

## THE SIMULTANEOUS ELECTRO-DEPOSITION OF LEAD AND LEAD PEROXIDE.

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## PART I—INTRODUCTION.

*General.* For many years it has been known that one may obtain the deposition of either metallic lead upon the cathode or lead peroxide upon the anode by the electrolysis of an aqueous solution of lead nitrate, depending upon the conditions maintained during the electrolysis. Many experiments under varied conditions have shown that lead may be quantitatively deposited on the anode as the peroxide from a solution of the nitrate containing 10 to 20 per cent nitric acid of Sp. G. 1.35-1.40.<sup>1</sup> A quantitative deposition of the lead in the metallic state has not been accomplished from aqueous solutions of the nitrate except through the addition of other compounds, such as those recommended by Stähler and Alders.<sup>2</sup> They accomplished this by separating the lead as amalgam from a solution of the nitrate (0.0997 g. lead) and of mercuric chloride (0.0855 g. mercury) together with 1 cc. of concentrated nitric acid and 1.5 cc. of phosphoric acid. Also Vortmann<sup>3</sup> states that lead can be quantitatively separated as an amalgam from a solution containing 1.4 g. of the lead salt, 1.2 g. mercuric chloride, 3-5 g. sodium acetate, 1 cc. of a concentrated solution of potassium nitrite, and enough acetic acid to dissolve any white precipitate formed.

In connection with two other investigations<sup>4</sup> lead amalgams were used which were made by electrolyzing a 10 per cent solution of the nitrate with a weighed amount of mercury for the cathode and a platinum foil electrode for the anode. After electrolyzing for 2 to 3 hours with a current of approximately 20 milliamperes, sufficient lead was deposited in the mercury to show a considerable amount of solid along with the liquid amalgam. This solid was taken to be the compound  $Pb_2Hg$ , described by Fay and North.<sup>5</sup> A comparatively thick, adherent deposit of lead peroxide was always obtained on the anode. In this previous work a coulometer was included in the electrical circuit, the assumption being that a quantity of lead would be deposited in the mercury cathode equivalent in amount to the metal deposited in the coulometer. Then, knowing the weight of the lead deposited and the weight of the mercury, one could readily calculate the percentage composition of the amalgam. Such a procedure, with a silver coulometer, has been used by Henderson<sup>6</sup> for zinc amalgams, and by Richards and Wilson<sup>7</sup> for

<sup>1</sup> Smith—Electro-Analysis, p. 109 (1918).

<sup>2</sup> Ber. 42, 2685 (1909).

<sup>3</sup> *Ibid.* 22, 2756 (1891).

<sup>4</sup> Henderson and Stegeman—J. Am. Chem. Soc. 40, 84 (1918). Mellon and Henderson—*Ibid.* 42, 676 (1920).

<sup>5</sup> Am. Chem. J. 25, 216 (1901).

<sup>6</sup> Phys. Rev. 29, 507 (1909).

<sup>7</sup> Carnegie Inst. Pub. 118, 1 (1909).

amalgams of thallium, indium and tin. Meyer<sup>1</sup> has used a hydrogen coulometer for similar work.

The validity of the above assumption regarding lead has seemed questionable, and the purpose of the present work has been to ascertain, first, the relative amounts of the two deposits; and, second, the relation between each of these amounts and the amount of silver deposited in a silver coulometer placed in the circuit in series with the cells containing the solution of lead nitrate. The latter quantities should enable one to answer the question as to whether there is deposited in the mercury a weight of lead equivalent to the weight of silver deposited in the coulometer, and, therefore, whether one can calculate the per cent of lead in the amalgam from the amount of silver deposited.

*Previous Work.* Although "Lead most readily of all the elements forms oxide on the anode during electrolysis,"<sup>2</sup> there is a considerable tendency for this element to separate from an aqueous solution of the nitrate partly as metallic lead on the cathode and partly as lead peroxide on the anode. Various individuals<sup>3</sup> have noted this division of the lead between the two electrodes and have studied the factors influencing the formation of the two deposits. Electrolysis from a neutral solution gives both the metal and the peroxide. An addition of nitric acid seems to improve the conditions for obtaining the peroxide; for with 15-20 per cent of the acid present, all the lead deposits in this form. Even with these higher concentrations of acid, however, a small amount of metallic lead may deposit, but it gradually dissolves as the decomposition proceeds. Easily oxidizable substances, such as lactose, glycerine, etc., hinder or prevent the formation of the peroxide. Oxalic acid, for example, is said to be very efficient for this purpose.

