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CHEMICAL REACTIONS IN THE LEAD STORAGE BATTERY

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ABSTRACT

Although the double-sulphate theory of reactions in the lead storage battery has been generally accepted, its validity has often been challenged because of disagreement between the theory and certain experimental results. One of the chief difficulties in the experimental work lies in determining the amount of electrolyte within the cell, including that portion held in the pores of the plates. The method of mixtures, not previously applied to this problem, has many advantages, and has enabled the authors to determine not only the number of equivalents of acid used per faraday, but also the number of equivalents of water formed. As a result of nine discharges the mean value of the equivalents of acid per faraday was found to be 2.02±0.03 as compared with 2.00 equivalents demanded by the theory. Two equivalents of water were formed under the same conditions. In these experiments the weight of electrolyte was determined at both the beginning and end of discharge.

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I. INTRODUCTION

The "double-sulphate" theory of chemical reactions in the lead storage battery has been accepted by battery engineers generally, but its validity has often been questioned because of disagreement between the theory and certain experimental results. Quantitative proof of the theory involves experimental difficulties that have doubtless been responsible for the variety of results previously obtained. With improved technique for determining the quantity of electrolyte in the cell, a new series of experiments to determine the amount of acid consumed during discharge has been made. The results of these experiments support the double-sulphate theory.

Gladstone and Tribe[1] proposed the double-sulphate theory in 1882 on the basis of their observations that lead sulphate is formed at both positive and negative plates during discharge of the cell and that lead sulphate can be oxidized at one plate and reduced at the other during charge. Their theory is expressed conveniently by the familiar equation

$$PbO_2+2H_2SO_4+Pb \rightleftarrows 2PbSO_4+2H_2O$$

When the cell discharges the reaction proceeds to the right, but this reaction is reversed during charge.

If the equation is true, the passage of one faraday of electricity (96,500 coulombs) in the direction of discharge should result in the consumption of one equivalent each of PbO_2 and Pb and two equivalents of sulphuric acid, while two equivalents each of lead sulphate and water are formed. Numerous experiments to determine the relationship between the quantity of electricity passing through the cell and the materials formed or consumed are recorded in the technical literature.

Gerard[2] suspended the element of a cell from the arm of a balance and determined the changes in weight of the element as it was charged or discharged. He concluded that his results were concordant with the double-sulphate theory. Ayrton, Lamb, and Smith[3] found the quantity of PbO_2 in the positive plates to increase or decrease proportionately to the quantity of electricity passing on charge or discharge, accompanied by equivalent changes in the amount of lead sulphate in both plates. Mugdan[4] concluded from his experiments that the quantity of lead sulphate formed during discharge is essentially that required by the double-sulphate theory.

Many more investigations have been made of the changing density of the electrolyte during charge or discharge. Aron,[5] Crova and Garde,[6] and Kohlrausch and Heim[7] found changes in density of the electrolyte to correspond to their calculations based on the double-sulphate theory. More recently the experiments of Knobel,[8] and Cassel and Tödt[9] have shown that two equivalents of sulphuric acid are consumed per faraday of electricity.

On the other hand, a considerable number of experimenters have found the consumption of sulphuric acid per faraday to be materially less than the two equivalents called for by the double-sulphate theory. Their results vary from 1.2 to 1.8 equivalents of acid per faraday, averaging about 1.5 equivalents. Schenck and Farbaky,[10] Pfaff,[11] Smith,[12] and MacInness, Adler and Joubert[13] are included in this group.

Some writers have expressed the opinion that the active material of the positive plates is not PbO_2 but a higher oxide of lead. Reasons for this belief were based partly on analytical determinations of the

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[1] Nature **25,** 221, 461; **26,** 251, 342, 602; **27,** 583 (1882–1883).
[2] Lumière élec. **27,** 387 (1888).
[3] Elektrotech.Z. **12,** 66 (1891).
[4] Z. Elektrochem. **6,** 309 (1899).
[5] Elektrotech.Z. **4,** 58 and 100 (1883).
[6] Lumière élec. **16,** 471; **17,** 219 (1885).
[7] Elektrotech.Z. **10,** 327 (1889).
[8] Trans.Am.Electrochem. Soc. **43,** 99 (1923).
[9] Z.angew. Chem. **36,** 227 (1923).
[10] Dinglers polytech. J. **257,** 357 (1885).
[11] Centr. Accumulatoren **2,** 73 and 173 (1901).
[12] Mentioned in reference of footnote 13.
[13] Trans.Am.Electrochem.Soc. **37,** 641 (1920).

material and partly on values less than two for the equivalents of acid used per faraday. Drzewiecki,[14] Féry,[15] and Bary[16] have discussed the so-called "higher oxides." Féry proposed a theory for the reaction involving a higher oxide of lead at the positive plate and the formation of a subsulphate of lead at the negative plate. Féry's reaction would require the consumption of only one equivalent of acid per faraday of electricity. Determinations mentioned above, averaging about 1.5 equivalents, are therefore intermediate between requirements of the two theories and support neither.

