20	15	0.2228



The exact variation of conditions can best be seen from the table given above.

Conclusion.

(1) Comparison of the rates of precipitation under like conditions of current, volume of solution, etc., shows that, although the rate of precipitation with the rotating anode is greater than with the stationary anode, it is not sufficiently so to recommend the use of so much more complex a piece of apparatus.

(2) The results obtained by this method are as accurate as those obtained by means of other mercury cathode methods.

(3) With the different metals determined it is possible to use about the same conditions as for the determination by means of the rotating anode and the mercury cathode.

University of Arizona, Tucson.

CORRECTIONS.

"*A Simple System of Thermodynamic Chemistry Based upon a Modification of the Method of Carnot*" and "*The Fundamental Law for a General Theory of Solutions.*"—The two papers which appeared under the above titles in the April and May numbers of This Journal require the following corrections:

Page 479, line following equation (12), for V read *v*.