In this earlier work there is included no mention of quantitative results on the relative amounts of the deposits of metallic lead on the cathode and lead peroxide on the anode, under the different conditions of electrolysis. Any of the quantitative determinations have been made with the aim of separating all the lead, either as peroxide or as the metal.

*Present Problem.* The object of the present investigation has been the determination of the quantity of lead deposited at each electrode, under varying conditions of electrolysis, together with a determination of the quantity of silver deposited in a coulometer placed in the electrical circuit. This has involved, first, the arrangement of apparatus suitable for the electrolysis; and, second, the selection of satisfactory analytical

<sup>1</sup> Z. Phys. Ch. 7, 481 (1891).

<sup>2</sup> Mathers—Trans. Am. Electrochem. Soc. 23, 178 (1913).

<sup>3</sup> Luckow—Z. anal. Ch. 19, 15 (1876); Ibid. 22, 485 (1883).

Schucht—Ann. Chim. Phys. (5) 13, 508 ( ).

Frechland—D. R. P. 140, 317; J. Ber. 9, 660 (1903).

Thomälsen—Chem. Ztg. 18, 1355 (1894).

Vortmann—Ann. 351, 238 (1907).

Gooch and Beyer—Am. Jr. Sci. (4) 25, 249 (1908); 27, 59 (1909).

Fairchild—J. Ind. Eng. Chem. 3, 902 (1911).

Smith—J. Am. Chem. Soc. 27, 1287 (1905).

Tenney—Am. Jr. Sci. (4) 5, 413 (1883).

methods for the determination of the lead peroxide on the anode, the metallic lead in the mercury of the cathode, and the metallic silver in the coulometer.

·PART II—EXPERIMENTAL PROCEDURE AND DATA.

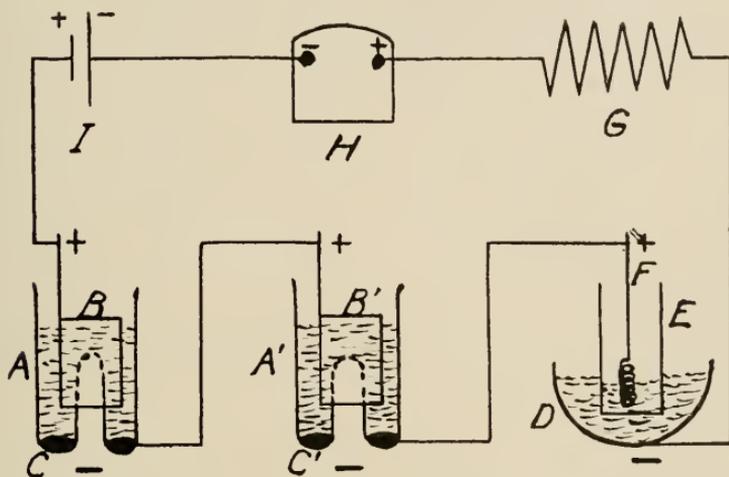


Fig. 1

*Apparatus.* The arrangement of apparatus used is illustrated by Fig. 1, in which A, A' represent special glass cells containing the solution of lead nitrate—these were about 6 cm. in diameter and of such a form that 40 g. of mercury easily covered the platinum points in the bottom; B, B' are anodes of platinum foil 2.5 cm. in diameter and 5 cm. in length; C, C' are the mercury cathodes, the electrical contact being made with them by means of three short pieces of platinum wire sealed through the glass; D is a platinum dish 7 cm. in diameter serving as the cathode in the silver coulometer; E is the porous cup, 3.5 cm. in diameter, and F the anode of 15 gauge coiled silver wire; G is an adjustable rheostat; H a milliammeter and I a storage cell.

*Analytical Methods.* The weight of silver deposited was determined by weighing the platinum dish after drying to constant weight at 105° C.

In order to determine the lead in the deposit of peroxide, the original intention was to follow the volumetric method suggested by Scott.<sup>1</sup> This consists in dissolving the peroxide from the electrodes with a hot mixture of 15 cc. of fifth normal oxalic acid and 10 cc. of nitric acid (Sp. G. 1.2) and titrating the excess of oxalic acid with tenth normal potassium permanganate. The end point in the titration with the potassium permanganate proved to be so indefinite that the method was abandoned for a procedure essentially that recommended by Smith.<sup>2</sup>

<sup>1</sup> Standard Methods of Chemical Analysis, p. 240 (1917).