MacInness, Adler and Joubert[17] showed that the active material of freshly charged positive plates had the same composition and electrical potential as lead dioxide prepared chemically or by anodic deposition on platinum. Their results make any reaction based on a higher oxide of lead seem very questionable.

The formation of a basic sulphate during discharge has been suggested in explanation of less than two equivalents of acid being used per faraday. Such a suggestion is apparently favored by Knobel[18] as an explanation of departures which he observed at high rates of discharge. Riesenfeld and Sass,[19] however, consider a basic lead sulphate as the normal product of discharge at the positive plate.

Within recent years the X-ray spectrograph has been used to identify chemical compounds in the storage battery. It would seem that this method should provide an unequivocal answer to the problem, but differences in opinion have arisen. Mazza[20] studied the compounds of the reaction by the use of X-rays and found battery plates in the charged condition to consist of lead dioxide (positives) and lead (negatives). In the discharged condition lead sulphate was found in both positive and negative plates, in addition to the original materials. Barrett[21] confirmed the conclusions of Mazza. Riesenfeld and Sass[22] on the other hand have found evidence that during discharge basic lead sulphate is formed at the positive plates and that this changes on standing to the neutral sulphate. In support of their theory, they cite experiments in which the acid consumption per faraday was found to be materially less than two equivalents.

Recently, Kameyama[23] has refuted the argument of Riesenfeld and Sass on thermodynamic grounds.

The work of others might be cited in support of or in opposition to the double-sulphate theory, but the conflict of opinion is clearly apparent. The question at the present time hinges on the correct determination of the amount of acid used per faraday. We believe the varying results obtained in the past have been due chiefly to the difficulty in determining the amount of acid in the cell. The free electrolyte in the cell can be measured easily, but to this must be added the electrolyte in the pores of the plates and separators. Porosity of the plates changes during discharge, making corrections for the amount of electrolyte held in the pores uncertain. If the plates are washed or dried before placing them in a measured quantity of electrolyte, their condition is not normal.

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[14] Bul.soc.int.élec. **6**, 414 (1889).

[15] Lumière élec. **34**, 305 (1916); Rev.gén.élec. **1**, 10 (1917); **19**, 296 (1926).

[16] Rev.gén.élec. **6**, 195 (1919).

[17] See footnote 13.

[18] Trans.Am.Electrochem.Soc. **43**, 99 (1923).

[19] Z. Elektrochem. **39**, 219 (1933).

[20] Atti.accad.Lincei [6] **4**, 215; **5**, 117, 688 (1927).

[21] Ind.Eng.Chem. **25**, 297 (1933).

[22] See footnote 19.

[23] J.Electrochem.Assn. (Japan) **1**, 3 (1933).

We have used the "method of mixtures" for determining the amount of acid in the cell, both at the beginning and end of discharge. Our cell has not been dismantled at any time for the purpose of measuring the acid. In principle, it is based on the fact that if to a solution of known concentration but unknown weight a carefully measured portion of water or another solution differing in concentration be added, and the concentration again determined, the weight of both the original and final solution can be calculated. This method has not been used previously in this particular problem so far as we are aware. It has many advantages for the purpose and has enabled us to determine not only the number of equivalents of acid used per faraday, but also the number of equivalents of water formed.

II. DESCRIPTION OF THE CELL

The cell consisted of 11 pasted plates, 5 positives and 6 negatives, contained in a rectangular glass jar having a capacity of about one-half liter. Each plate was 9 by 2.5 by 0.3 cm. The grids were castings of pure lead having a volume 1.8 cm ^{3} and providing space for 5.7 cm ^{3} of active material. Each grid was provided with a long stem or terminal post, which was burned to the grid, using pure lead. The plates, which were made in the laboratory, were pasted with lead oxide mixed with dilute sulphuric acid. To the paste for negative plates, ⅜ percent of lampblack was added as an expander. The procedure for pasting the plates was similar to that previously described.[24]

The plates, after being pasted, were pickled in sulphuric acid of specific gravity 1.150 for 20 hours. They were formed at 0.4 ampere in a small tank containing sulphuric acid, initially 1.150 specific gravity. At the conclusion of formation the voltage across the cell was 2.63 volts, and cadmium voltages were +2.42 and −0.24 for the positive and negative groups, respectively.

