(1) The compounds produced by precipitation of copper solutions by carbonates are unstable and possess varying solubilities in solutions of carbon dioxide.

(2) On treatment with solutions of carbon dioxide these substances pass over into an apparently stable compound possessing a definite solubility in solutions of carbon dioxide of definite concentration, which solubility increases with the concentration of carbon dioxide.

(3) The addition of small amounts of sodium chloride or sodium sulphate causes no decided change in the solubilities. Larger amounts of these salts increase the solubilities.

(4) The action of calcium sulphate is not decidedly in either direction.

(5) Sodium carbonate and calcium carbonate both decrease the solubility strongly, and in about the same ratio.

The results with soluble salts are in line with what would be expected from the standpoint of the electrolytic dissociation theory. If the dissolved copper be supposed to exist in some combination which gives a carbonate ion on dissociation, the presence of the same ion derived from sodium or calcium carbonates ought to depress the solubility of copper—as it does. On the other hand, the presence of an ion which forms a soluble copper salt, as Cl^- or SO_4^-, ought to increase the solubility —as it does.

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THE ELECTROLYTIC FORMATION OF SELENIC ACID FROM LEAD SELENATE.

BY FRANK CURRY MATHERS.

Received June 23, 1908.

This paper gives the results of a series of experiments that were made to determine the best conditions for electrolytically changing lead selenate into metallic lead and selenic acid. It is a well known fact that many insoluble metallic salts, when in contact with the cathode, are changed into the metal and the acid by the nascent hydrogen that is formed during the electrolysis. Many of the salts of lead are decomposed in this manner. Lead oxide is easily reduced at the cathode.[1] The commercial process of Salom[2] for the electrolytic reduction of galena depends upon the fact that lead sulphide resting upon the cathode in a dilute solution of sulphuric acid is changed into metallic lead and hydrogen sulphide. Lead sulphate can also be changed into metallic lead and sulphuric acid as is shown by the negative plates of storage batteries during charging. In a

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[1] Lodyguine, *Trans. Am. Electrochem. Soc.*, 7, 221 (1905).

[2] J. W. Richards: *Electrochem. Met. Ind.*, 1, 18 (1902). A. J. Weightman: *Trans. Am. Electrochem. Soc.*, 1, 931 (1902).

similar manner, lead selenate in contact with the cathode is decomposed by the nascent hydrogen, according to this equation:

$$PbSeO_4 + 2H = Pb + H_2SeO_4.$$

In the experiments described in this paper, a platinum dish was used as cathode and a platinum wire coil served as anode. The lead selenate was placed in the dish which was then filled with distilled water. The dish was covered with a perforated watch glass to prevent spattering. The resistance of the solution, which was, of course, very high at the beginning of the electrolysis, rapidly decreased on account of the selenic acid that was formed. Part of the reduced lead adhered tightly to the dish and part remained loosely in the bottom of the dish. A little of the lead selenate went into solution and the anode became covered with a very thin deposit of lead peroxide, which weighed less than 0.2 mg. in a number of experiments.

Method of Analysis.—At the end of an experiment, the electrolyte was filtered and the selenic acid in the filtrate was determined by titration with 0.5 *N* sodium hydroxide, using methyl orange as indicator. This filtration must be made immediately at the close of the experiment, since the finely divided lead in the dish is acted upon by the selenic acid. After standing several hours the solution may even become neutral in reaction. A copper coulometer was run in series with each set of experiments.

Preparation of Lead Selenate.—The selenium was purified by the potassium cyanide method that has been completely described in a recent article.[1] The pure selenium, that was obtained by this method, was treated with nitric acid and the selenious acid thus formed was oxidized to selenic acid with potassium permanganate in a hot nitric acid solution. The manganese dioxide that precipitated was removed by filtration and the selenic acid in the filtrate was precipitated with lead nitrate. The lead selenate was filtered, washed, and finally dried at 100°, before using.