Chwala and Colle—Z. anal. Chem. 50, 209 (1911).

<sup>2</sup> Loc. cit.

This consisted in washing the deposits with water, placing the electrode in a platinum dish, and drying both in an electric furnace in which the temperature was maintained at approximately 250° C. by means of a pyrometer. While wet, the peroxide did not show any tendency to scale off during handling; but as soon as dried, it often did not adhere well. By drying in the platinum dish, any particles falling off were saved, since the dish and electrodes were weighed together.

It was planned to determine the weight of lead deposited at the cathode according to the method of Stähler and Alders,<sup>1</sup> that is, by obtaining the increase in weight of the mercury cathode after having decanted the electrolyte and washed the amalgam with water, alcohol and ether. Although it is stated that this procedure gives very good results, it was not found possible to handle the amalgams in this way without having marked evidence of oxidation on the surface of the amalgam, even with only a few hundredths of a gram of lead present. Sometimes a black scum formed on the surface, which was easily lost in the washing by decantation. Some of the preliminary results were obtained in this way, but the method was changed for one proving more satisfactory.

The procedure adopted consisted essentially in the replacement of the lead in the amalgam by another element, thus bringing the lead into aqueous solution from which it could be precipitated.<sup>2</sup> This was accomplished by washing the amalgam with water by decantation and then adding 25 cc. of a 10 per cent solution of copper nitrate. The solution remained on the amalgam from 15 to 24 hours, after which it was decanted and the resulting amalgam washed with water. Copper is less soluble in mercury than lead, and most of the determinations showed considerable brownish-red material in the beaker containing the amalgam, after standing in contact with the copper nitrate for several hours. This was found to be largely copper, along with some mercury, and the solution was always filtered from this precipitated matter. To the filtrate two or three drops of acetic acid were added, the solution heated to somewhat less than boiling, and the lead precipitated with potassium dichromate. The precipitate was handled and weighed according to the directions of Scott.<sup>3</sup>

*General Procedure.* The arrangement and manipulation of the silver coulometer followed rather closely the suggestions of Richards and Anderegg,<sup>4</sup> a porous porcelain cup and recrystallized silver nitrate being used. All the precautions noted in their papers were not followed, such as corrections for the amount of electrolyte included in the cathode deposit and protection from dust during electrolysis, since the nature of the present work did not seem to warrant it.

Each determination was made by placing 30 to 50 g. of mercury in each of the glass cells and adding 100 cc. of the solution of lead nitrate to be electrolyzed. The platinum foil anodes were suspended in the electrolyte about 1.5 cm. above the surface of the mercury. In-

<sup>1</sup> Loc. cit.

<sup>2</sup> Mellon and Reinhard—See following paper.

<sup>3</sup> Standard Methods of Chemical Analysis, p. 236 (1917).

<sup>4</sup> J. Am. Chem. Soc. 37, 7 675 (1915).

side the platinum dish serving as cathode for the coulometer, and about 0.5 cm. above the bottom, the porcelain cup was suspended. The silver wire in the form of a spiral was lowered close to the bottom of the cup. After filling the dish nearly full, and the cup slightly below this level, with a 5 per cent solution of silver nitrate, the current was allowed to pass from 1 to 3 hours. At the end of this time, the solutions in the three cells were siphoned off simultaneously, being replaced with distilled water until the ammeter in the electrical circuit indicated practically no current passing. The weights of silver and lead deposited were then determined according to the methods already outlined.

The solution of lead nitrate used as electrolyte for the determinations reported in Table II was made by dissolving an amount of the salt in water to produce an approximately 10 per cent solution. For the second series, the solution was made by diluting 40 cc. of concentrated nitric acid to 1 liter with the previous solution; and the third solution was made in the same way, using 80 cc. of the nitric acid.

The value for the lead equivalent of the silver deposited was obtained by multiplying the weight of the silver for each determination by the ratio obtained in dividing one-half of the atomic weight of lead (207.20) by the atomic weight of silver (107.88), this ratio being 0.9603. The factor used for lead in lead peroxide was 0.866.

The quantities reported for lead as lead peroxide and for lead as lead amalgam are the average of the two cells run in each experiment. The values reported as variations from the average indicate the amount by which each determination varied from the average of the two. The amperage showed some variation during the electrolysis, and the values recorded are taken as the average. Table I includes some preliminary results, and Table II those obtained in the later work.