After formation the plates were cycled ten times in sulphuric acid of specific gravity 1.250. Charging was done at 0.5 to 0.75 ampere and discharging at 1.5 ampere. During the preliminary cycling the capacity of the cell increased and the cadmium voltage of the negative plates changed to −0.28. This rather large numerical value is characteristic of plates not containing antimony.

When the plates were assembled in the cell they were spaced approximately 0.4 cm apart. The stems of individual plates were brought through holes in a hard-rubber cover and extended considerably above the cover. Glass tubes 6 to 7 cm long and extending above and below the cover were placed over each stem to provide additional insulation between adjacent terminals of opposite polarity. These glass tubes were supported by short sections of rubber tubing, which served also to seal the upper ends of the glass tubes.

Slotted-rubber separators and glass rods were placed between adjacent plates of opposite polarity. Wood separators were not used as we desired to have free circulation of the electrolyte.

Above the tops of the plates a free space of about 200 cm^3 provided for the addition of weighed amounts of water or relatively concentrated solutions of sulphuric acid as a means of changing the density of

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[24] Vinal, Craig and Snyder, BS J.Research **10**, 798 (1933) RP567.

solution within the cell. Vent holes in the cover, normally closed with cork stoppers, provided for adding or withdrawing samples of electrolyte from the cell and also for stirring the electrolyte by means of an air jet before making titrations or density determinations.

III. MANIPULATION OF THE CELL

1. NECESSARY CONDITIONS

The first requisite for the successful operation of the cell in determining the relation of electrochemical products to the quantity of electricity discharged is that the cell shall be in normal operating condition. That is, the cell must be operating on a program of charges and discharges without interruptions, such as removing the plates for determination of their weight or porosity. Any unusual operation on the cell before beginning the experiment leaves a doubt whether it is in normal condition.

The second requirement is that means must be provided to determine with high precision the weight and concentration of the electrolyte in the cell before and after each discharge.

The third requirement is that the cell shall be as free as possible from local action.

The fourth requirement calls for high accuracy in electrical measurements of the coulombs discharged by the cell and of its electromotive force before and after each discharge as a test of the stability of the cell. These requirements have been met as described in the following paragraphs.

We have prepared our cell by cycling it in the usual way up to the time for making the experiment and then determined the amount of electrolyte within the cell by observing the change in concentration when a carefully weighed portion of distilled water or sulphuric-acid solution is added. Such a change in equilibrium is essentially the same as occurs in the normal operation of the cell and it interferes in no way with the condition of the plates.

2. TESTS FOR EQUALIZATION OF ACID AND THE STABILITY OF THE CELL

After each addition of water or solution, it is necessary that the electrolyte be completely equalized throughout the vessel and the pores of the plates. We have two tests for determining when this is accomplished.

Since the electromotive force (emf) of the cell is dependent on the concentration of the electrolyte, constancy of emf is an indication that the electrolyte is homogeneous throughout the cell. To avoid the difficulty which often arises in measuring the emf of a storage cell because its emf exceeds the range of the ordinary potentiometer, we opposed the emf of the storage cell to the emf of a standard cell, and measured the difference directly on a potentiometer. The emf of the standard cell was determined daily in terms of the Bureau's primary standard of emf. This value added to the observed difference in emf between the cells gave the emf of the storage cell with high precision.

The rapidity with which equalization is accomplished and the stability of the cell thereafter is shown by the results in tables 1 and 2. Table 1 gives measurements of emf after the completion of the discharge of April 13. This table shows that the emf of the cell became practically constant in 2 hours. When the electrolyte was diluted 19 hours after concluding the discharge for the purpose of determining the amount of electrolyte in the cell, a period of about 2 hours was required before the emf again became constant to 0.3 millivolt. The constancy of emf when equalization is established shows the stability of the cell and its freedom from local action, electrical leakage, etc.