Effect of Contact with the Cathode.—It was thought that possibly the only lead selenate that was decomposed was that which was in solution and that the solid material was unacted upon. To settle this point, 0.5 gram of lead selenate and 150 cc. of water were placed in a beaker. A platinum wire was used for anode and a platinum foil of 100 sq. cm. area served as cathode. The cathode did not reach to the bottom of the beaker and so was not in contact with the solid lead selenate, that settled upon the bottom of the beaker. The electrolyte was stirred from time to time and the temperature was kept at 85°. A duplicate experiment was run in series with the above except that a platinum dish, which served as cathode, was used as the electrolyzing vessel.

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[1] Mathers and Schluederberg, THIS JOURNAL, 30, 211 (1908).

TABLE I.

	At start.		At end.		Time.	Current efficiency in
	Ampere.	Volts.	Ampere.	Volts.	Hours.	per cent.
Lead selenate upon the cathode	0.1	23.0	0.2	4.3	2	13.4
Lead selenate suspended in the solution	0.1	50.0	0.2	45.0	2	0.6

This shows that a good reduction is obtained only when the solid lead selenate is in contact with the cathode.

TABLE II.—EFFECT OF THE QUANTITY OF (CORRECTED) LEAD SELENATE THAT IS USED UPON THE CATHODE. TEMPERATURE, 35°.

$PbSeO_4$ upon cathode.	At start.		At end.		Time.	Current efficiency
Grams.	Ampere.	Volts.	Ampere.	Volts.	Hours.	in per cent.
0.3	0.15	33.0	0.2	5.8	2	6.4
0.5	0.1	16.0	0.2	4.3	2	9.7
2.0	0.18	32.0	0.2	3.9	2	9.7
3.0	0.2	15.0	0.3	4.4	5	11.6

This table shows that the current efficiency is increased by using larger amounts of lead selenate upon the cathode.

TABLE III.—EFFECT OF TEMPERATURE.

	At start.		At end.		Current efficiency
Temperature.	Ampere.	Volts.	Ampere.	Volts.	in per cent.
85°	0.18	20.0	0.3	5.0	11.6
35°	0.18	25.0	0.3	6.0	8.1
85°	0.04	16.0	0.2	4.0	12.6
35°	0.04	20.0	0.2	5.0	9.7

In these experiments, 1 gram of lead selenate was used and each experiment was run for two hours. This table shows that the effect of an increase in temperature is to increase the current yield.

TABLE IV.—EFFECT OF CURRENT DENSITY.

Temperature, 85°; lead selenate, 1 gram; volume of electrolyte, 60 cc.; time of experiment, 2 hours; cathode, Classen dish.

At start.		At end.		Current efficiency
Ampere.	Volts.	Ampere.	Volts.	in per cent.
0.1	24.0	0.2	3.8	13.1
0.1	23.0	0.2	4.3	13.4
0.18	20.0	0.3	5.0	11.6
0.1	30.0	0.6	5.3	6.4
0.12	63.0	0.85	3.1	3.0

This table shows that the highest current yields are obtained with low current densities at the cathode. With high current densities much hydrogen is evolved and this stirs up the solution so that the lead selenate does not make good contact with the cathode and Table I showed that good contact was needed for a high current yield.

TABLE V.—YIELD OF SELENIC ACID FROM THE LEAD SELENATE.

$PbSeO_4$. Grams.	At start.		At end.		H_2SeO_4 formed. Gram.	Efficiency yield in per cent.
	Ampere.	Volts.	Ampere.	Volts.		
0.3	0.15	33.0	0.2	5.8	0.1074	86.4
0.5	0.09	63.0	0.1	3.4	0.1814	87.6
2.0	0.15	94.0	0.2	7.0	0.6444	77.8
3.0	0.2	10.0	0.2	4.4	0.9630	78.3