TABLE I.  
Deposition of Lead from Aqueous Solutions of Lead Nitrate.

No.	Time in Hours	Milliamperes	Lead as Peroxide	Lead as Amalgam	Ratio of Anode Lead to Cathode Lead
1	3.0	20	0.2383	0.2329	1.0232
2	3.0	20	0.2489	0.2294	1.0850
3	3.0	20	0.2505	0.2384	1.0508
4	3.0	24	0.3098	0.2979	1.0399
5	5.5	10	0.1993	0.1870	1.0657
6	4.0	14	0.2099	0.1932	1.0864
7	4.0	19	0.3229	0.3040	1.0621

The investigation reported in this paper was begun at The Ohio State University in 1919 by C. C. Curran under the direction of the senior author. The results in Table I, obtained at that time, when compared with those in Table II, show the effect of employing more refined methods of analysis.

In this earlier work a copper coulometer was used, but the results obtained with it indicated inaccurate manipulation. The lead peroxide was weighed after drying at 105° C.; and the metallic lead was obtained from the increase in weight of the mercury cathode, after being washed with water, alcohol and ether. These determinations include

TABLE II.  
Deposition of Lead from Aqueous Solutions of Lead Nitrate

No.	Time (Min)	Amperage	Pb Equiv. of Silver	Lead as Peroxide	Variation from Ave. of 2 Cells	Lead as Amalgam	Variation from Ave. of 2 Cell	Ratio of Anode Pb to Pb Equiv. of Silver	Ratio of Cathode Pb to Pb Equiv. of Silver	Ratio of Anode Pb to Cathode Pb
(Series I—No. HNO <sub>3</sub> )										
1	70	44	0.2044	0.2031 0.2062 0.2963	±0.0001	0.2025	±0.0000	0.9936 1.0088 0.9858	0.9907	1.0026 1.0187 1.0018
2	107	44	0.3006	0.3008 0.1567	0.0004	0.2958	0.0002	1.0008 0.9831	0.9840	1.0171 1.0021
3	51	44	0.1594	0.1591 0.4183	0.0003	0.1564	0.0003	0.9981 0.9893	0.9810	1.0172 1.0030
4	130	46	0.4238	0.4257 0.3667	0.0005	0.4178	0.0004	1.0044 0.9942	0.9860	1.0189 1.0120
5	240	22	0.3688	0.3723 0.2290	0.0003	0.3624	0.0003	1.0094 0.9914	0.9826	1.0273 1.0144
6	250	20	0.2310	0.2325 0.3911	0.0001	0.2258	0.0003	1.0065 0.9974	0.9773	1.0297 1.0091
7	200	30	0.3922	0.3971 0.3919	0.0000	0.3876	0.0002	1.0126 0.9872	0.9884	1.0245 1.0061
8	75	70	0.3970	0.3979	0.0003	0.3896	.....	1.0023	0.9813	1.0214
(Series II—40cc HNO <sub>3</sub> per L)										
9	140	46	0.4473	0.4490	0.0005	0.4367	0.0000	1.0038	0.9763	1.0282
10	145	30	0.2879	0.2776	0.0000	0.2764	0.0013	0.9642	0.9600	1.0043
11	130	40	0.2445	0.2408	0.0003	0.2382	0.0012	0.9849	0.9742	1.0105
12	85	40	0.2308	0.2347	0.0013	0.2291	0.0012	1.0169	0.9928	1.0244
(Series III—80cc HNO <sub>3</sub> per L)										
13	105	60	0.4346	0.4287	0.0001	0.4244	0.0020	0.9864	0.9719	1.0101
14	.....	.....	0.5377	.....	.....	0.5202	0.0030	.....	0.9674	.....
15	130	65	0.5385	0.5257	0.0050	0.5142	0.0045	0.9762	0.9349	1.0223
16	75	60	0.3232	0.3171	0.0025	0.3232	.....	0.9811	1.0000	0.9811

the errors resulting from drying the peroxide at a temperature too low to expel all the water, and from the oxidation of the amalgam during washing and drying. The former values are then too high and the latter too low, thus increasing the ratio of the former to the latter. No nitric acid was used in these determinations.

Table I does not include the deposits of copper in the coulometer. It will be noted in these earlier results that the ratios of the deposit of lead at the anode to that at the cathode are distinctly higher and more variable than is the case with the new results for Series I shown in Table II.