TABLE 1.—*Measurements of electromotive force at 24° C*

Experiment of April 13, 1934

(Time is reckoned from termination of the discharge)

Time		Emf	Remarks
Hours	*Minutes*	*Volts*	
0	0	----------	Discharge stopped.
----------	10	1.977	Electrolyte stirred at 0 hr, 5 min.
1	20	2.0334	
1	40	2.0348	Electrolyte stirred at 1 hr, 25 min.
2	20	2.0346	
6	30	2.0349	Electrolyte stirred at 6 hr, 35 min.
17	30	2.0352	Electrolyte stirred at 17 hr, 35 min.
18	30	2.0349	
19	0	----------	Electrolyte diluted and stirred.
19	30	1.9897	Electrolyte stirred at 19 hr, 35 min.
19	40	1.9879	
20	35	1.9811	Electrolyte stirred at 20 hr, 40 min.
21	30	1.9789	Electrolyte stirred at 21 hr, 35 min.
21	45	1.9798	
29	0	1.9794	Electrolyte stirred at 29 hr, 05 min.
30	0	1.9794	
42	0	1.9795	
90	0	1.9795	
114	0	1.9796	

Table 2 shows the results of repeated measurements of concentration of the solutions following the discharge of November 30. As in the preceding table, constancy is attained by allowing the cell to stand. The observed change in concentration which occurred between 3 hours 50 minutes and 13 hours 35 minutes after stopping the discharge amounted only to 5 parts in 1,000 of the total change resulting from the discharge of the cell. The electrolyte was then concentrated for the purpose of determining the quantity of electrolyte. Between 27 and 50 hours the change was within the experimental error.

TABLE 2.—*Measurements of concentration of electrolyte*

Experiment of November 30, 1934

(Time is reckoned from termination of the discharge)

Time		Concentration	Remarks
Hours	*Minutes*	*Percent*	
0	0	----------	Discharge stopped.
3	50	23.534	Stirred at 3 hr, 20 min.
11	35	23.594	Stirred at 11 hr, 20 min.
12	10	23.582	
12	35	23.588	Stirred at 12 hr, 20 min.
13	35	23.579	
14	20	----------	Concentrated acid added and stirred.
27	20	[a] 34.153	Stirred at 26 hr, 50 min.
50	50	[a] 34.164	Stirred at 50 hr, 20 min.

[a] Average of three determinations.

3. TEMPERATURE CONTROL AND PRECAUTIONS AGAINST EVAPORATION

The earlier experiments were made while the storage cell was immersed in a thermostatically controlled oil bath. The object in controlling the temperature was to permit making precise measurements of electromotive force before and after discharge as a test of complete equalization of electrolyte throughout the cell. Although the cell was closed by a cover, evaporation was not completely prevented.

Experiment 8, which was made in two parts with great care, showed conclusively that evaporation was appreciable. Frequent weighings of the cell were made on a balance sensitive to 0.1 gram. The progressive loss in weight of the cell accompanied by a progressive increase in density of electrolyte while the cell was on open circuit indicated that additional precautions against evaporation were necessary.

The loss of water by evaporation depends on temperature and atmospheric conditions as well as on concentration. No corrections for this loss during the earlier experiments could be made. The amount probably varied from 0.5 to 1.0 gram or even more per day. This is a relatively large percentage of the total amount of water formed during discharge.

In all the later experiments, therefore, the use of the thermostatically-controlled oil bath was abandoned and the cell was kept under a sealed bell jar, except when the discharge was actually in progress. At such times it was in a covered glass vessel. Repeated weighings of the cell showed that its weight was much more constant under these conditions. It then became possible to determine with accuracy the water formed during discharge as well as the acid consumed.

4. MEASUREMENT OF COULOMBS DELIVERED

In some of the earlier measurements the current was measured by a calibrated ammeter, but in the later experiments we used a precision 1/10-ohm shunt, measuring the fall in potential across its terminals on a potentiometer. Readings were taken at frequent intervals and the time integral of the current obtained. Time was measured by reference to the Bureau's standard clocks. In all experiments an ampere-hour meter was included in the circuit as a check, but we have preferred to base the coulombs delivered by the cell on the more accurate measurements of current and time.

5. RANGE OF CURRENT AND CONCENTRATION

The electric current and concentration of electrolyte have been varied purposely from one experiment to another in order that the results of the experiments may not be limited to any particular conditions. The largest current used in any of the experiments was 1.8 amperes and the smallest was 0.6 ampere. These currents correspond approximately to the 5-hour and 20-hour rates for the cell. The highest initial concentration of the electrolyte was 42 percent and the lowest 21 percent. At the end of the discharge the highest concentration was 38 percent and the lowest about 9 percent. Experiment 8 was made in two parts and the equivalents of acid used per faraday for each part were compared. Notwithstanding these variations in current, concentration, or part of the discharge, no significant differences in the equivalents of acid used per faraday were found.