These experiments were conducted at a temperature of 35° and very low yields resulted at temperatures of about 85°. A 50 per cent. yield of selenic acid and a current yield of 3.1 per cent. resulted with 1.2 ampere hours at 0.2 ampere per square decimeter of cathode surface and 0.5 gram of lead selenate. An additional 4.5 ampere hours raised the yield of selenic acid to 87.6 per cent. while the current yield dropped practically to zero at the end. During the electrolysis, a part of the selenic acid is reduced[1] to lead selenide or some other insoluble reduction product that remains in the residue when the electrolyte is filtered. This reduction product is shown to be insoluble by the fact that when the filtrates were treated with a current of sulphur dioxide gas, they did not yield a precipitate of selenium. Also, the filtrates, when made acid with nitric acid and heated to boiling, did not use up potassium permanganate solution. If the electrolysis is continued for an excessive time or if the electrolyte is heated, the efficiency yield is very low, probably on account of this reduction. There is no way to easily determine when the formation of selenic acid is complete, so the electrolyte should be filtered every four or five hours, the residue washed back into the platinum dish and the electrolysis continued. This procedure is repeated until a filtrate is obtained that contains only an inappreciable amount of acid.

Lead Selenate in Contact with the Anode.—It was supposed that lead selenate, when resting upon the anode, would be decomposed according to this equation:

$$PbSeO_4 + O + H_2O = PbO_2 + H_2SeO_4.$$

A few experiments were made placing the lead selenate upon the anode, but only very small amounts of selenic acid were formed. These experiments were discontinued since reduction at the cathode was found to give so much better results.

Summary.

Selenic acid can be made from lead selenate by electrolyzing a dilute solution of selenic acid in a platinum dish that serves as cathode and upon which rests the lead selenate that is to be decomposed.

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[1] E. F. Smith, "Electro-Analysis," 4th Ed., 66. This states that prolonged electrolysis of sulphuric acid at a copper cathode results in a partial reduction, copper sulphide being formed. Selenic acid, under similar conditions, should be more easily reduced.

Some reduction products of selenic acid are formed during the electrolysis but these are insoluble and may be removed from the selenic acid solution by filtration.

The best efficiency yield, amounting to 87 per cent., was obtained with a low current density at the cathode, room temperature and a thin layer of lead selenate upon the cathode.

The best current yield, amounting to about 13 per cent., was obtained with a low current density, a hot solution (85°) and a large amount of lead selenate upon the cathode.

Only small amounts of selenic acid are formed from lead selenate in contact with the anode.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ELECTROLYTIC DETERMINATION OF NITRIC ACID.[1]

BY OWEN L. SHINN.

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In 1880 Lukow[2] found that nitric acid alone or in presence of sulphuric acid was not reduced to ammonia when electrolyzed between platinum electrodes. If, however, copper sulphate was added to the solution, reduction did take place, and if enough of the copper sulphate was added the reduction to ammonia was complete. He recognized the importance of an acid solution, as, in a solution which is alkaline, the change is oxidizing and ammonia is changed into nitric acid.

Lukow was satisfied with qualitative results and it remained for Vortmann[3] to develop the idea of making the operation a quantitative method for the determination of nitric acid. He also found that no ammonia was produced, even when the current was run continuously for several days, unless some metallic salt was added to the solution. He found copper sulphate to be the most satisfactory, but salts of other metals gave good results.

Easton[4] studied the conditions of this method with potassium nitrate and obtained good results. The method used was to add to a quantity of potassium nitrate an equal weight of copper sulphate, acidulate with sulphuric acid and electrolyze in a dish with a current of 0.2 to 3 ampere and a pressure of 3 to 8 volts. The time varied from one and one-half hours to seven hours, depending upon the current used. When the operation was complete the solution was poured off, the ammonia liberated

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[1] Read at the New Haven Meeting of the American Chemical Society.

[2] *Z. anal. Chem.*, **19**, 11.

[3] *Ber.*, **13**, 2798.

[4] THIS JOURNAL, **25**, 1042.