*Discussion of Results.* As shown in Table II, the results for solutions containing free nitric acid are so variable for the different experiments and so inconsistent for the two cells in each experiment, that one seems justified only to conclude the action of some variable and uncontrolled factor. However, even from these acid solutions, the deposits of lead at both the anode and cathode are approximately equivalent to the corresponding deposit of silver, and also, for a distinct change in concentration of nitric acid, there is not any marked change in the ratio of the amount of lead deposited at the anode to that deposited at the cathode.

For the experiments in which no nitric acid was added to the solution of lead nitrate, the results are distinctly less variable, both for the separate experiments and for the two cells in each experiment. Using some variation in the amperage for the different experiments, and with a considerable difference in the time each ran, there is a fair constancy in the ratios for each of the two deposits of lead to the silver in the coulometer, and, consequently, for the one deposit to the other; and also there is a fairly satisfactory agreement in the amount of the deposits in the two cells. It will be noted that, with one exception, the amount of lead found in the anodic deposit was always more than the lead equivalent of the silver, and that in the cathodic deposit was always less.

Apparently, then, for the solutions made up by dissolving lead nitrate in water, one must conclude either that there is not deposited (under the conditions maintained in this work) at the cathode or at the anode an amount of lead equivalent to the amount of silver, the former being less and the latter greater; or that some error in the manipulation of the apparatus or in the methods of analysis has prevented the recognition of the deposit of an electrochemical equivalent of lead at either of the electrodes.

The average of the ratios of the lead deposited at the anode to the lead equivalent of the silver is 1.0053 for the eight experiments; and for the cathodic ratio the average is 0.9864. These averages indicate the deposition at the anode of an amount of lead 0.5 per cent more, and at the cathode 1.4 per cent less, than the electrochemical equivalent of the silver. The variation of the individual ratios from these averages is approximately 0.5 per cent.

In considering the explanation of the cause of these variable results, one comes first to the question of the accuracy of the coulometer. Many careful researches have resulted in the adoption of the porous

cup type of silver coulometer as the standard for the measurement of electrical current. As already mentioned, the manipulation of the coulometer in the present work would not give the high degree of accuracy attained by Richards and Anderegg, but it seems probable that the error involved in these measurements is small.

The second source of error to be considered is in the analytical methods used for the determination of the lead. In the handling of the peroxide the chief difficulty has been in drying the deposit under conditions that will remove all the water and yet not convert any of the peroxide to monoxide. This determination has been worked over many times and Smith finally recommends drying at a temperature of at least 200° C., when the error involved is stated to be small. The drying in this work was made from 230° to 300° C. No appearance of the yellow monoxide was noted; if there had been some undetected, the results calculated would be lower than otherwise, owing to the fact that the deposit would weigh less than if there were no such conversion. In one set the values for the peroxide were checked by conversion to the monoxide and weighing as such. Although it may be possible that the combined errors of the coulometer and the general manipulation could account for the difference between the lead at the anode and the lead equivalent of the silver, it does not seem probable.

If one uses the empirical factor 0.853 of Hollard<sup>1</sup> for lead in lead peroxide instead of the theoretical value of 0.866 in calculating the results for Table II, a considerable difference is noted in the relationships involved. These values have been inserted in the table in the parentheses. It will be noted that the ratio of the lead deposited at the anode to the lead equivalent of the silver falls in all the cases considered to values much closer those for the ratio of the lead deposited at the cathode to the lead equivalent of the silver. In some cases they are very close together. The average of these anodic ratios becomes 0.990 as compared with 0.986 for the cathodic ratios. These values indicate the deposition of an amount of lead at each electrode slightly less than the electrochemical equivalent of the silver deposit.

For the determination of the lead in the amalgam the data presented by the authors in the preceding paper indicates that the method employed is accurate. These results showed that the weight of lead not recovered by this procedure was less than 0.1 per cent of that originally added to the mercury. The error in this determination would not seem to account for the variation of 1.4 per cent between the lead found and the lead equivalent of the silver.

### PART III—SUMMARY.

In this work involving the electro-deposition of lead from aqueous solutions of the nitrate, there has been presented:

1. A review of the investigations bearing upon the division of lead between the two electrodes during the electrolysis.
2. Data associated with the quantitative relationship between the anodic and cathodic deposits of lead, and the relationship between these and the deposit of silver in a coulometer.

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<sup>1</sup>Ibbotson and Aitchison—*Analysis of Non-Ferrous Alloys*, p. 60 (1915).