IV. METHOD OF DETERMINING CONCENTRATION AND AMOUNT OF ACID

1. DETERMINATION OF CONCENTRATION OF ELECTROLYTE

Three methods were used for measuring the concentration of the acid. In the first two experiments the samples of acid withdrawn from the cell were titrated with CO_2-free sodium-hydroxide solution. The sodium-hydroxide solution, approximately 0.2 *N*, was standardized with acid potassium phthalate.

In experiments 3 to 5, the accuracy of the acid determinations was improved by making all titrations by weight. To the weighed sample to be titrated, a weighed amount of 0.2 *N* sodium hydroxide was added, stopping short, however, of the final end point, which was then determined volumetrically by using a solution of 0.02 *N* sodium hydroxide. The latter was freshly prepared and standardized before each experiment. All titrations were done in triplicate, the individual measurements agreeing to 0.01 percent of sulphuric acid.

For experiments 6 to 12, we used a third method for determining the amount of sulphuric acid in the electrolyte. The density $\frac{26.5^\circ \text{ C}}{4^\circ \text{ C}}$ was determined with a pycnometer immersed in a thermostatically-controlled water bath. Density determinations were then calculated to percentages of sulphuric acid by using data in the International Critical Tables. In some experiments, interpolation of data in the Critical Tables was carried to five figures. This was done in those cases where the density was very nearly the same after the final concentration as it was at the beginning of the discharge.

The pycnometer was a bulb of Pyrex glass of about 15-ml capacity and provided with a graduated capillary stem. It was filled and emptied by a capillary glass tube. Repeated measurements were made, the agreement being indicated by the following group of density measurements, which were part of the experiment of November 30: 1.16308, 1.16299, 1.16304, 1.16297, giving an average value 1.16302. The maximum difference of a single observation from the mean is 5 parts in 100,000.

Accuracy in determining the concentration of acid in the solutions is important, because the determination of the weight of electrolyte in the cell depends on the difference in concentration produced when a weighed portion of water or sulphuric-acid solution is added to the electrolyte in the cell. The factor which cannot readily be controlled is the difference in solubility of lead sulphate in sulphuric-acid solutions of various concentrations. For the extreme range in concentrations which we have used, the solubility of lead sulphate as given by Dolezalek [25] ranges from 0.01 mg-mol of $PbSO_4$ in 1 gram-mol of sulphuric acid to 0.07 mg-mol of $PbSO_4$ in 6 gram-mols of sulphuric acid per liter. In other words, the lead sulphate in solution varied from 3 to 16 parts per million. We have not attempted to make correction for this dissolved lead sulphate.

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[25] Theory of the Lead Accumulator, page 145.

2. METHOD OF CALCULATING WEIGHT OF ELECTROLYTE

When a weighed portion of water or of sulphuric acid of specified concentration is added to another portion of sulphuric acid of known concentration, but unknown weight, it is possible to determine both the weight of the latter and of the mixture on the basis of the concentration of the resulting solution. Thus determinations of the weight of electrolyte in the cell at the beginning and end of a discharge have been made for all experiments except 1 and 7. For these the respective weights of electrolyte have been determined only at the end of the experiments. Particular care has been taken to equalize the electrolyte in all portions of the cell (see page 453) before attempting to determine the weight of electrolyte.

The method of calculating the weight of electrolyte by mixing two portions of unlike concentration is shown in the following example In all cases the mixtures were made within the cell. Samples removed for titration were carefully weighed and allowance made for them.

The following data apply to experiment 11 of December 7: (concentrations are expressed as the weight fraction)—

Initial concentration of electrolyte		0. 22783
Acid added: concentration	0. 59820	
Acid added: weight	117. 684 g	
Concentration of resulting mixture		0. 33447

Let y=weight of electrolyte after mixing

$$\frac{0.33447y-(0.59820\times 117.684)}{y-117.684}=0.22783$$

whence	y=408. 73 g
Deduct for sample removed	60. 66 g
Net weight of electrolyte at start of discharge	348. 07 g

A similar method was used to determine the weight of electrolyte at the end of discharge. The percentage strength and weight of electrolyte for each experiment are given in table 3.

TABLE 3.—*Amounts of sulphuric acid consumed and water formed in discharging a lead storage battery*

Experiment	Date	Discharge data		Percentage of H_2SO_4 (by weight)		Weight of solution		Acid used	Water formed
		Time	Coulombs	Start	Finish	Start	Finish		
	1934	*Hours*				*Grams*	*Grams*	*Grams*	*Grams*
1	Mar. 9	10. 42	45252	35. 53	24. 82	--------	311. 2	--------	--------
2	Mar. 20	7. 81	34992	36. 60	29. 17	358. 77	330. 60	34. 87	6. 70
3	Mar. 27	8. 00	35833	28. 061	18. 933	341. 78	307. 65	37. 66	3. 53
4	Apr. 6	8. 83	39116	30. 885	21. 684	358. 71	324. 73	40. 38	6. 40
5	Apr. 13	4. 83	31232	32. 518	25. 607	364. 20	337. 88	31. 91	5. 59
6	Oct. 5	10. 60	42088	28. 21	17. 89	355. 33	317. 20	43. 49	5. 36
7	Oct. 17	5. 84	23130	42. 714	38. 246	--------	345. 92	--------	--------
8a	Oct. 31	5. 03	19786	20. 951	15. 850	347. 73	--------	--------	--------
8b		5. 80	22316	15. 850	8. 898	--------	[a] 284. 98	--------	--------
9	Nov. 23	5. 75	22638	41. 24	36. 72	360. 85	340. 28	23. 86	3. 29
10	Nov. 30	19. 87	44173	33. 948	23. 584	351. 22	315. 14	44. 91	8. 83
11	Dec. 7	6. 73	31237	33. 447	26. 276	348. 07	323. 13	31. 51	6. 57
12	Dec. 27	13. 42	38152	31. 141	22. 298	359. 09	326. 87	38. 94	6. 72

[a] Between the two discharges 18.62 grams of electrolyte were removed for density determinations.

V. EXPERIMENTAL RESULTS

1. DIRECT CALCULATION OF ACID USED AND WATER FORMED

In the course of most of our experiments we determined the weight and percentage strength of electrolyte at the beginning and end of discharge. Sufficient data were provided thereby to calculate directly the amount of acid consumed and water formed as a result of the reaction. No assumptions regarding the correctness or applicability of any theory of chemical reactions in the battery are necessary, therefore, in computing the number of equivalents of acid and water taking part in the reaction. We know of no previous attempt to determine the amount of water formed by the process of discharge, nor of calculations of the acid consumed, which are thus independent of theoretical assumptions.

Nine of the twelve experiments reported in table 3 give directly the amounts of acid and water taking part in the reaction. Of the remaining three experiments, the first and seventh lack the initial weight of electrolyte and the eighth was subject to error in determining the water because of evaporation. These three experiments will be discussed later.

Table 4 gives the results of nine experiments in terms of the equivalents of acid consumed and water formed per faraday. The number of equivalents of H_2SO_4 consumed per faraday is equal to

$$\frac{F}{C}\frac{(pw-qw')}{49.04},$$

and the number of equivalents of H_2O formed per faraday is equal to

$$\frac{F}{C}\frac{(pw-qw')-(w-w')}{9.01}.$$

In these expressions

w = weight of electrolyte at beginning of discharge
w' = weight of electrolyte at end of discharge
p = weight fraction of sulphuric acid at beginning of discharge
q = weight fraction of sulphuric acid at end of discharge
c = coulombs of electricity discharged
F = value of faraday = 96500 coulombs
Equivalent weight of sulphuric acid = 49.04 g
Equivalent weight of water = 9.01 g

It can be seen that the expressions for the equivalents of H_2SO_4 and H_2O per faraday involve no assumptions regarding the reaction and that each of the unknown quantities can be determined experimentally. The average result of the equivalents of acid used per faraday is 2.02 ±0.03, whether all the experiments are included in the average or only the last four. The water determinations show more variation as would be expected. The mean of the last four experiments, in which evaporation was avoided, is 1.96 ±0.19 equivalents per faraday.

Direct determinations of the acid used and water formed afford a severe test of the accuracy of the work. The average amount of electrolyte in the cell was about 335 grams, but the actual change in weight of the electrolyte from the beginning to end of a discharge averaged only 35 grams. If an error as large as 1 gram were made in determining the total weight of electrolyte, the percentage error would be only 0.3 percent, but in calculations based on the difference of the initial and final weights it would be 3 percent, or an error ten times as great. The water formed is a still smaller part of the change in weight of electrolyte and the supposed error of 1 gram in weight of the whole solution becomes about 15 percent of the water determination. It is apparent, therefore, that the weight of electrolyte must be determined very accurately if the direct calculations of water formed and acid used are to be sufficiently precise to prove any particular theory.

TABLE 4.—*Equivalents of acid consumed and water formed per faraday during discharge of the lead storage battery*

Experiment	Equivalents per faraday	
	H_2SO_4	H_2O
2	1.96	2.05
3	2.07	1.06
4	2.03	1.75
5	2.01	1.92
6	2.03	1.36
9	2.07	1.56
10	2.00	2.14
11	1.99	2.25
12	2.01	1.89
Mean of all	2.02	1.78
Average deviation	±0.03	±0.30
Mean of last four	2.02	1.96
Average deviation	±0.03	±0.19

In experiments 3 and 6 the observed amount of water was proportionally less than that of several other experiments. In attempting to find why this should be, experiment eight was made with great care and an unusually long time was required for many repetitions of the density measurements. The results obtained by calculating the water formed in this experiment were even worse than before. The cell was weighed periodically and found to be losing weight by roughly 0.5 gram per day, while the density of the electrolyte was gradually increasing. Weighings were made on a balance sensitive to 0.1 gram. All the evidence indicated evaporation to be the cause of the discrepancy in amount of water.

Evaporation of water from the electrolyte was doubtless a source of error in several of the earlier experiments, particularly 3 and 6, for which the percentage strength of the acid was low. We have no way of correcting for loss of water in these experiments, but beginning with the ninth experiment added precautions were taken to prevent evaporation. The weight of the cell in these last experiments remained nearly constant. The results of water determinations of the last four experiments are regarded, therefore, as more reliable than those which preceded.

Clearly the results in table 4 show that two equivalents of acid are consumed per faraday and that two equivalents of water are formed simultaneously. Comparing these figures with the requirements of the several theories mentioned on page 451, it is found that they satisfy exactly the requirements of the double-sulphate theory, but fail to support any of the other theories.

Previous calculations of the equivalents of acid used per faraday have been based on a single determination of the weight of electrolyte, usually at the beginning of discharge. Such calculations assumed that an equal number of equivalents of acid and water were involved in the reaction. This had not been proved, but the assumption now appears to have been entirely justified.

We are now in a position to calculate the results of all of our experiments, including the three which were omitted from table 4. By doing this our results are presented in a manner analogous to that of previous investigators and accidental errors in determining the weight of solution become far less important than when we are dealing with the difference in weight at the beginning and end of a discharge.

2. VALUE OF THE FUNCTION ϕ

The equivalents of sulphuric acid which were consumed per faraday of electricity, ϕ,[26] were calculated by the method used by some previous experimenters, that is from the change in concentration of the electrolyte during the experiment and the known weight of the electrolyte at either the beginning or end of discharge. In those of our experiments for which we determined the weight of electrolyte both at the beginning and end of discharge, it is possible to compute two independent values for ϕ, table 5. One computation serves as a check on the other, but they are independent inasmuch as each is based on independent determinations of the weight of electrolyte.

TABLE 5.—*Equivalents of sulphuric acid consumed per faraday in discharging a lead storage battery*

Experiment	Value of ϕ		Method for determining acid concentration
	Equation 1	Equation 2	
1		2.04	Titration by volume.
2	1.97	1.97	Do.
3	2.026	2.000	Titration by weight.
4	2.017	2.010	Do.
5	2.005	2.003	Do.
6	2.008	1.988	Density.
7		2.019	Do.
8a	2.026		Do.
8b		2.007	Do.
9	2.025	2.015	Do.
10	2.008	2.013	Do.
11	2.001	2.008	Do.
12	2.002	1.999	Do.
Mean	2.009	2.006	
Mean of all	2.007		
Average deviation from mean	±0.011.		

Using the weight of electrolyte determined at the beginning of discharge

$$\phi=\frac{wF(p-q)}{c\,(49.04-40.03q)}=\frac{2410.7\ w\ (p-q)}{c\,(1.2251-q)} \tag{1}$$

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[26] Reference footnote 8, Trans. Am. Electrochem. Soc. 43, 99 (1923).

Similarly, using weight of electrolyte determined at end of discharge

$$\phi=\frac{w'\,F\,(p-q)}{c\,(49.04-40.03\,p)}=\frac{2410.7\,w'\,(p-q)}{c\,(1.2251-p)} \qquad (2)$$

Applying the formulas 1 and 2 to the data of experiment 11 of December 7, as given in table 3, ϕ is calculated to be

By formula 1 .... $\phi=2.001$
By formula 2 .... $\phi=2.008$
Using formula 1 based on the weight of electrolyte at the beginning of each discharge, the average result for all the experiments is .... $\phi=2.009$
Probable error of mean .... $\pm.003$
Similarly, using formula 2 based on the weight of electrolyte at the end of each discharge, the average result for all the experiments is .... $\phi=2.006$
Probable error of mean .... $\pm.003$

The two values for ϕ agree, therefore, within probable errors.

The average of 22 determinations of ϕ is .... $\phi=2.007$
Average deviation of a single observation .... $\pm.011$

This value for ϕ agrees closely with the theoretical value, 2, given by the equation representing the double-sulphate theory.

VI. DISCUSSION OF RESULTS

Throughout the experiments the cell was unusually stable. Repeated measurements of its electromotive force and of the concentration of its electrolyte have shown constant values after sufficient time had elapsed for equalization of the acid. During the 6 months from April 13 to October 5 when experiments were not in progress, the cell stood in a partially charged condition without harmful sulphation occurring or visible liberation of gas from the negative plates. We believe this stability was the result of constructing the cell with pure-lead grids, the use of reagent grade of sulphuric acid for the electrolyte, and the insulation of the terminal of each plate with a long glass tube. Such a cell may be expected to hold its charge for 6 months or a year.

Although pure sulphuric acid was used for the electrolyte, small amounts of lead sulphate dissolved in it as the cell was worked. The amount varied with the concentration of the acid, but in any case probably did not exceed 0.1 mg-mol per liter. We were justified, therefore, in basing calculations of percentage strength on data applying to pure sulphuric-acid solutions. We do not have sufficient data on the variation of the solubility of lead sulphate with acid concentration to warrant applying a correction for it.

Tables 4 and 5 show that most of our determinations of the equivalents of acid used per faraday are slightly above the theoretical value, 2, based on the double-sulphate theory. Several possible causes for this may be mentioned although it is not certain that any one of them was responsible. First, the unequal solubility of lead sulphate in the stronger solutions at the beginning of discharge as compared with the more dilute solutions at the end may have produced a slight effect. Second, an unobserved precipitate of lead sulphate may have introduced a small error in the density determinations. We guarded against such a possibility by repeating density measurements at intervals of one-half to one hour after stirring the electrolyte. If a precipitate was settling out, concordant results could not have been obtained.

Riesenfeld and Sass [27] in commenting on the work of Cassel and Tödt [28] emphasized the fact that the latter obtained two equivalents of acid used per faraday only after the lapse of considerable time following each discharge. Determinations made shortly after completion of discharge, on the other hand, were less than two by significant amounts. Cassel and Tödt have attributed low values to incomplete equalization of electrolyte, but Riesenfeld and Sass believe that the low values cannot be accounted for in such a manner. The latter think that a chemical reaction occurs during the period of standing, by which basic lead sulphate is transformed to neutral sulphate. We have examined the records of our experiments in which samples of electrolyte were taken soon after the termination of discharge and have computed values of ϕ, which are given in table 6. In all cases, values approximating two were obtained, including the measurement made only 15 minutes after the conclusion of the discharge when equalization of the acid in the pores of the plate was probably incomplete. Our work in this respect does not confirm the hypothesis of Riesenfeld and Sass.

TABLE 6.—*Effect of time of sampling on values calculated for* ϕ

Experiment	Time of sampling after discharge		Value of ϕ	Remarks
	Hours	*Minutes*		
8	0	15	1.976	
	3	30	2.010	
	15	0	2.026	Steady value.
9	1	45	2.024	
	4	45	2.022	
	19	0	2.024	Steady value.
10	4	0	2.016	
	13	0	2.008	Steady value.

The results of our work are entirely consistent with the double-sulphate theory and we have shown that 2.02±0.03 equivalents of acid are used and 1.96±0.19 equivalents of water formed by the passage of one faraday of electricity through the cell in the direction of discharge. We have found no evidence of the formation of basic sulphate or any spontaneous change occurring in the cell when on open circuit after discharge.

WASHINGTON, January 19, 1935.

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[27] Z.Elektrochem. **39,** 219 (1933).
[28] Z.angew.Chem. **36,** 227 (1923).